

The use of Raman spectroscopy to study
fatigue type processes in polycrystalline
diamond (PCD)

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Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

(Signature of candidate)

_____ day of _____-20 _____ in _____

Abstract

Polycrystalline diamond (PCD) cylindrical tool-bits used in oil well drilling are susceptible to fracture due to the hostile environment of randomly occurring high impact loads. These tool-bits generally comprise of a PCD layer sintered onto a tungsten carbide substrate. The metallic phase primarily aids the formation of the diamond to diamond bonds, however during application the same cobalt expands much quicker than the diamond, breaking the very same bonds it helped to form in the first place, leading to premature failure of the tool bits. Because the PCD is virtually a two phase material comprising of cobalt and diamond, substantial volumes of the metallic phase can be removed through a leaching process without compromising the cohesiveness of the diamond matrix with reported improved wear resistance and thermal stability. The fact that the tool-bits fail after repeated use gives rise to the possibility of fatigue-type processes in diamond.

X-ray diffraction and Raman spectroscopy techniques were used to investigate residual stresses in leached and unleached polycrystalline diamond disc samples. The 514.5 nm line of an Ar^+ ion laser was used as an excitation source with an 1800 grooves/mm grating in the single spectrograph mode of a Jobin-Yvon *T64000* Raman spectrometer. Raman stress measurements at room temperature were carried out using a 36 point mapping array in area close to the size of the PCD samples. The mapping points provided histograms of the magnitude and nature of these small individually stressed regions

showing a general compressive stress for the lower numbers of fatigue cycles which deteriorates to a high proportion of tensile regions. The data are also illustrated by 2-D surface maps as an alternative mode of presentation again confirming the change from surface stresses being dominantly compressive to dominantly tensile with exposure to the higher numbers of fatigue cycles.

A systematic investigation and evaluation of the average in-plane residual stress fields on a fatigue loaded leached and unleached PCD disc sample was also conducted using the Bruker D8 Discover machine equipped with a graphite monochromator and a *Cu* X-ray tube of wavelength 1.544 Å operated at a voltage of 40 kV and a current of 40 mA. To determine the full stress tensor, samples were measured at 6 different azimuth angles = 0°; 180°; 90°; 270°; 45°, and 225°. Whilst the Raman technique showed a progress shift of the residual stresses state on the surface of the samples, from a compress stress state to an average tensile stress state with increasing number of loading cycles, the X-ray diffraction method recorded compressive stresses for all the measurements even at the highest number of loading cycles.

Whilst the results are seemingly in disagreement the non destructive nature of the two techniques employed in the study has been shown. Whilst the two methods are considered to be surface techniques there exists fundamental differences in way they determine the residual stress, which can be used to explain the divergent set of results for the two methods. Scanning electron microscope (SEM) images showing evidence of possible localized damage at large numbers of cycles for some of the unleached samples, were obtained using a JEOL JSM7500F field emission scanning electron microscope operating at 15 keV in a vacuum of 5.1×10^{-4} Pa. Using the same equipment elementary analysis was done for the unleached samples and the observations indicated that the samples had similar chemical compositions.

Dedication

This thesis and the Doctor of Philosophy degree are dedicated to the love of my life Patience Tarisayi and our two beautiful kids Nicole and Jayden. Words are not enough to express how grateful I am for your love. I hope I have made you proud.

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Contents

1	Introduction	1
1.1	Previous Work	2
1.2	Aims of the Work	4
2	Literature Review	6
2.1	Diamond Structure and Bonding	6
2.2	Diamond and Graphite	8
2.3	Commercial Synthesis of Diamond	9
2.4	Thermodynamics of Diamond Synthesis	10
2.5	PCD Synthesis and Properties	11
3	Fatigue	14
3.1	Introduction	14
3.2	Fundamentals of Fatigue Life	15
3.3	The Griffith Energy Theory	17
3.4	Fracture Toughness	20
3.4.1	Modes of Crack Propagation	21
3.5	Paris' Law - The Fatigue Crack Growth Rate Curve	22
3.6	Classification of Tool Fracture	24

4	Residual Stress Measurement Techniques	26
4.1	Residual Stress	26
4.2	Residual Stress Measurement Methods	27
4.3	Mechanical (Destructive) Methods	28
4.3.1	Curvature Method	28
4.3.2	Hole drilling	29
4.3.3	Ring Core	30
4.4	Non-Destructive stress measurement techniques	31
4.4.1	X-ray diffraction stress measurement technique	31
4.4.2	Bragg's law	32
4.4.3	Uniaxial stress Measurements	34
4.4.4	Biaxial Stress Measurements	37
4.4.5	Grazing Angle method	39
4.4.6	Raman Spectroscopy.	44
4.4.7	Classical Theory Approach	45
4.4.8	Quantum Theory Approach	48
4.5	Raman Spectroscopy as an Optical Characterisation Technique	50
4.6	Stress and the Raman Line	50
4.6.1	Stress classification	52
4.6.2	The Hydrostatic Piezo-Raman Coefficient	53
4.7	Advantages and Limitations of Raman Spectroscopy	56
4.8	Typical Raman Spectra for Diamond	57
5	Methods and Results: Unleached PCD	59
5.1	Sample Dimensions and Preparation	60
5.2	Quasi-Static Loading Test Procedure	61

5.3	Fatigue Test	63
5.4	Raman Experimental Arrangement	66
5.5	Laser	67
5.6	The Raman Spectrograph	69
5.6.1	Single Spectrograph Mode	70
5.6.2	Triple Spectrograph Modes	71
5.6.3	Charge Coupled Device (CCD) Detector	71
5.6.4	Raman Microscope	72
5.7	Raman 2D Mapping Details	72
5.8	Results and Discussion	75
5.9	Raman Spectra of Diamond	76
5.10	Average Spectra for all the Samples	77
5.11	Further Raman Measurements	81
5.12	Sample A	81
5.13	Sample B	82
5.14	Sample E	90
5.15	Sample F	96
5.16	Sample G	102
5.17	Scanning Electron Microscope and Energy Dispersive Spectro- scopy Measurements	111
5.17.1	Sample B	111
5.17.2	Sample E	113
5.17.3	Sample F	114
5.17.4	Sample G	115
5.18	Summary of Results	117

6	Methods and Results: Leached PCD	119
6.1	Introduction	119
6.2	Methodology	121
6.2.1	Fatigue Experiments - Methodology	121
6.3	X-Ray diffraction stress measurements	123
6.3.1	The highest Bragg Peak	123
6.3.2	Peak with the highest Intensity	124
6.3.3	Experimental Procedure	124
6.4	Raman stress measurements	126
6.5	Results : Raman Stress Results	126
6.5.1	Sample D16_C	127
6.5.2	Sample D16_D	143
6.5.3	Sample D16_F	155
6.6	X-ray Diffraction Stress Results	168
6.6.1	Sample D16_C	169
6.6.2	Sample D16_D	173
6.6.3	Sample D16_F	176
6.7	Summary of the Results	179
6.8	Comparison with Published Work	183
7	Conclusions	186
7.1	Future work	189
	Bibliography	190
A	Conferences and Publications	201

List of Figures

2.1.1 Arrangement of atoms in the diamond structure	7
2.2.1 Phase diagram for carbon	9
2.3.1 The equilibrium line as predicted by Berman and Simon	10
3.2.1 Stages of fatigue life	15
3.2.2 Graphical representation of fatigue life	17
3.3.1 Griffith crack model	18
3.4.1 Showing the three basic modes of crack tip deformation	22
3.5.1 Typical fracture mechanics fatigue crack propagation behaviour	23
4.3.1 Residual stress measurement methods: hole-drilling	29
4.4.1 Diffraction of X-rays by a crystal lattice	33
4.4.2 Rod in tension, with X-rays reflected from planes parallel to axis.	35
4.4.3 Stresses at the surface of a stressed body	37
4.4.4 Definition of the laboratory coordinate system L_i and sample coordinate system S_i	40
4.4.5 Definition of the laboratory coordinate system L_i , sample co- ordinate system S_i and the angles α and ψ	41
4.4.6 The laboratory coordinate system L_3 , X-ray incident and dif- fraction directions, and the angle α	42

4.4.7 Energy level diagrams showing (a) Rayleigh scattering, (b) Stokes Raman scattering, and (c) anti-Stokes Raman scattering . . .	49
4.4.8 Stokes and anti-Stokes Raman lines	50
4.8.1 Typical Raman spectra for a single crystal diamond and for polycrystalline diamond.	57
5.1.1 Showing the schematic of a typical cylindrical cutter with dimensions of the PCD layer.	61
5.1.2 (a) Ball on three balls configuration. (b) Isometric view of the balls relative to the sample.	61
5.2.1 The 5500R Instron machine in the Element Six laboratory, used for the quasi-static loading test.	62
5.2.2 Results of quasi - static loading test. (<i>Curves for specimen 1 and 3 are almost superimposed one on top of the other</i>). . . .	63
5.3.1 Schematic of the Instron SYN 179 servo-hydraulic test machine.	65
5.3.2 Constant amplitude cyclic loading characteristics as described as in the text	66
5.5.1 Schematic representation of a four-level laser transition scheme	68
5.5.2 The Ar-ion laser energy diagram	69
5.6.1 Schematic diagram of the Raman spectrograph showing the beam path	70
5.7.1 The three different map sizes used in this work; the distributions of the mapping points are illustrated.	73
5.7.2 The expected stress field for the ball on three balls test.	74
5.8.1 Raman spectra for the three different map sizes for one of the PCD samples (sample A).	76

5.10.1 Comparison of the average Raman surface spectra for the samples A to I as a function of number of cycles.	79
5.10.2 Variation of Raman peak position as a function of number of cycles for the nine samples used (<i>sample A through to sample I</i>).	80
5.10.3 Variation of stress as function of number of cycles for the nine sample used (sample A through to sample I).	80
5.12.1 Comparison of the measured Raman spectra for sample A as a function of map size.	82
5.13.1 The measured Raman spectra as a function of number of cycles for sample B	83
5.13.2 Stress variation as a function of the number of cycles for sample B.	84
5.13.3 Point to point stress variation as a function of the number of cycles for Sample B	85
5.13.4 Point to point stress variation as a function of the number of cycles for Sample B Continue.. . . .	86
5.13.5 2D Surface maps showing the nature and distribution of stress as a function of the number of cycles for sample B.	87
5.13.6 A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample B.	89
5.14.1 The measured Raman spectra as a function of number of cycles for sample E.	90
5.14.2 Stress variation as a function of number of cycles for sample E.	91
5.14.3 Point to point stress variation as a function of the number of cycles for Sample E.	92
5.14.4 Point to point stress variation as a function of the number of cycles for Sample E.	93

5.14.5 2D maps showing the nature and distribution of stresses as a function of number of cycles for sample E Continue..	94
5.14.6 A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample E.	95
5.15.1 Raman peak position and the full width measured at half maximum for sample F.	97
5.15.2 Stress variation as a function of number of cycles for sample F.	97
5.15.3 Point to point stress variation as a function of the number of cycles for Sample F.	99
5.15.4 Point to point stress variation as a function of the number of cycles for Sample F Continue..	100
5.15.5 2D maps showing the nature and distribution of stresses as a function of number of cycles for sample F.	101
5.15.6 A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample F.	102
5.16.1 Measured Raman spectra showing peak position as a function of number of cycles for sample G.	103
5.16.2 Stress variation as a function of number of cycles for Sample G.	104
5.16.3 Point to point stress variation as a function of the number of cycles for Sample G.	105
5.16.4 Point to point stress variation as a function of the number of cycles for Sample G Continue..	106
5.16.5 2D surface maps showing the distribution of the stress as a function of number of cycles for sample G.	107
5.16.6 A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample G.	108

5.16.7	Average surface stress variations as a function of the number of cycles for samples B, E, F and G.	109
5.16.8	The number of mapping points exhibiting tensile stress as a function of the number of fatigue cycles for samples B, E, F and G.	110
5.17.1	SEM images showing the cobalt pools and the diamond grains for sample B.	112
5.17.2	Energy dispersion spectra for sample B.	112
5.17.3	SEM images showing the cobalt pools and the diamond grains for sample E.	113
5.17.4	Energy dispersion spectra for sample E.	113
5.17.5	SEM images showing the cobalt pools and the diamond grains for sample F.	114
5.17.6	Energy dispersion spectra for sample F.	115
5.17.7	SEM images for sample G	116
5.17.8	Energy dispersion spectra for sample G.	117
6.2.1	Sample dimensions of the PCD layer used for the experiments and the map sizes employed for the Raman stress measurements.	121
6.3.1	X-ray diffraction instrument at NECSA.	125
6.5.1	Sample D16_C average residual stress comparison for map size.	127
6.5.2	Graph of the number of mapping points exhibiting tensile stresses, for Sample D16_C's Leached side.	130
6.5.3	Point to point stress variation as a function of the number of cycles for Sample D16_C's Leached side.	131
6.5.4	Point to point stress variation as a function of the number of cycles for Sample D16_C's Leached side.	132

6.5.5 Point to point stress variation as a function of the number of cycles for Sample D16_C's underside	134
6.5.6 Point to point stress variation as a function of the number of cycles for Sample D16_C's underside.	135
6.5.7 2D surface maps for Sample D16_C's Large map on the leached side.	137
6.5.8 2D surface maps for Sample D16_C's small map on the Leached side.	138
6.5.9 2D surface maps for Sample D16_C's large map on the underside.	140
6.5.10 2D surface maps for Sample D16_C's small map on the underside side.	141
6.5.11 Graph of the FWHM for Sample D16_C.	142
6.5.12 Sample D16_D average residual stress comparison for map size.	143
6.5.13 Graph of the number of mapping points exhibiting tensile stresses, for Sample D16_D.	145
6.5.14 Point to point stress variation as a function of the number of cycles for Sample D16_D's leached side.	146
6.5.15 Point to point stress variation as a function of the number of cycles for Sample D16_D's leached side Continue...	147
6.5.16 Point to point stress variation as a function of the number of cycles for Sample D16_D's underside.	148
6.5.17 Point to point stress variation as a function of the number of cycles for Sample D16_D's underside.	149
6.5.18 2D surface maps for Sample D16_D's large map on the leached side.	151

6.5.19 2D surface maps for Sample D16_D's Small map on the leached side.	152
6.5.20 2D surface maps for Sample D16_D's large map on the underside side.	153
6.5.21 2D surface maps for Sample D16_D's small map on the underside.	154
6.5.22 Graph of the FWHM for Sample D16_D.	155
6.5.23 Sample D16_F average residual stress comparison for map size.	156
6.5.24 Graph of the number of mapping points exhibiting tensile stresses, for Sample D16_F.	157
6.5.25 Point to point stress variation as a function of the number of cycles for Sample D16_F's leached side.	159
6.5.26 Small map point to point stress variation as a function of the number of cycles for Sample D16_F's leached side.	160
6.5.27 Large map point to point stress variation as a function of the number of cycles for Sample D16_F's underside.	161
6.5.28 Small map point to point stress variation as a function of the number of cycles for Sample D16_F's underside.	162
6.5.29 2D surface maps for Sample D16_F's Large map on the Leached side.	164
6.5.30 2D surface maps for Sample D16_F's Small map on the Leached side.	165
6.5.31 2D surface maps for Sample D16_F's Large map on the Underside.	166
6.5.32 2D surface maps for Sample D16_F's Small map on the Underside.	167
6.5.33 Graph of the FWHM for Sample D16_F.	168

6.6.1	Sample D16_C scatter plot showing stress variation on the Leached side.	170
6.6.2	Sample D16_C scatter plot showing stress variation on the underside.	172
6.6.3	Sample D16_C stress graph plot showing stress variation.. .	172
6.6.4	Sample D16_D scatter plot showing stress variation on the leached side.	174
6.6.5	Sample D16_D scatter plot showing stress variation on the underside.	175
6.6.6	Sample D16_D stress graph showing stress variation.	175
6.6.7	Sample D16_F scatter plot showing stress variation on the leached side.	177
6.6.8	Sample D16_C scatter plot showing stress variation on the underside.	178
6.6.9	Sample D16_F stress graph showing stress variation.	178

List of Tables

2.1	A comparison of the mechanical properties of the single crystal diamond and PCD	13
4.1	Experimental values for the hydrostatic pressure coefficient . .	54
5.1	Quasi - static loading test results.	64
5.2	Fatigue loading settings used for the unleached samples	66
5.3	Average peak position and FWHM for all samples	78
5.4	Table indicating Raman peak position and full width measured at half maximum for sample B.	83
5.5	Number of tensile points for Sample B	88
5.6	Raman Peak position for Sample E	90
5.7	Number of tensile points for Sample E	95
5.8	Raman Peak position for Sample F	96
5.9	Number of tensile points for Sample F	101
5.10	Raman Peak position for Sample G	103
5.11	Number of tensile points for Sample G	108
5.12	EDS results for sample B.	112
5.13	EDS results for sample E.	114
5.14	EDS results for sample F.	115

5.15	EDS results for sample G.	116
6.1	Quasi - static loading test results for the leached samples. . . .	122
6.2	Fatigue loading settings used for the leached samples.	122
6.3	: Parameters settings on D8 GADDS diffractometer.	126
6.4	Table of Raman results for Sample D16_C.	129
6.5	Table of Raman results for Sample D16_D.	144
6.6	Table of Raman results for Sample D16_F.	157
6.7	Table showing the measured stress values and the error for Sample D16_C on the leached side.	170
6.8	Table Showing the measured stress values and the error for Sample D16_C on the underside.	171
6.9	Table showing the measured stress values and the error for Sample D16_D on the leached side.	173
6.10	Table showing the measured stress values and the error for Sample D16_D on the underside.	174
6.11	Table showing the measured stress values on the leached side of the Sample D16_F.	176
6.12	Table showing the measured stress values on the underside of the Sample D16_F.	177

Chapter 1

Introduction

Diamond is a remarkable material and its unique properties have made it useful for many applications [1]. It is composed of a single element, carbon, which is one of the most abundant elements on earth and is found in three allotropic forms, amorphous carbon, graphite and diamond. Carbon atoms form very strong bonds with each other yielding solid crystalline materials like graphite and diamond [2]. The symmetrical tetrahedral bonding in diamond causes it to be the strongest known material while the unsymmetrical resonance and π bonding in graphite causes it to have high material strength within a plane due to the covalent bonding but it has weak inter-planar strength due to weak van der Waals bonding [3].

Following the discovery that diamond was pure carbon in 1797, there were several efforts and claims of diamond synthesis. Most of these claims were documented between 1879 and 1928 but after careful analysis most of these were not confirmed [4]. Earliest apparent successes were reported by J. Ballantyne in 1879 and Ferdinand F. Henri Moissan in 1893 [5]. Their method involved heating charcoal up to 3500 °C with iron inside a carbon crucible in a furnace. The molten iron was then rapidly cooled by immersion in water. The contraction generated by the cooling supposedly produced the high

pressure required to transform graphite to diamond. Sir Charles Algernon Parsons, a prominent scientist and engineer spent 40 years trying to reproduce the experiments of Moisson and Hannay and in 1928 he stated his belief that no synthetic diamonds (including those of Moisson and others) had been produced up to that date [4]. The first commercially successful synthesis of diamond was achieved by Hall in 1954. His breakthrough was using a “belt” press, which was capable of producing pressures above 10 GPa and temperatures above 2000 °C [6]. The belt press used a pyrophyllite container in which graphite was dissolved within molten nickel, cobalt or iron. These metals acted as a solvent-catalyst which both dissolved carbon and accelerated its conversion into diamond.

The successful synthesis of diamond paved the way for the manufacture of polycrystalline diamond (PCD) cylindrical tool-bits used in the oil and gas drilling industries [4]. These cutting tools are also widely used for machining non-ferrous metals and alloys as well as highly abrasive composite materials. During the drilling exercise the drill bits are subjected to repeated loads, fluctuating or cyclic and rapidly applied loads [7]. Such hostile cutting conditions with fluctuating loads induce cyclic stresses that often result in failure by fatigue. This failure in some instances inevitably leads to premature degradation of the cutter’s ability to drill and results in catastrophic failure [8]. Developing an understanding of the mechanism of fatigue crack growth behaviour in PCD materials in the quest for improved lifetime of the PCD tools is important both for the manufacturers and the customer.

1.1 Previous Work

Several authors have conducted work investigating and demonstrating evidence of fatigue in polycrystalline diamond. Lin *et al.*[8] studied the effects of

residual stress on PCD as well as calculating their magnitudes, these being as high as 1.4 GPa. They also highlighted factors that influence these residual stresses in PCD tool-bits consisting of a PCD layer sintered onto a tungsten carbide substrate and these include:

- (a) The thickness ratio of the diamond layer to the tungsten carbide substrate;
- (b) The effect of the cutter diameter.

They showed that the diameter of the cutter determines only the size of the uniform stress regions and has little influence on the magnitude of the residual stress. The larger the cutter diameter the larger the region of uniform stress distribution [9].

In the Hertz ring-crack test, Bell *et al.* [10] observed that a single indentation on a diamond surface had no perceptible effect, but on the order of 100 to 1000 indentations produced cracks. They concluded that the cracks were a result of fatigue damage. Paggett *et al.* [11] also did studies on residual stresses and stress gradients in PCD compacts using neutron diffraction. They recorded average in-plane stress in the diamond layer in the range of -250 MPa to -582 MPa, where the negative sign indicates that the stresses were compressive in nature. In other studies Dunn and Lee [12] conducted fatigue tests on sintered polycrystalline diamond where they showed that the maximum strength of the sintered diamond compacts is reduced under cyclic loading. In most of these works PCD tool-bits were used. Fatigue testing is discussed in more detail in sections 5.2 and 5.3.

Residual stresses play a critical role in the fatigue life of any engineering component or structure and as such their evaluation is equally critical. Since the early 1950s X-ray diffraction has been the standard technique for the measurement and evaluation of residual stresses. Whilst the majority of the applications of the techniques have been focussed mainly on steel materials, the

techniques has been applied in the diamond materials industry and research. In one such paper Haker et al. [13] recorded residual stress magnitudes of 0.5 - 0.8 GPa in free standing 0.5 - 2 mm thick samples of polycrystalline diamond. In 1995, Rats et al. [14] investigating the the crystalline quality as well as residual stresses in diamond films chemically vapour deposited on silicon substrates, made use of the Raman and x-ray diffraction techniques and measured stress in the range of -0.59 to 0.01 GPa. More recently Jia et al. [15] conducted tests to study the effects of initial crystal size of the diamond powder on the residual stress and morphology of the resulting PCD layers. For evaluating the stresses they employed X-ray diffraction and reported stress values slightly below $+0.22$ GPa.

In the current work only the PCD layers detached from their tungsten carbide cobalt (WC-Co) substrates were used as this configuration was required for the ball on three balls fatigue test employed.

1.2 Aims of the Work

The aims of this work were:

- Firstly to carry out a literature review on the theory of wear behaviour of polycrystalline diamond (PCD).
- Secondly to investigate fatigue type behaviour in non- leached PCD by the careful analysis of samples fatigued at room temperature.
- Conduct fatigue measurements on leached PCD samples for comparison with non leached PCD results.
- Conduct the literature review on the two techniques for residual stress analysis to be employed in this work, namely Raman Spectroscopy and X-ray diffraction stress measurement techniques.

- Conduct analysis of residual stress as determined by the X-ray diffraction and Raman spectroscopy methods on the surfaces of the PCD samples.
- Finally it was hoped that the characterization of the fatigue behaviour of leached and non-leached PCD will contribute towards understanding of the science behind the fatigue type processes which leads to premature failure of PCD tool bits, thus contributing to their improved lifetime.

Chapter 2

Literature Review

2.1 Diamond Structure and Bonding

All carbon-based molecules are covalently bonded since there are no electro-positive atoms present and the extra electrons needed to fill the valence shell of the electronegative atoms must be obtained by sharing electrons [16]. A perfect diamond is made up purely of carbon atoms. Each atom has four sp^3 orbitals and shares one with four other neighbouring carbon atoms [17]. This produces a tetrahedral structure containing five carbon atoms with extremely strong molecular bonds of length 0.154 nm and bond angle of 109.5° as shown in Figure 2.1.1a [2]. Each carbon atom in the structure lies at the centre of a tetrahedron, with an equidistant tetrahedral neighbour creating the structure of diamond (a build up of collective tetrahedrons), as shown in Figure 2.1.1b [2].

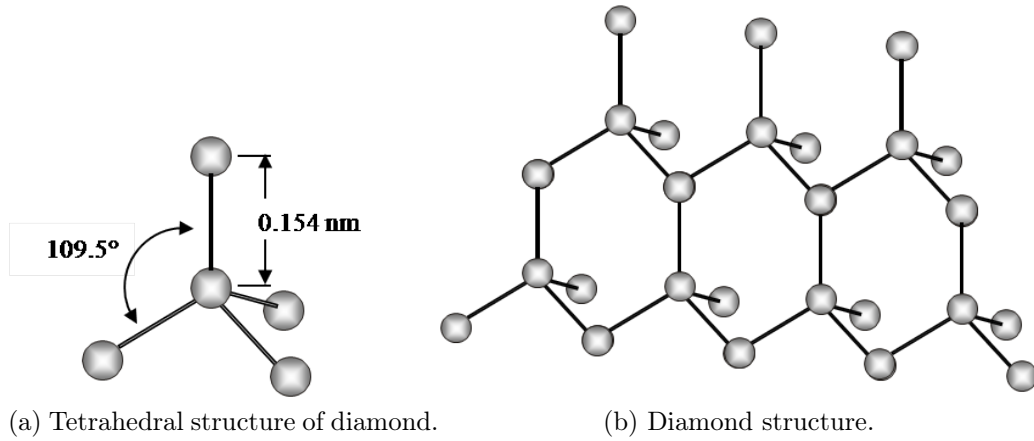


Figure 2.1.1: Arrangement of atoms in the diamond structure [2].

A disadvantage with single crystal diamond for many applications is the anisotropy of most of its properties [18]. It is well established that directionally dependent elastic and plastic anisotropy exists in single crystal diamond [19]. Brookes et al. [20] showed that the Knoop micro-hardness of single crystal diamond depended on the $\{111\} \langle 110 \rangle$ slip system. The hardness value measured is thus a property of the crystallographic plane pairs tested. The anisotropy of the Young's modulus and Poisson's ratio for diamond was also investigated by Klein et al. [21] and they observed that these properties were directional and functions of the symmetry of the crystal structure. Table 2.1 highlights this directionality as well as the mechanical properties of single crystal diamond when compared with PCD. In order to reduce the undesirable effects caused by the hardness anisotropy of single crystal diamond in abrasive applications, polycrystalline diamonds which are formed by sintering diamond powder in the presence of a suitable solvent catalyst, are used. Consisting of an extended diamond structure, made up of randomly oriented diamond-diamond bonded crystallites, the composite nature of these materials provide more homogeneous properties [4]. The random orientation prevents uneven wear due to varying hardness as a function of direction and catastrophic failure along the $\{111\}$ plane is retarded [22]. Polycrystalline diamond also have

greater toughness compared to single crystal diamond, due to the Hall-Petch effect and the composite nature of the material, and offers more homogeneous properties, [23], while still maintaining a reasonably high thermal conductivity [24]. The Hall-Petch effect describes the dependence of material strength on grain size, which influences slip resistance.

2.2 Diamond and Graphite

The relationship between diamond and graphite is both thermodynamic and kinetic in nature, as illustrated in the phase diagram shown in Figure 2.2.1. At normal temperatures and pressures, graphite is more stable than diamond by only a few eV and the fact that diamond exists at all is due to the very large activation barrier for conversion between the two [25]. There is no easy mechanism of converting between the two as interconversion requires almost as much energy as destroying the entire lattice and rebuilding it [26]. Therefore once diamond is formed, it cannot convert back to graphite under standard room temperature and pressure because the energy barrier is too high. Thus diamond is said to be metastable since it is kinetically stable but not thermodynamically stable [27]. For direct conversion of graphite to diamond high temperatures and pressures are required to overcome the large difference in the Gibbs energy between these two structures of carbon so that there is a rapid transition from one to the other. As highlighted earlier the barrier to be overcome here is the breaking of the bonds in the graphite so that the atoms are free to re-bond in the form of diamond [27].

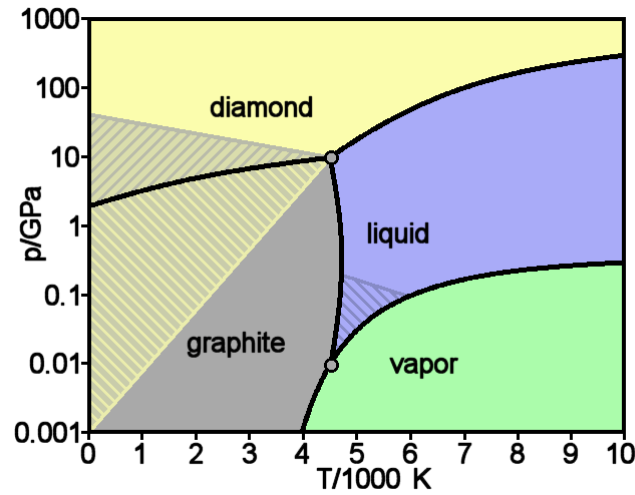


Figure 2.2.1: Phase diagram for carbon [25].

2.3 Commercial Synthesis of Diamond

The first synthetic diamond successfully made and the results published was in 1955 by General Electric. Berman and Simon produced a successful prediction of an equilibrium line for the transition from graphite to diamond [28], see Figure 2.3.1. This was done using the high pressure high temperature (HPHT) process, which is an attempt to imitate the conditions under which natural diamond forms deep in the earth. Graphite in the presence of a metallic solvent-catalyst is put into a huge press at high temperatures and pressure and converts to diamond over a period of hours. Generally the diamond crystals produced are typically a few millimetres in size which are sometimes too flawed to use as gemstones, but are extremely useful as hard wearing edges on cutting tools and drill bits [29]. However with improved methods it is possible to synthesise crystals of gemstone quality [30]. The synthesis of the PCD which is used in this current study is discussed in section 2.5.

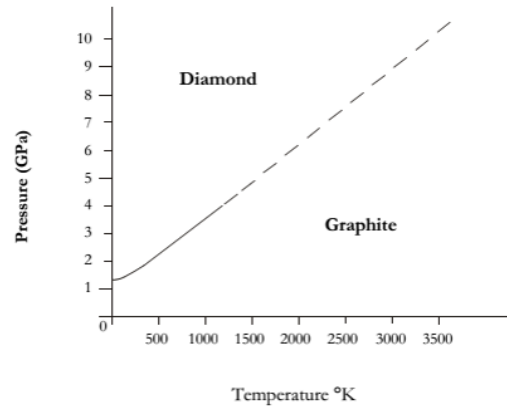


Figure 2.3.1: The equilibrium line as predicted by Berman and Simon [28].

2.4 Thermodynamics of Diamond Synthesis

Berman discusses the stability of the two allotropes of carbon in terms of Gibbs free energy G [2]. The difference between the free energies of graphite and diamond changes with pressure. This can be expressed as

$$(\delta\Delta G/\delta P)_T = \Delta V, \quad (2.4.1)$$

$\Delta G = G_d - G_g$, where G_d is the free energy of diamond and G_g is the free energy of graphite. $\Delta V = V_d - V_g$, where, V_d is the volume of diamond, V_g is the volume of graphite.

The subscripts d and g refer to the diamond and graphite respectively [31]. ΔV is negative since diamond is much denser than graphite ($3.52 \times 10^6 \text{ kg.m}^{-3}$ compared with $2.2 \times 10^6 \text{ kg.m}^{-3}$) [32]. ΔV decreases as pressure increases therefore according to equation 2.4.1, ΔG must also decrease with increasing pressure. At $\Delta G = 0$, diamond and graphite are in equilibrium. This alone however is not sufficient to have a conversion from graphite to diamond because of the large and positive activation energy [25]. This is due to the existence of a transition state with an increased volume, requiring higher

temperatures to overcome the activation energy, which in turn requires higher pressures. The metallic solvent/catalyst then provides an alternative lower energy reaction path for the conversion [27].

2.5 PCD Synthesis and Properties

As in single crystal diamond synthesis, sintered polycrystalline diamonds are synthesised by the application of high temperatures and high pressures with the difference being that instead of graphite as the starting material, diamond powder is used. Micro-sized diamond powder is thoroughly mixed with a metallic catalyst or binder phase, typically cobalt, and enclosed in a protective metal can [33]. In the case of the PCD tool-bits used in the present work, the powder is placed in contact with a previously sintered WC-Co compact from which the required catalyst is obtained by melting and diffusion of the Co binder phase [27]. A cylindrical holder is used to hold the substrate and the diamond powder and an electrically conducting sleeve surrounds the assembly to act as the heating element at high pressure. The holder is then placed in the HPHT press with an appropriate gasket in place to act as a pressure seal. This is then first pressurized to a typical pressure of 5 GPa and then heated to the carbon/catalyst eutectic temperature, which is typically 1500 °C [33]. Infiltration of the cobalt takes place and sintering of the mixture occurs by the dissolution of the diamond crystals at their edges and points of contact, followed by the epitaxial growth of diamond on faces and sites of low-angle contact between crystals [34]. Thus the binder phase is effectively excluded from the crystal contact points and true diamond to diamond bonds are formed [33]. This is then followed by cooling down in the press and de-pressurising. Due to the different thermal expansion coefficients between diamond and the tungsten carbide substrate, differential cooling takes place

with the substrate contracting more than the PCD layer and thus introducing compressive residual stress in the layer. Assuming that the stresses are transmitted uniformly through diamond layer regardless of thickness, the thermal stress due to the differential cooling can be calculated using the equation 2.5.1,

$$\sigma_{thermal} = \frac{E}{1 - \nu} \int_{293K}^T (\alpha_f - \alpha_s) dT. \quad (2.5.1)$$

where E is the Young's Modulus of diamond, ν the Poisson's ratio of diamond, α_f and α_s are the thermal expansion coefficients of the diamond film and the substrate respectively, and T being the growth temperature.

Assuming $E = 900$ GPa, $\nu = 0.2$, $\alpha_f = 4.2 \times 10^{-6} - 4.6 \times 10^{-6}$ K⁻¹, $\alpha_s = 5.4 \times 10^{-6}$ K⁻¹ and $T = 1700$ °C and applying equation 2.5.1, then the resulting induced compressive stresses will be between 1.51 GPa and 2.27 GPa. These theoretically derived values are extremely high compared to values reported by the authors cited in section 1.1.

One aspect that can play a role in tool service behaviour is the residual macro-stress state that is created as a result of this difference in coefficients of the thermal expansion between the diamond layer and WC-Co substrate [35]. At the completion of the process small pockets of the binder phase remain in the interstices of the continuous diamond network. Typically diamond concentration in PCD is 90 -97%. The synthesised PCD has some important characteristics such as those listed below and shown in Table 2.1

- PCD approaches the hardness of single crystal diamond but exhibits isotropic mechanical properties as a result of the random orientation of the diamond crystals [36].
- Residual stresses in the PCD layer are high as a result of reasons given earlier. The nature of these residual stresses is important to the manu-

facturers and the end users. Compressive residual stresses are known to inhibit the initiation and the propagation of cracks and so are desirable to obtain a long lifetime for the PCD tool. On the other hand tensile residual stresses promote the development of cracks and their propagation which result in a shorter tool lifetime [37].

Table 2.1: A comparison of the mechanical properties of the single crystal diamond and PCD [37].

Material	Knoop hardness ($kg.mm^{-2}$)	Tensile Strength (GPa)	Compressive Strength (GPa)	Young Modulus (GPa)	Poisson Ratio	Fracture Toughness ($MPa.m^{1/2}$)
Single Crystal Diamond						
(110) <110>	9500					
(111) <110>	9000	4.5 – 5.8	8.68 – 16.53	1000	0.1-0.29	3.4
(100) <110>	8600					
PCD	8000	0.34 – 1.50	1.9 – 6.9	900	0.2	6.0 – 8.8

Chapter 3

Fatigue

3.1 Introduction

The majority of mechanical engineering failures are caused by fatigue and this is because the materials used in these fields usually operate under alternating loads which are sufficiently severe to result in failure [7]. By definition, fatigue failure can be considered to be the tendency of a material or structure to fracture by means of progressive brittle cracking under repeated stress of any intensity considerably below the normal strength of the material or structure [38]. Polycrystalline diamond tools used in the oil drilling industry sometimes fail during use and the fact that they fail after being subjected to alternating varying loads gives rise to the possibility of the failure being a result of fatigue type processes during operation [8]. Diamond is a brittle material and the suggestion that diamond fatigues under a repeated stress at room temperature would seem at first sight surprising [39], since dislocations in diamond are immobile at room temperature [10]. However results suggesting that sintered diamond compacts can exhibit fatigue in drilling experiments have been given by Dunn *et al.* [12]. Fatigue in most materials (excluding polymers) is usually associated with either dislocation motion or a

combination of stress and chemical effects; with diamond however the process is thought to be a slow development of submicroscopic cracks to observable dimensions [24]. Grain boundaries in polycrystalline materials can constitute sites where cracks can form preferentially by a variety of mechanisms [36]. The fracture of ductile materials is in general attributed to cyclic plasticity due to relatively unimpeded dislocation motion. In total contrast polycrystalline materials invariably lack dislocation mobility due to the randomly oriented crystals leading to dislocation pile ups, static extrusions in the form of ledges and stress concentration along the boundaries where neighbouring grains meet [40]. Micro-cracks soon ensue and grow to some critical length resulting in failure. As such fatigue then plays a crucial role in determining the life of the material or structural component [41].

3.2 Fundamentals of Fatigue Life

Fatigue life of a material or component comprises of both the crack initiation stage and the crack propagation stages [36]. The life is determined by the number of elapsed cycles required to initiate a crack and to propagate the crack from submicroscopic dimensions to some critical size [42]. Crack initiation and the micro-crack growth phases generally account for most of the fatigue life, especially in low stress-long life regimes [11]. Figure 3.2.1 shows the different stages of fatigue.

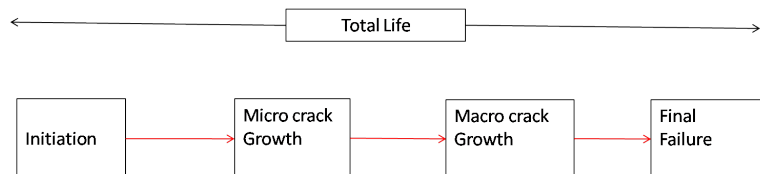


Figure 3.2.1: Stages of fatigue life [42].

With many engineering materials two fracture modes are possible and these are *ductile* and *brittle* fracture [38]. Classification is based on the ability of the

material to experience plastic deformation and the mode of fracture is highly dependent on the mechanism of crack propagation [42]. For brittle fracture, the cracks may spread very rapidly, with minimal plastic deformation [9]. Such cracks are said to be unstable and crack propagation once started will continue spontaneously without an increase in the magnitude of the applied stress. The crack initiation and propagation in the fatigue life of a material can be represented mathematically as shown in equation 3.2.1, namely

$$N_f = N_i + N_p \quad (3.2.1)$$

where N_f is the total fatigue life, which is a sum of the initiation and propagation lives;

N_i is the number of cycles required to initiate a crack, and

N_p is the number of cycles required to propagate the crack to a critical size [42].

Figure 3.2.2 details the the sequential stages of of cyclic deformation until fatigue failure. Stage I is dominated by crack initiation and in metals this would included a bit of work-hardening. Once the crack(s) have been formed then crack growth and propagation ensues and this is in stage II of the fatigue life. The area represented by stage III is the region of fatigue failure depending on the alternating stresses related to the number of loading cycles.

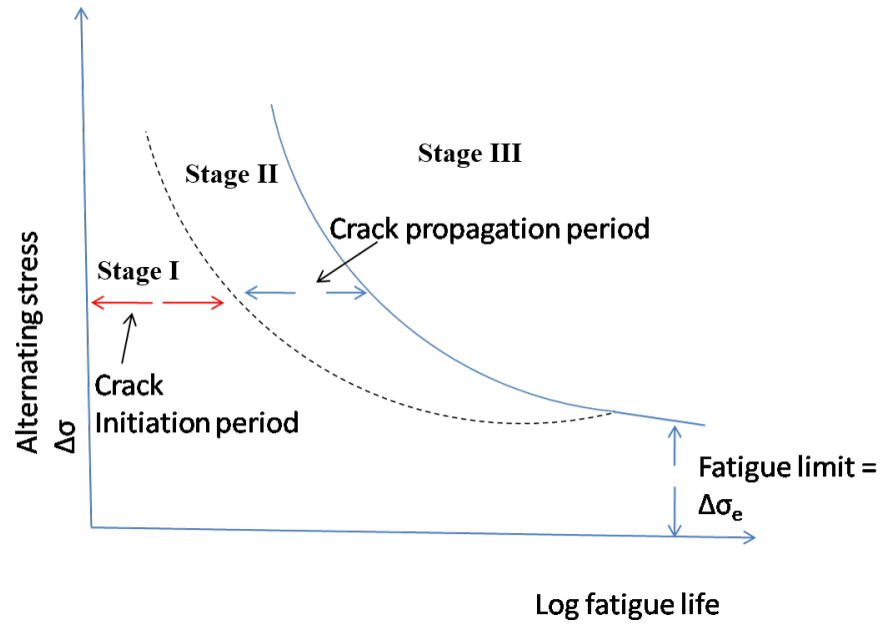


Figure 3.2.2: Schematic illustration of the four stages of fatigue [42].

3.3 The Griffith Energy Theory

In 1924 Griffith derived a criterion for crack growth using an energy approach. The approach is based on the theory that energy has to be conserved in all processes [42]. He proposed that when a crack grows the change (decrease) in the potential energy stored in the system, U is balanced by the change (increase) in surface energy, S due to the creation of new crack faces [43]. The analysis is based on the assumption that incipient fracture in ideally brittle materials occurs when the magnitude of the elastic energy supplied at a crack tip is greater or equal to the magnitude of the elastic energy required to advance the crack by an incremental increase [44]. If one considers an infinite plate of unit thickness that contains a through-thickness crack of length $2a$ and that is subjected to uniform tensile stress σ , applied at infinity, the total potential energy of the system, U may be written as shown in equation 3.3.1, namely

$$U = U_0 - U_a + U_\gamma \quad (3.3.1)$$

where U_0 is the elastic energy of the uncracked plate, U_a is the decrease in the elastic energy caused by introducing the crack in the plate, and U_γ is the increase in the elastic-surface energy due to the formation of the crack surfaces.

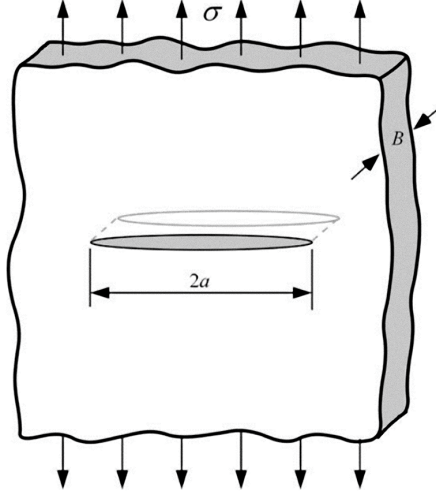


Figure 3.3.1: Griffith crack model [44].

Griffith used the stress analysis that was developed by Inglis [45], to show that [44],

$$U_a = \frac{\pi\sigma^2 a^2}{E}, \quad (3.3.2)$$

where E is the Young's Modulus of the material. The elastic surface energy, U_γ is equal to the product of the elastic-surface energy of the material γ_e and the new surface area of the crack; thus

$$U_\gamma = 2(2a\gamma_e). \quad (3.3.3)$$

Consequently the total energy of the system, U , is

$$U = U_0 - \frac{\pi\sigma^2 a^2}{E} + 4a\gamma_e. \quad (3.3.4)$$

The equilibrium condition for crack extension is obtained by setting the first derivative of U with respect to the crack length a , equal to zero. The resulting equation can be written as

$$\sigma^2 a = \frac{2E\gamma_e}{\pi}. \quad (3.3.5)$$

Equation 3.3.5 can be re-written as

$$\sigma\sqrt{a} = \sqrt{\frac{2E\gamma_e}{\pi}}. \quad (3.3.6)$$

This indicates that crack extension in ideally brittle materials is governed by the product of the applied nominal stress and the square root of the crack length and by the material properties E and γ_e [42]. The right hand side of equation 3.3.5 is equal to a constant value that is characteristic of a given ideally brittle material. Hence equation 3.3.6 indicates that crack extension in such materials occurs when the product $\sigma\sqrt{a}$ attains a constant critical value. Equation 3.3.5 can be rearranged as equation 3.3.7

$$\frac{\pi\sigma^2 a}{E} = 2\gamma_e. \quad (3.3.7)$$

The left hand side has been designated as the energy release rate, G , and represents the elastic energy per unit crack surface area that is available for infinitesimal crack extension. The right hand side represents the material's resistance to crack extension, R [12].

In 1948 Irwin suggested that the Griffith Fracture criterion for brittle material could be modified to also include metals that exhibit plastic deformation [45]. The modification recognized that a material's resistance to crack extension is equal to the sum of the elastic surface energy and the plastic-strain work γ_p accompanying crack extension [44]. Equation 3.3.7 then becomes

$$\frac{\pi\sigma^2 a}{E} = 2(\gamma_e + \gamma_p), \quad (3.3.8)$$

with the quantities as defined previously.

3.4 Fracture Toughness

Toughness can be defined as the amount of energy per unit volume, that a material can absorb before it fractures. It is also considered to be the resistance of a material to brittle fracture in the presence of a flaw or a crack. The toughness of a material can be evaluated by calculating the total area under a stress/strain curve up to the point of fracture [44]. The fracture toughness or critical stress intensity factor K_c of a material is a measure of the resistance to crack propagation and is related to the Young's Modulus, E , and the energy absorbed in making the crack γ by equation 3.4.1, namely

$$K_c = \sqrt{2E\gamma}. \quad (3.4.1)$$

If the thickness of the sample is close to the dimensions of the crack then the condition of plane stress exists i.e. the normal component will be $\sigma_z = 0$ and K_c decreases with increasing specimen thickness [27]. When K_c becomes independent of thickness the condition of plane strain is said to exist and use is made of the constant value K_{Ic} which is a measure of the plane strain fracture toughness defined by equation 3.4.2, namely

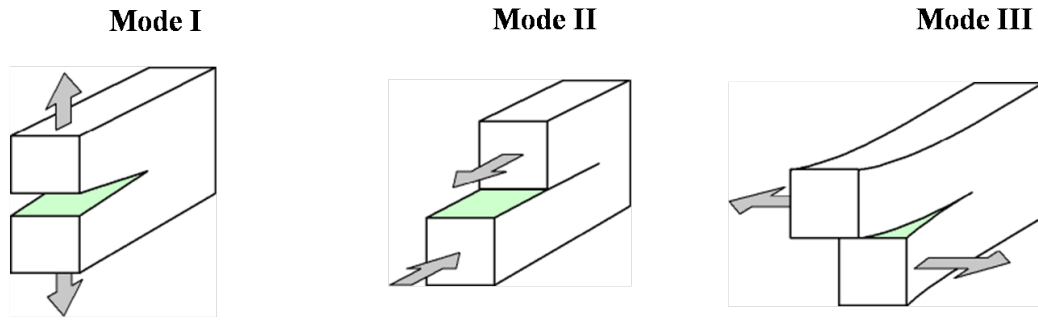
$$K_{Ic} = Y\sigma_c\sqrt{\pi a}, \quad (3.4.2)$$

where Y is a dimensionless parameter dependent on the material and crack geometry, σ_c is the critical applied tensile stress for fracture, a is the crack

length and the subscript I indicates mode I (see fig 3.4.1) cracking. Morrell et al. [46] determined the fracture toughness for polycrystalline diamond to be approximately $10 \text{ MPa} \cdot \text{m}^{\frac{1}{2}}$, however Miess and Rai [47], concluded that the toughness is a function of the starting diamond powder grain size, after they used the Brazilian disc test to determine the fracture toughness of pre-notched polycrystalline discs. McNamara [48] whilst agreeing with the work done by Miess and Rai [47], suggests that to improve the measured value of the fracture toughness of PCD, it is necessary to accurately analyse the underlying failure mechanics and define the structure-property relationship linking fracture initiation and microstructure.

3.4.1 Modes of Crack Propagation

In stress analysis for plane cracks the three basic modes of crack-surface displacement are as shown in Figure 3.4.1. Mode I (opening mode) corresponds to normal separation of the crack walls under the action of tensile stresses; Mode II (sliding mode) corresponds to longitudinal shearing of the crack walls in a direction normal to the crack front; Mode III (tearing mode) corresponds to lateral shearing parallel to the crack front. Of the three modes, the first is by far the most pertinent to crack propagation in highly brittle solids [45].



Mode I : Opening or Tensile Mode

Mode II : Sliding or In-Plane Shear Mode

Mode III : Tearing or Anti-Plane Shear Mode

Figure 3.4.1: Showing the three basic modes of crack tip deformation [41].

3.5 Paris' Law - The Fatigue Crack Growth Rate Curve

For constant amplitude loading one can make use of the correlation between fatigue crack growth rate da/dN and the stress intensity factor range ΔK . The proposal that the rate of crack propagation per cycle should be controlled by the range of the stress intensity factor for the cycle was first made by P.C. Paris as part of his research work [49]. The general relationship now known universally as the Paris Law is as follows:

$$\frac{da}{dN} = C (\Delta K)^m, \quad (3.5.1)$$

where da/dN is the rate of crack growth per cycle, ΔK is the range of stress intensity factor at the crack tip, and C and m are constants that depend on the material environment, frequency, temperature and stress ratio.

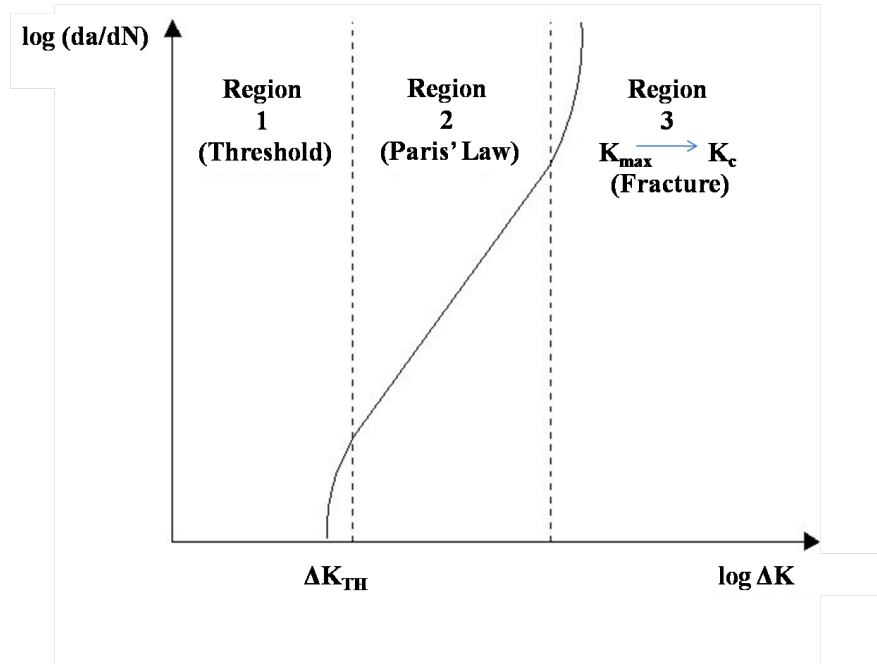


Figure 3.5.1: Typical fracture mechanics fatigue crack propagation behaviour [41].

The characteristic sigmoidal shape of a $\log(da/dN)$ vs $\log \Delta K$ fatigue crack growth rate curve is shown in Figure 3.5.1. The curve is divided into three regions according to curve shape and the mechanisms of crack extension.

Region I

There is a threshold value ΔK_{th} below which cracks do not propagate. Above this value the crack growth rate increases relatively rapidly with increasing ΔK .

Region II

There is often a linear log-log relationship between da/dN and ΔK .

Region III

The crack growth rate curve rises to an asymptote where the maximum stress intensity factor K_{max} , in the fatigue stress cycle becomes equal to the critical stress intensity factor K_c [49].

3.6 Classification of Tool Fracture

Tool fracture is mainly influenced by the strength of the material and the stress it is being exposed to [50]. In terms of the amount of plastic deformation taking place before or at the event, tool fracture can usually be classified into two categories, namely, plastic fracture and brittle fracture [51]. Since ceramic tool materials are of brittle nature, plastic fracture is very rare due to a tool's high hardness and high compressive strength [51]. Premature or early fracture and late fracture are the two forms of brittle fracture of ceramic tools. The latter often is a result of fatigue, which as highlighted in earlier text, is the progressive build up of localized damage. The most prevalent modes of brittle fracture are: chipping, spalling and cracking [52].

Chipping : This is a type of premature/early fracture which usually occurs on the cutting edge or in the area near the tool nose during operation [53]. It may be a result of either continuous or interrupted cutting operations. It usually results in the formation of one or several small notches on the cutting edge. The tool can however still be used as long as the size of the chip area is within the wear criteria [51].

Cracking : This is often a result of fatigue effect after a long period of cutting. Two kinds of cracks are formed in these cutting tools. The first are mechanical fatigue cracks which result from mechanical impacts and often run parallel to the cutting edge or form a network. The second are thermal cracks caused by thermal shock [53].

Spalling : This is when a layer of tool material is stripped off the tool rake face or flank face. Depending on the contact point of the impact cutting force on the tool faces, the fractured fragment, which is often a shell-like shape, may be at the cutting edge or a small distance away from it. This is the kind of fracture most often encountered when using ceramic tools in operations

such as milling. Czichos [54] put forward a “spalling theory of wear” based on the studies he did on the plastic-elastic stress fields in the sub-surface regions of sliding asperity contacts and the possible dislocation interactions [53]. He states that the generation of sheet-like wear particles is explained on the basis of a chain of events which are;

- transmittance of stresses at contact points,
- incremental plastic deformation per cycle,
- sub-surface void and crack nucleation,
- crack formation and propagation,
- formation of sheet like wear particles.

Chapter 4

Residual Stress Measurement Techniques

4.1 Residual Stress

Residual or internal stresses can be defined as the stresses that remain in the bulk of a material in the absence of any external load [55]. Accordingly the state of the residual stresses is self-equilibrating meaning they have to be globally balanced with the resultant force and moment being equal to zero i.e.

$$\int \sigma dA = 0 \quad (4.1.1)$$

$$\int \sigma z dA = 0 \quad (4.1.2)$$

Where σ is the residual stress at a point, dA is an infinitesimal area in the material or body and z is the distance measured from a reference point.

These stresses can be either macro or micro in nature and both can be present in a component at any one time [56]. It is possible to classify the stresses as:

- *Type I*: Macro residual stress that develop in the body of a component on a scale larger than the grain size of the material;
- *Type II*: Micro residual stresses that vary on the scale of an individual grain;
- *Type III*: Micro residual stresses that exist within a grain, essentially as a result of the presence of dislocations and other crystalline defects.

Residual stresses generally develop in a structure due to non-uniform plastic deformation and are stored within the structure as a tangled network of dislocations [57]. Due to the numerous sources of origination, it is also possible to classify the residual stresses using their origin as follows;

- differential plastic flow
- differential cooling rates
- phase transformations with volume change.

These categories can easily be listed as mechanical, thermal and metallurgical groupings of the origin of residual stresses, respectively. Due to the important role they play in the fatigue life of the material it is important to be able to measure them precisely and incorporate them into the material and structure designs.

4.2 Residual Stress Measurement Methods

Residual stress measurement is of critical significance to the integrity as well as the reliability of engineering components. It is therefore critical that reliable methods of measurement be employed when measuring them coupled with a good understanding of the information the subsequent measurement conveys,

[58]. In the past few decades several methods for measuring residual stresses in different components have been developed. These methods can be broadly classified as destructive and non-destructive methods. In this chapter a few of these methods will be highlighted but more emphasis is accorded to the Raman spectroscopy and the X-ray diffraction techniques, which are the two techniques employed in this current work for the stress analysis.

4.3 Mechanical (Destructive) Methods

Also known as destructive or semi-destructive, these techniques are usually applied in the measurement of type I residual stresses. These methods rely on the strict monitoring of changes in component distortion either during the generation of the residual stresses or their effect if already present, by deliberately removing materials to allow stresses to relax [59]. Whilst these techniques are widely applied for stress evaluation in steel and metal materials, they are generally not applicable to PCD due to the hardness and toughness of PCD. Only a few of these destructive methods are discussed here.

4.3.1 Curvature Method

Curvature measurements are mainly used to establish the stresses within coatings and layers. The layer deposition process can induce stresses which causes the substrate to curve and this resulting change makes it possible to calculate the corresponding variations in stress as a function of layer thickness [60]. The curvature can be measured using contact methods (e.g profilometry, strain gauge) allowing curvatures down to 0.1 m^{-1} to be routinely characterized. Measurements are normally made on narrow strips ($width/length < 0.2$) to avoid multi-axial curvature and mechanical instability. The Stoney equation is often applied to relate the deflection g of a thin beam of length l and

stiffness E to the stress σ along the beam [61],

$$\sigma = -\frac{4}{3}E \frac{h^2}{l^2} \frac{dg}{dh} \quad (4.3.1)$$

where h is the layer thickness.

Curvature measurements can also be used to determine the stresses by incremental layer removal [62]. This method is also known as the back-grinding method.

4.3.2 Hole drilling

This is the most mature and widely employed destructive method for measuring residual stresses. The hole-drilling method involves drilling a shallow hole around which the local surface deformations are measured by a specially designed strain-gauge rosette [59].

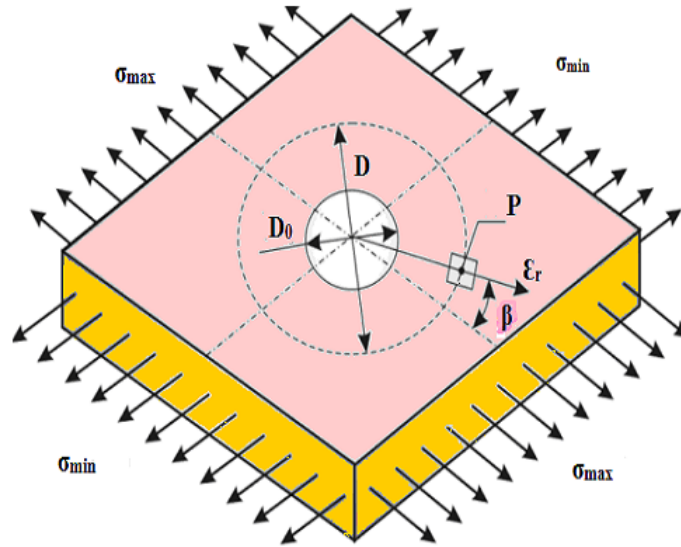


Figure 4.3.1: Residual stress measurement methods: hole-drilling [62].

The small drilled hole is usually 1 to 5 mm in diameter and depth, right in the centre of the specialized strain gauge rosette. In most cases the residual stresses are assumed to be uniform through the depth of the structure or

material, thereby simplifying the calculation procedure [63]. The stress can then be calculated using the relationship between the relieved strain and the originally existing residual stress, i.e.

$$\varepsilon_r = A(\sigma_{max} + \sigma_{min}) + B(\sigma_{max} - \sigma_{min}) \cos 2\beta \quad (4.3.2)$$

where ε_r relieved strain measured by a radially aligned strain gage centered at P , σ_{max} and σ_{min} are the maximum and minimum principal residual stresses respectively, β is the angular coordinate measured anticlockwise from the maximum principal stress direction. A and B are the calibration coefficients that have to be determined and D and D_0 are the diameter of the gauge circle and the diameter of the drilled hole respectively.

4.3.3 Ring Core

The ring-core method is a linear elastic theory based mechanical technique used to quantify the principal residual stresses within a specified depth of material or structure [59]. This method was developed almost simultaneously with the development of the hole-drilling method, thus the operational principles of the method are based on the hole-drilling method with the main deviation being that, instead of drilling a hole through the middle of a strain gauge rosette, a groove is milled around the rosette [64]. A small annular groove in the surface of the specimen is milled concentrically around a strain gauge rosette, leaving the upper part of the core separated from the surrounding material. This separation causes the relaxation of the residual stresses presented in core, which is represented by deformation of the core [65]. These deformations can be measured by strain gauges designed for measuring relieved strains by the Ring-Core method. The annular groove can be machined with a suitable cutter, like a ring saw. This method is less sensitive to errors

involved in the positioning of the cutting tool relative to the strain gauge and stress can be measured more accurate up to the yield stress of material [59].

4.4 Non-Destructive stress measurement techniques

Traditionally the main non-destructive techniques in stress measurement have been X-ray diffraction, neutron diffraction and ultrasonic techniques and more recently the Raman spectroscopy technique. These methods do not require the specimen to be damaged in order for the stress to be evaluated. Due to this non-destructive component in the evaluation of residual stresses, they are more desirable for use [66]. However due to their no-destructive nature, these techniques generally surface values.

The ultrasonic method utilizes the relationship between sound wave speed and any residual stresses in a material. In general the change in the wave speed is proportional to the average residual stress present [59]. The neutron diffraction technique is based on an analogous principle to the X-ray diffraction method as such a detailed discussion of only the X-ray diffraction and the Raman spectroscopy techniques will be given in the next sections.

4.4.1 X-ray diffraction stress measurement technique

The method of residual stress measurements using the X-Ray diffraction (XRD) technique is well established [67]. Application of XRD stress measurement to practical engineering problems began in the early 1950s. The advent of X-Ray diffractometers and the development of the plane-stress residual stress model allowed the successful application of the technique to hardened steels [67]. Today measurements are routinely performed in ceramic, inter-metallic,

composite and fine grained crystalline material. Though the term stress measurement is widely used, stress is actually an extrinsic property and must be calculated from a directly measurable property such as strain or force and area [68].

The underlying principle of this method is the determination of the change in inter-atomic spacing d of a particular set of crystallographic planes when the crystal or polycrystalline aggregate is strained homogeneously [69]. The deformations cause changes in the spacing of the lattice planes from their stress free value to a new value that corresponds to the magnitude of the applied stress. This new spacing will be the same in any similarly oriented planes, with respect to the applied stress and the crystal lattice therefore effectively acts as a very small strain gauge [57]. For the determination of elastic strains only, the method is fundamentally a measurement of a set of inter-atomic spacings altered by elastic stresses. The governing elasticity assumes a material whose stress state is being measured to be elastic, homogeneous, and isotropic [70]. The diffraction of X-rays from an atomic plane in a crystalline material can be described by Bragg's law.

4.4.2 Bragg's law

A crystal can be defined as a solid composed of atoms arranged in a pattern periodic in three dimensions [71]. When monochromatic X-Rays are incident on the crystal, these periodic planes of atoms can cause constructive and/or destructive interference patterns by diffraction. The nature of the interference depends on the inter-planar spacing d , and the wavelength of the incident radiation λ . Figure 4.4.1 shows one such crystal in which atoms are arranged in a periodic manner with interatomic spacing d . A narrow beam of monochromatic x-Ray of wavelength λ is allowed to fall on a crystal with the crystal

acting as a diffraction grating. In other words the atoms would act as the opaque part whilst the interatomic spacing could act as the transparent slits to the passage of x-rays.

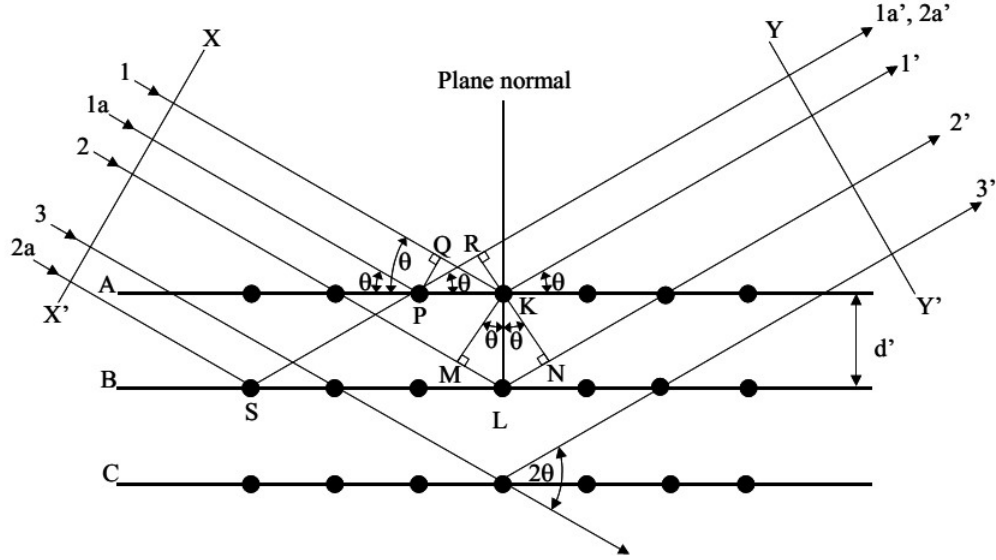


Figure 4.4.1: Diffraction of X-rays by a crystal lattice [56].

Consider a single plane of atoms, (row A in Figure 4.4.1). Ray **1** and **1a** strike atoms **K** and **P** in the first plane of atoms and are scattered in all directions. Only in directions **1'** and **1a'** are the scattered beams in phase with each other, and hence interfere constructively. Constructive interference is observed because the difference in their path length between the wave fronts **XX'** and **YY'** is equal to zero. That is

$$QK - PR = PK \cos \theta - PK \cos \theta = 0 \quad (4.4.1)$$

Any rays that are scattered by other atoms in the plane that are parallel to **1'** will also be in phase and thus add their contributions to the diffracted beam, thereby increasing the intensity. Now consider the condition necessary for constructive interference of rays scattered by atoms in different planes. Rays **1** and **2** are scattered by atoms **K** and **L**. The path difference for rays **1K1'**

and $2\mathbf{L2}'$ can be expressed as

$$ML + LN = d' \sin \theta + d' \sin \theta \quad (4.4.2)$$

This term also defines the path difference for reinforcing rays scattered from atoms $\mathbf{S}$ and $\mathbf{P}$ in the direction shown in Figure 4.4.1, since in this direction there is zero path difference between rays scattered by atoms $\mathbf{S}$ and $\mathbf{L}$ or $\mathbf{P}$ and $\mathbf{K}$. Scattered rays $\mathbf{1}'$ and $\mathbf{2}'$ will be in phase only if the path difference is equal to a whole number n of wavelengths, that is if

$$2d' \sin \theta = n\lambda \quad (4.4.3)$$

where λ is the wavelength of the incident radiation, d' the inter-planar spacing and θ the Bragg angle, which is the angle the incident beam makes with the diffracting plane [58]. This is commonly known as Bragg's Law and it forms the fundamental basis of X-ray diffraction theory. When the relation is satisfied, the diffracted rays that are in phase will result in constructive interference and those out phase in destructive interference. The three-dimensional symmetry of the unit cell was not taken into consideration in the derivation of Bragg's law [56]. Due to the particular positions of the atoms in the unit cell Bragg's law is necessary but not sufficient condition for diffraction [59]. The total diffraction intensity from a unit cell can be determined by summing up the waves from each atom.

4.4.3 Uniaxial stress Measurements

The simplest way to approach the X-ray diffraction method is through the case of pure tension, where the stress acts only in a single direction. Consider a cylindrical rod with cross-sectional area A that is stressed elastically in

tension by a force F as shown in figure 4.4.2.

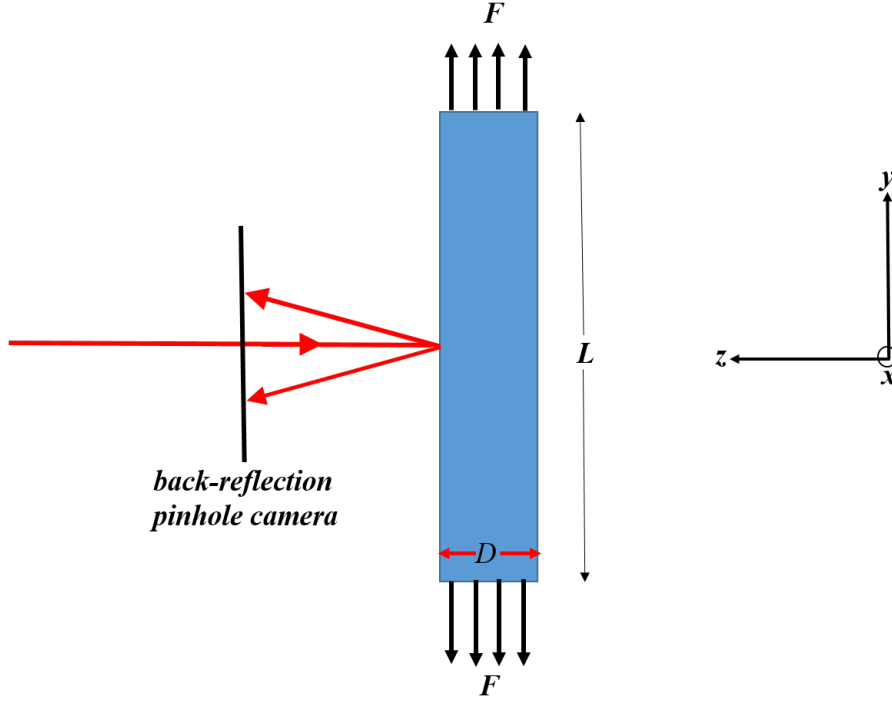


Figure 4.4.2: Rod in tension, with X-rays reflected from planes parallel to axis.

There is some stress in the y -direction given by,

$$\sigma_y = \frac{F}{A} \quad (4.4.4)$$

In the x and z directions no stresses are being experienced. It is important to note that in the y - direction only the normal stress is being considered as any shear stresses present are not directly measurable by the x-ray diffraction method. This stress σ_y produces a strain ε_y in the y -direction given by

$$\varepsilon_y = \frac{\Delta L}{L} = \frac{L_f - L_0}{L_0} \quad (4.4.5)$$

Where L_0 and L_f are the original and final lengths of the rod. This strain is related to the stress by,

$$\sigma_y = E\varepsilon_y \quad (4.4.6)$$

Where E is the Young's Modulus. Elongation of the rod consequently results in a decrease in the diameter D of the rod. Strains in the x and z directions are thus given by

$$\varepsilon_x = \varepsilon_z = \frac{D_f - D_0}{D_0}. \quad (4.4.7)$$

Where D_0 and D_f are the original and final diameters of the rod. If the material of the rod is isotropic, these strains are related by the equation,

$$\varepsilon_x = \varepsilon_z = -\nu\varepsilon_y. \quad (4.4.8)$$

Where ν is the Poisson's ratio for the material of the rod. To determine ε_y would require diffraction from planes perpendicular to the axis of the bar [71]. This is physically impossible hence there is a need to make use of the reflecting planes parallel to the axis of the bar by making the back reflection x-ray measurement as indicated in figure 4.4.2. Using this configuration a measurement of the strain in the z direction can be obtained since this is given by

$$\varepsilon_z = \frac{d_n - d_0}{d_0} \quad (4.4.9)$$

Where d_n is the spacing of the planes parallel to the rod axis under stress and d_0 is the spacing of the same planes in the absence of stress.

Combining equations 4.4.7, 4.4.8 and 4.4.9 yields

$$\sigma_y = -\frac{E}{\nu} \left(\frac{d_n - d_0}{d_0} \right) \quad (4.4.10)$$

and this gives the required uniaxial stress.

4.4.4 Biaxial Stress Measurements

In a rod subject to pure tension the normal stress acts only in a single direction, however in a more general case there will be stress components in two or three directions at right angles to one another forming a biaxial or triaxial stress system[58]. Generally the stress at right angles to a free surface is always zero at that surface, thus we only deal with two stress components and these lie in the plane of the surface. Only in the interior of a body can the stresses be triaxial [71]. Within a stressed body, whatever the stress system, three mutually perpendicular directions (1, 2 and 3) can be found which are normal to planes on which no shear stress acts. These are called the principal directions, and the stresses acting in these directions (σ_1 , σ_2 and σ_3) are called the principal stresses [71].

Consider a portion of the surface of a stressed body as shown in figure 4.4.3.

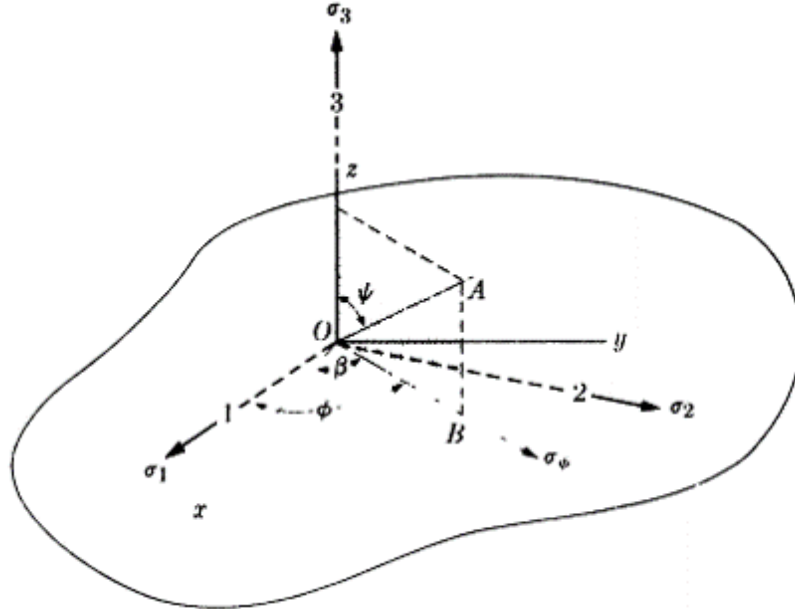


Figure 4.4.3: Stresses at the surface of a stressed body [71].

Principal stresses σ_1 and σ_2 are parallel to the surface, and σ_3 is zero, however

ε_3 , the strain normal to the surface, is not zero as it has a finite value given by the Poisson's contractions due to σ_1 and σ_2 , thus,

$$\varepsilon_3 = -\nu(\varepsilon_1 + \varepsilon_2) = -\frac{\nu}{E}(\sigma_1 + \sigma_2) \quad (4.4.11)$$

The value of ε_3 can be found by measuring the spacing d of planes parallel to the surface and is given by equation 4.4.9, and substituting this value into equation 4.4.11 yields,

$$\frac{d_n - d_0}{d_0} = -\frac{\nu}{E}(\sigma_1 + \sigma_2) \quad (4.4.12)$$

Thus in the general case, only the sum of the principal stresses can be obtained from such a measurement, and the value of d_0 is required. Normally, however we want to measure the stress σ_ϕ acting in some specified direction, such as OB as shown in figure 4.4.3, where OB makes an angle ϕ with principal direction 1 and an angle β with the x-axis. This is done by taking two exposures, one with the incident beam normal to the surface and one with it inclined along OA at some angle ψ to the surface normal are needed. OA lies in a vertical plane through the direction OB in which it is desired to measure the stress, and ψ is usually made equal to 45° . The normal-incidence pattern measures the strain approximately normal to the surface, and the inclined-incidence pattern measures the strain approximately parallel to OA [71]. These measured strains are therefore approximately equal to ε_3 and ε_ψ , respectively, where ε_ψ is the strain in a direction at an angle ψ to the surface normal. Elasticity theory for an isotropic solid shows that the strain along the inclined line OA is, [71],

$$\varepsilon_\psi = \frac{1}{E} [\sigma_\phi (1 + \nu) \sin^2 \psi - \nu(\sigma_1 + \sigma_2)] \quad (4.4.13)$$

Subtracting equation 4.4.11 from equation 4.4.13 yields,

$$\varepsilon_\psi - \varepsilon_3 = \frac{\sigma_\phi}{E} (1 + \nu) \sin^2 \psi \quad (4.4.14)$$

But,

$$\varepsilon_\psi = \frac{d_i - d_0}{d_0} \quad (4.4.15)$$

where d_i is the spacing of the inclined reflecting planes, approximately normal to OA , under stress, and d_0 is their stress-free spacing.

Expressing the strain in terms of plane spacings yields,

$$\frac{d_i - d_0}{d_0} - \frac{d_n - d_0}{d_0} = \frac{d_i - d_n}{d_0} = \frac{\sigma_\phi}{E} (1 + \nu) \sin^2 \psi \quad (4.4.16)$$

Since d_i , d_n and d_0 are very nearly equal to one another, $(d_i - d_n)$ is small compared to d_n and so d_0 can be replaced with d_n with very little error, hence equation 4.4.16 becomes

$$\sigma_\phi = \frac{E}{(1 + \nu) \sin^2 \psi} \left(\frac{d_i - d_n}{d_n} \right) \quad (4.4.17)$$

This is known as the $\sin^2 \psi$ method. This equation allows us to calculate the stress in any chosen direction from plane spacings and is valid whether the stress system is uniaxial or is biaxial. From the equation it is not necessary to know the unstressed plane spacing d ; the measurement is therefore non-destructive, because there is no necessity for cutting out part of the specimen to obtain a stress free sample [65].

4.4.5 Grazing Angle method

The following discussion is based on the work by Huang and colleagues,[72]. The traditional $\sin^2 \psi$ stress measurement method is based on the measure-

ment of the shift of a diffraction peak position recorded for different ψ angles. A specific diffraction plane is carefully selected and the inter-planar spacing is measured from a coupled $\theta - 2\theta$ scan [standard Bragg–Brentano (B-B) geometry] of the specimen at different specimen tilt angles ψ —the angle between the diffracting plane normal and the specimen surface normal [73]. To ensure higher sensitivity to strain higher 2θ angles are usually used. Unfortunately for highly textured materials or single crystalline-like materials under the symmetric B-B diffraction geometry only a few (hkl) peaks appear with other Bragg peaks hardly visible. This can be solved by making use of the grazing angle technique [72].

The underlining principle of the grazing angle X-ray residual stress measurement method is exactly the same as the traditional $\text{Sin}^2\psi$ method. It is based on the measurements of the lattice parameters determined from a fixed (hkl) Bragg reflection but at different tilt angle ψ [72]. Unlike the traditional $\text{Sin}^2\psi$ method, this method employs an asymmetric B-B XRD geometry, with the incident X-ray beam making a grazing angle γ with respect to the specimen surface-tilting axis S_1 (Fig 4.4.4 - Fig 4.4.6) where the angle γ is the ω angle in traditional four circle diffractometer geometry [66].

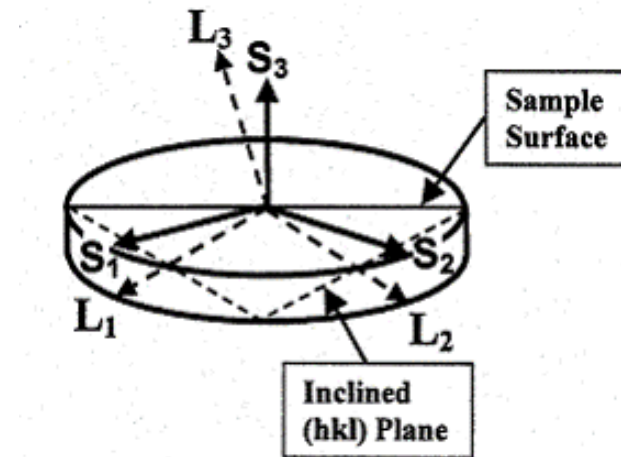


Figure 4.4.4: Definition of the laboratory coordinate system L_i and sample coordinate system S_i [72].

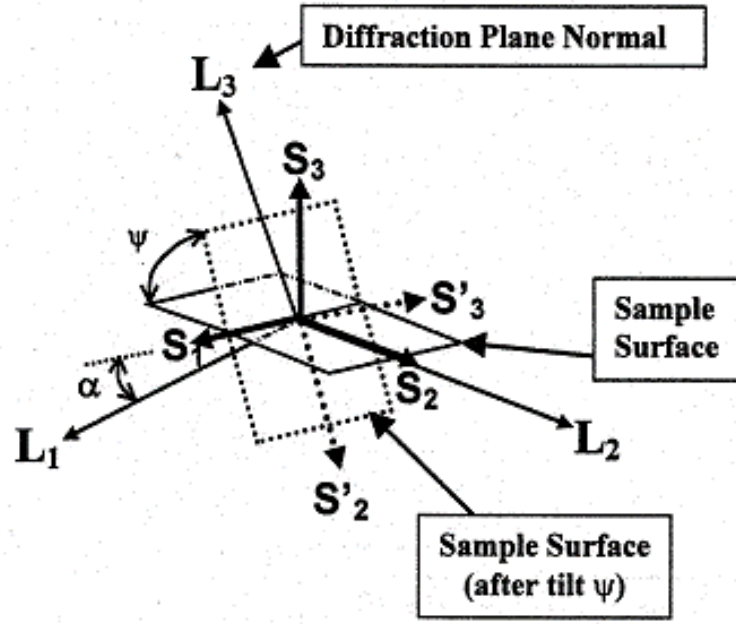


Figure 4.4.5: Definition of the laboratory coordinate system L_i , sample coordinate system S_i and the angles α and ψ [72].

The orthogonal coordinate systems used in the following discussion are shown in figure 4.4.4. The axes S_i define the co-ordinate system of the thin-film specimen, with S_1 , S_2 contained in the sample surface plane, and S_3 being the specimen surface normal. The laboratory system L_i is defined such that L_3 is the normal of diffraction planes (hkl) for which spacing is measured by X-rays. L_1 and L_2 are the two orthogonal axes lying on the (hkl) plane. The S_1 , S'_2 , and S'_3 are the new specimen axes when the specimen is rotated about the S_1 axis for an angle ψ . As observed in figure 4.4.5, the L_2 axis makes an angle ψ with respect to S'_2 after the tilting. (In a four-circle geometry, rotation along the S_1 axis is known as the x rotation.) At the same time, L_1 is kept at a constant angle α with S_1 . Here the angle α calculated as $\alpha = \theta_0 - \gamma$ where θ_0 is the reference Bragg angle of the observed plane (hkl) at $\psi = 0^\circ$, θ_0 and γ is the grazing angle as shown in figure 4.4.6. The strain from the residual stress on the plane (hkl) along L_3 can be obtained when the lattice spacing $d_{\alpha\psi}$ is derived from the position of the diffraction peak for a given reflection (hkl); it is shown as the following formula [58]:

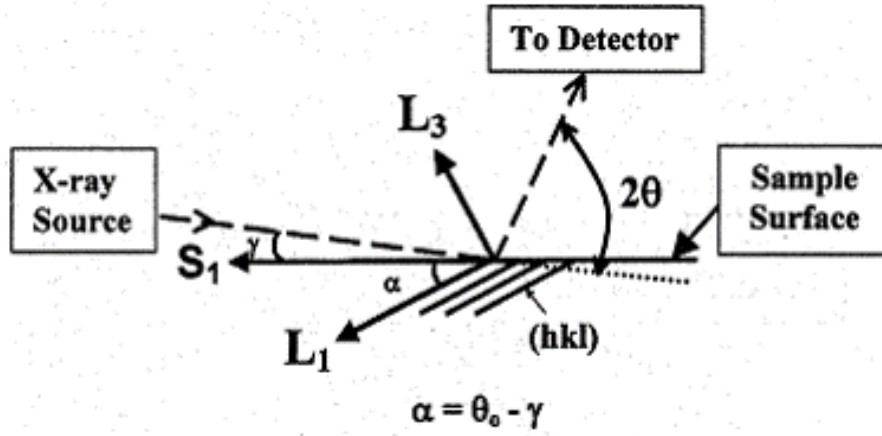


Figure 4.4.6: The laboratory coordinate system L_3 , incident X-ray and diffraction directions, and the angle α [72].

$$\left(\varepsilon'_{33} \right) = \frac{d_{\alpha\psi} - d_0}{d_0} \quad (4.4.18)$$

where d_0 is the initial lattice spacing when $\psi = 0$. The strain $\left(\varepsilon'_{33} \right)_{\alpha\psi}$ may be expressed in terms of the strain ε_{ij} in the co-ordinate system of the film by a tensor transformation:

$$\left(\varepsilon'_{33} \right)_{\alpha\psi} = \alpha_{3k} \alpha_{3l} \varepsilon_{kl} \quad (4.4.19)$$

where α_{3k} , α_{3l} are the direction cosines between L_3 and S_k , S_l , respectively.

The direction cosine matrix for this case is:

$$\alpha_{ik} = \begin{vmatrix} \cos\alpha & 0 & -\sin\alpha \\ \sin\alpha\sin\psi & \cos\psi & \cos\alpha\sin\psi \\ \sin\alpha\cos\psi & -\sin\psi & \cos\alpha\cos\psi \end{vmatrix} \quad (4.4.20)$$

Substituting for α_{3k} , α_{3l} in equation 4.4.19 gives:

$$\begin{aligned}
 \left(\varepsilon'_{33} \right)_{\alpha\psi} &= \frac{d_{\alpha\psi} - d_0}{d_0} = \sin^2\alpha \cos^2\psi \varepsilon_{11} - \sin\alpha \sin 2\psi \varepsilon_{12} \\
 &\quad + \sin 2\alpha \cos^2\psi \varepsilon_{13} + \sin^2\psi \varepsilon_{22} \\
 &\quad - \sin 2\psi \cos\alpha \varepsilon_{23} + \cos^2\alpha \cos^2\psi \varepsilon_{33}
 \end{aligned} \tag{4.4.21}$$

if the material is isotropic (i.e the Poisson's ratio, $\nu^{hkl} = \nu$, and Young's modulus $E^{hkl} = E$), the strain becomes,

$$\varepsilon_{ij} = \frac{1 + \nu}{E} \sigma_{ij} - \delta_{ij} \frac{\nu}{E} \sigma_{kk} \tag{4.4.22}$$

which, upon substitution into equation 4.4.21, yields:

$$\begin{aligned}
 \frac{d_{\alpha\psi} - d_0}{d_0} &= \frac{1 + \nu}{E} (\sigma_{22} - \sigma_{11} \sin^2\alpha - \sigma_{33} \cos^2\alpha) \sin^2\psi \\
 &\quad + \frac{1 + \nu}{E} (\alpha_{11} \sin^2\alpha + \sigma_{33} \cos^2\alpha) - \frac{\nu}{E} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \\
 &\quad - \frac{1 + \nu}{E} (\sigma_{12} \sin\alpha + \sigma_{23} \cos\alpha) \sin 2\psi
 \end{aligned} \tag{4.4.23}$$

It is evident from equation 4.4.23 that, if the stress existing in the films is biaxial, the stress tensor assumes the following form:

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{4.4.24}$$

Thus equation 4.4.23 becomes,

$$\begin{aligned}
 \frac{d_{\alpha\psi} - d_0}{d_0} &= \frac{1 + \nu}{E} (\sigma_{22} - \sigma_{11} \sin^2\alpha) \sin^2\psi \\
 &\quad + \frac{1 + \nu}{E} \alpha_{11} \sin^2\alpha - \frac{\nu}{E} (\sigma_{11} + \sigma_{22}) \\
 &\quad - \frac{1 + \nu}{E} \sigma_{12} \sin\alpha \sin 2\psi
 \end{aligned} \tag{4.4.25}$$

For $\sigma_{11} = \sigma_{22}$ and $\sigma_{12} = 0$ the stress tensor is as follows [72]:

$$\begin{bmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.4.26)$$

as a result equation 4.4.26 becomes

$$\frac{d_{\alpha\psi} - d_0}{d_0} = \frac{1 + \nu}{E} \sigma \cos^2 \alpha \sin^2 \psi + \frac{1 + \nu}{E} \sigma \sin^2 \alpha - \frac{2\nu}{E} \sigma \quad (4.4.27)$$

The $(d_{\alpha\psi} - d_0)/d_0$ vs. $\cos^2 \alpha \sin^2 \psi$ plot will be linear according to equation 4.4.27. The residual stress can be obtained by determining the slope of the linear fitting between the fractional change in lattice spacing and the term $\cos^2 \alpha \sin^2 \psi$. Therefore, the slope is equal to $\frac{1+\nu}{E} \sigma$, and the intercept, when $\cos^2 \alpha \sin^2 \psi = 0$, is $\frac{1+\nu}{E} \sigma \sin^2 \alpha - \frac{2\nu}{E} \sigma$.

4.4.6 Raman Spectroscopy.

Raman scattering is a fundamental form of vibrational spectroscopy which can be used to obtain information about the structure and properties of molecules and crystals from the vibrational transitions [74]. The property involved is the change in the polarizability of the molecule with respect to its vibrational motion. The interaction of the molecule with the incoming radiation creates an induced dipole moment in the molecule and the radiation emitted by this induced dipole contains the observed Raman scattering [75].

Historically, Raman scattering has been described in two ways, the classical theory and the quantum theory. The older classical theory is based on the wave theory of light and is deficient in that it does not take into account the quantized nature of vibrations. It is also not able to explain as much about the relationship between the molecular properties and Raman scattering as a

quantum theory [76].

4.4.7 Classical Theory Approach

Although the classical theory is generally considered to not deal with all the aspects of Raman scattering adequately, it does provide a useful insight into the frequency dependence and selection rules [77]. The classical approach assumes that the Raman effect arises as a result of the interaction of an incident photon and the electric dipole of a molecule [78]. The relation between the induced electric dipole moment of a molecule and the dynamic electric field which produces it, is characterized by $\mathbf{E}$. This is the time dependent vector of the incident radiation, which is a monochromatic plane wave of frequency ν [77]. The total time-dependent induced electric dipole moment vector of a molecule can be written as the sum of a series of time-dependent induced electric dipole moment vectors $\boldsymbol{\mu}^{(1)}, \boldsymbol{\mu}^{(2)}, \boldsymbol{\mu}^{(3)} \dots$ as

$$\boldsymbol{\mu} = \boldsymbol{\mu}^{(1)} + \boldsymbol{\mu}^{(2)} + \boldsymbol{\mu}^{(3)} + \dots \quad (4.4.28)$$

This is a rapidly converging series with $\boldsymbol{\mu}^{(1)} \gg \boldsymbol{\mu}^{(2)} \gg \boldsymbol{\mu}^{(3)}$. The relationship between $\boldsymbol{\mu}^{(1)}, \boldsymbol{\mu}^{(2)}, \boldsymbol{\mu}^{(3)}$ and $\mathbf{E}$ has the forms

$$\boldsymbol{\mu}^{(1)} = \alpha \mathbf{E}$$

$$\boldsymbol{\mu}^{(2)} = \frac{1}{2} \beta \mathbf{E} \mathbf{E}$$

$$\boldsymbol{\mu}^{(3)} = \frac{1}{6} \gamma \mathbf{E} \mathbf{E} \mathbf{E}$$

where $\mathbf{E} \mathbf{E}$ and $\mathbf{E} \mathbf{E} \mathbf{E}$ are the second and third terms of the power series.

This means $\boldsymbol{\mu}^{(1)}$ is linear in $\mathbf{E}$, while $\boldsymbol{\mu}^{(2)}$ and $\boldsymbol{\mu}^{(3)}$ are non-linear in $\mathbf{E}$, with $\boldsymbol{\mu}^{(2)}$ quadratic and $\boldsymbol{\mu}^{(3)}$ cubic in $\mathbf{E}$. The equation 4.4.28 can be expressed as

$$\boldsymbol{\mu} = \alpha \mathbf{E} + \frac{1}{2} \beta \mathbf{E} \mathbf{E} + \frac{1}{6} \gamma \mathbf{E} \mathbf{E} \mathbf{E} + \dots, \quad (4.4.29)$$

where α is the polarizability, β the hyperpolarizability and γ the second hyperpolarizability. The non-linear terms in the above equation are usually very small compared to the first term; as a result their contribution in linear Raman scattering is negligible [77].

The expression for the induced dipole moment vector can therefore be simplified to

$$\boldsymbol{\mu} = \alpha \mathbf{E}. \quad (4.4.30)$$

This can be expressed in matrix form as

$$\begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

where the nine coefficients α_{ij} are the components of the polarizability tensor α . Variation of the molecular polarizability as a function of the normal coordinates is expressed in terms of the Taylor series

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum \left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_k \partial Q_l} \right) Q_k Q_l + \dots \quad (4.4.31)$$

where $(\alpha_{ij})_0$ is the value of the polarizability tensor in the equilibrium position and Q_k is the k th normal coordinate amplitude associated with vibrations of frequency ν_k . For small vibrations near the equilibrium position equation

4.4.31 can be written as

$$\alpha_k = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k. \quad (4.4.32)$$

Taking the normal vibrations of the molecule as being harmonic, the time dependence of Q_k is given by

$$Q_k = Q_{ko} \cos 2\pi\nu_k t, \quad (4.4.33)$$

where Q_{ko} is the normal coordinate amplitude. The change in the electric field of the incident radiation of frequency ν_0 with time is given by

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu_0 t. \quad (4.4.34)$$

An electric dipole oscillating at a frequency ν is itself a source of electromagnetic radiation of frequency ν . Combining equations 4.4.30, 4.4.32, 4.4.33 and 4.4.34 the linear induced dipole moment vector is given by

$$\begin{aligned} \boldsymbol{\mu} &= \alpha_0 \mathbf{E} + \left(\frac{\partial \alpha}{\partial Q_k} \right) Q_{ko} \mathbf{E}_0 \cos 2\pi\nu_0 t \cos 2\pi\nu_k t \\ &= \alpha_0 \mathbf{E} + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 Q_{k0} \mathbf{E}_0 [\cos 2\pi(\nu_0 - \nu_k)t + \cos 2\pi(\nu_0 + \nu_k)t]. \end{aligned} \quad (4.4.35)$$

From equation 4.4.35 above the induced dipole has three distinct frequency components. The first term $\alpha_0 \mathbf{E}_0 \cos 2\pi\nu_0 t$ describes the Rayleigh scattered light at ν_0 . The second term $(\nu_0 - \nu_k)$ represents the Stokes Raman process and the third term $(\nu_0 + \nu_k)$ represents the anti-Stokes Raman process. The intensity of the Raman scattering depends on the derived polarizability tensor

α_k also called the Raman tensor [75].

$$\alpha_k = \left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0. \quad (4.4.36)$$

It represents the sensitivity of the molecular polarizability to changes of nuclear configuration along the normal coordinates of vibration. To be Raman active, at least one component of the polarizability tensor must change during the vibration, i.e.

$$\left(\frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 \neq 0. \quad (4.4.37)$$

Whilst the above discussion is for the case of molecules, it is still applicable in the same way to inter-atomic vibrations in unit cells in crystals as well as vibrations between unit cells.

4.4.8 Quantum Theory Approach

The quantum approach considers Raman scattering as a two photon process. A photon of incident radiation is absorbed raising the system to a virtual state. This virtual state has a very short lifetime (10^{-14} s) hence the system makes a downward transition, creating or absorbing a phonon of given energy and scattering a photon in the process [77]. Rayleigh scattering is when the energy of the scattered photon is the same as that of the incident photon, see Figure 4.4.7a. Conventionally the scattering of light with a decrease in frequency is referred to as Stokes Raman scattering, see Figure 4.4.7b. If the system was initially in an excited state, it can make a transition from the virtual state to a lower energy state than the initial one, see Figure 4.4.7c. Its energy will therefore be higher than that of the incident photon, corresponding to anti-Stokes Raman scattering [77]. At thermal equilibrium, the populations of the different levels follows the Boltzmann distribution. So the population

of the ground level is higher than the excited level. In experimental conditions in this work the Stokes transition is much more probable than the anti-Stokes transition [79].

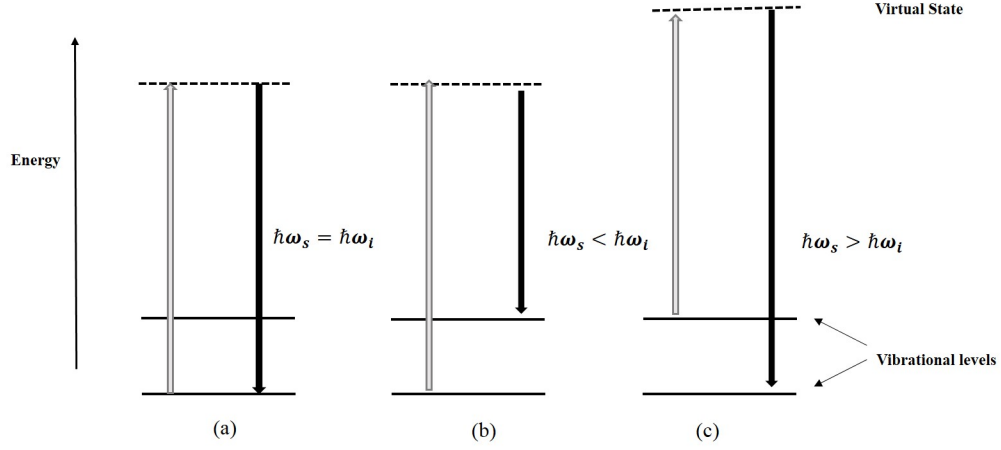


Figure 4.4.7: Energy level diagrams showing (a) Rayleigh scattering, (b) Stokes Raman scattering, and (c) anti-Stokes Raman scattering [77].

Energy and momentum are conserved in the Raman scattering process. If any incoming photon of angular frequency ω_i causes a phonon of angular frequency ω_{ph} to be created or absorbed in the scattering of a photon of angular frequency ω_s then by conservation we have

$$\hbar\omega_i = \hbar\omega_s \pm \hbar\omega_{ph}$$

$$\vec{q}_i = \vec{q}_s \pm \vec{q}_{ph} \quad (4.4.38)$$

where $\pm$ represents a Stokes or anti-Stokes process, see Figure 4.4.8 and $\vec{q}_i$, $\vec{q}_s$ and $\vec{q}_{ph}$ are the wave vectors of the incident photon, scattered photon and emitted or absorbed phonon respectively [75].

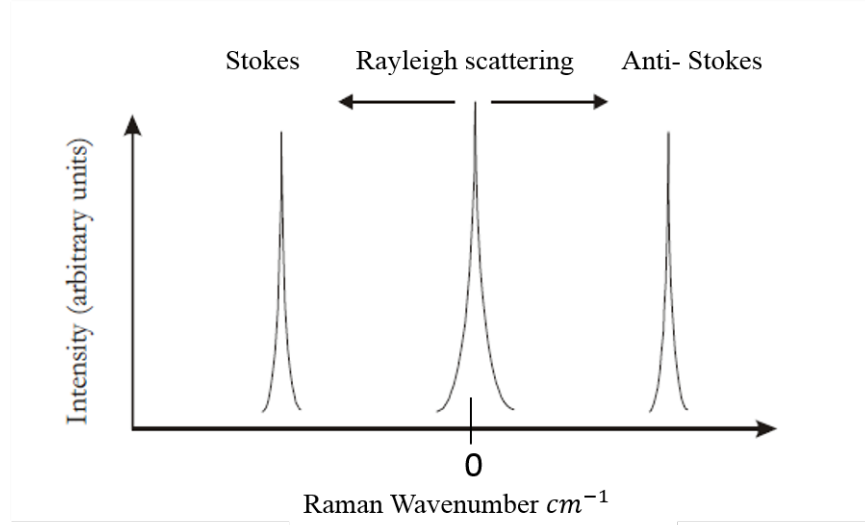


Figure 4.4.8: Stokes and anti-Stokes Raman lines [78].

4.5 Raman Spectroscopy as an Optical Characterisation Technique

As discussed in subsections 4.4.7 and 4.4.8, if the frequency of an incident photon is ν_i and that of the emitted is ν_s then the frequency shift is,

$$\nu_s - \nu_i = \Delta\nu \quad (4.5.1)$$

Its magnitude is referred to as a Raman frequency and the set of frequencies of the scattering species constitutes its Raman spectrum [74]. Figure 4.4.8 shows the Stokes and Anti-Stokes Raman lines expressed mathematically in equation 4.4.35.

4.6 Stress and the Raman Line

Since the Raman effect is a result of the interaction between photons and vibrational mode(s) in a crystal, it is then expected that stress applied to a

crystal which has Raman active vibrational modes would cause changes in the observed Raman bands [76]. As the crystal is subjected to stress, be it externally imposed or due to internal imperfection, the frequency of the lattice phonons is affected and thus also the position of the Raman peak. A slight compression of the unit cell results in a change in the force constant of the vibration and consequently the vibrational frequency will be altered as well. If the unit cell experiences a tensile stress and dilates due to the applied stress, a similar argument as in the compression state holds. However if the applied stress is isotropic then no changes will be observed with respect to the shape of the Raman band since the symmetry of the unit cell would not have been compromised in any way, but a change in the Raman peak position will be observed [79]. Careful measurements of the shift of the Raman peak relative to its unstressed position can yield information about the stresses present in a sample[80]. Compressive residual stresses in the material result in a shift of the peak to higher frequencies and tensile residual stress to lower frequencies. By making use of the coefficient of stress induced shift (so called piezo-Raman shift) it is therefore possible to determine the stress state within the sample material using equation 4.6.1

$$\nu_r - \nu_s = \sigma\alpha \quad (4.6.1)$$

where ν_s is the measured position of the Raman line, ν_r is the position of the stress free Raman line, α is the piezo-Raman coefficient and σ is the calculated stress present. In general, equation 4.6.1 is applicable where an isotropic stress state is assumed.

The intensity of a characteristic Raman line is to a fair approximation proportional to the volume concentration of the species in question, and the Raman intensity measurements provide a basis for quantitative analysis [79]. The

sharpness of the Raman bands gives an indication of the state of crystallinity, hence a distinct sharp peak at the correct wavenumber for a specific material indicates that there is little deformation or significant stress in the crystal [27]. The width of the Raman peak normally measured as the full width at half maximum (FWHM) provides a qualitative measure of the degree of disorder in a crystal and is useful as a ranking indicator [27]. The Raman line-width of natural diamond is related to the average lifetime of the phonons created in the Raman process. In imperfect crystals the phonons created in the Raman process can decay (scatter) at grain boundaries and at defect sites, thereby reducing the average lifetime and broadening the Raman line [81]. The theory of homogeneous spectral lines predicts that the line-width is inversely proportional to the phonon lifetime and that the line shape is expected to be Lorentzian [82].

4.6.1 Stress classification

The fatigue experiments in the present work are such that the Raman measurements determine the in-plane stresses in the diamond layer samples. A bi-axial stress model is applied and is discussed further in section 4.6.2. A certain classification system for the stress in the diamond is commonly used in the industry. The stresses can be classified under one of three possible types which are :

1. Type I - macro-stresses. These are considered over distances of approximately component size. Causes range from changes to the sample as a whole to differential thermal expansion during the synthesis processes
2. Type II - affects distances of approximately grain size and can be spread over grain boundaries. They are generally as a result of processing e.g sintering. They can also result as a result of the anisotropy of individual

crystallites with the sample.

3. Type III -these stresses are at atomic level and are generally as a result of point defects as well as line defects in the material under study. They are within individual grains.

The measured residual surface stresses at each point are thus a combination of type II and type III stresses. The macroscopic type I stresses are not expected to significantly change over the dimensions of the sample, thus are common to each point on the sample. The type II stresses show more variation from point to point and contribute to the variations observed in the data. The averaging of the mapping points (discussed in section 5.8) to yield a single stress value for a sample is thus used to calculate a representative macroscopic value.

4.6.2 The Hydrostatic Piezo-Raman Coefficient

In section 4.6 it has been shown that lattice deformations caused by mechanical stresses affect the phonon frequencies. According to Mohrbacher *et al.* [83] any stress tensor can be decomposed into a hydrostatic component and a deviator. The hydrostatic component would have an effect of change in the volume of the unit cell whilst the deviator induces a distortion of the bond angles. Changes in the volume due to the hydrostatic stress result in a linear shift of the triply degenerate Raman line in diamond. The Raman shift $\Delta\nu_H$ relative to the stress-free state is related to the magnitude of the hydrostatic stress σ by [84],

$$\Delta\nu_H = \frac{\nu_0\gamma}{B}\sigma. \quad (4.6.2)$$

where ν_0 is the frequency of the particular photon in question, B is the bulk modulus and γ is the mode Grüneisen parameter. The linear relationship

between the peak position of the Raman line and the applied stress for diamond was confirmed by Grimsditch *et al.* [85]. It was proven that when a compressive stress is applied to diamond, the peak position of the Raman line shifts linearly with stress to a higher frequency. This dependence of the Raman shift $\Delta\nu$ on the applied stress σ is

$$\Delta\nu = \nu_r - \nu_s = \alpha\sigma \quad (4.6.3)$$

where α is the piezo-Raman coefficient while ν_r and ν_s are the Raman peak of the unstressed and stressed diamond. Conversely, a shift of the Raman peak position to lower wavenumbers is indicative of the presence of tensile stress in the diamond.

In choosing the value of the piezo-Raman coefficient careful consideration was given to previous work of other authors. Catledge *et al.*[86] measured peak shifts in the range of 3 cm^{-1} and calculated stresses up to 1.3 GPa. Erasmus *et al.* [80] also measured similar peak shifts and subsequently calculated stresses in the same range. Both authors made use of the value employed by Bergman and Nemanich [31] which is $\alpha = 1.9 \text{ cm}^{-1}/\text{GPa}$. In these above mentioned investigations the authors made use of PCD tool-bits that consisted of a diamond layer sintered onto a WC-Co substrate.

Table 4.1 below shows values of the coefficient reported to have been obtained under truly hydrostatic conditions using high pressure diamond anvil cells.

Table 4.1: Experimental values for the hydrostatic pressure coefficient

Author	$\alpha(\text{cm}^{-1}).\text{GPa}^{-1}$
Mitra <i>et al.</i> [84]	2.8 ± 0.3
Boppart <i>et al.</i> [87]	2.87 ± 0.1
Whalley <i>et al.</i> [88]	2.96 ± 0.11

Mohrbacher *et al.* [83] derived the hydrostatic coefficient from theory. They

argue that any tensor can be decomposed into a hydrostatic component and a deviator. The hydrostatic component as mentioned before is responsible for the change in the volume of the unit cell and the deviator will distort the bond angles. They suggest that if a balanced bi-axial stress state is assumed the tensor can be represented in the $\begin{bmatrix} 1 & 0 & 0 \end{bmatrix}$ plane of the cubic lattice by the sum of the hydrostatic and deviator components as shown below,

$$\begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{2}{3}\sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{1}{3}\sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \quad (4.6.4)$$

The piezo-Raman coefficient of the centroid can then be evaluated by multiplying the value of the coefficient from the hydrostatic model with the factor $\frac{2}{3}$. Since the hydrostatic component is invariant to rotation this coefficient remains the same for any other crystallographic orientation.

In the present work a bi-axial stress model is assumed and in light of the theory behind the piezo-Raman coefficient, an average of the experimentally determined values for the hydrostatic stress state given in Table 4.1 and multiplied by the factor $\frac{2}{3}$ was calculated. The calculated coefficient value was found to be $1.92 \pm 0.11 \text{ cm}^{-1} \text{ GPa}^{-1}$, in good agreement with that used previously by Bergman and Nemanich [31] and Erasmus *et al.* [80].

In the present work, only the PCD layer detached from the substrate was used (see section 5.2). It is common to observe the splitting of the Raman peak when significant non-hydrostatic stresses are present in the PCD; however in the present work no peak splitting was observed. This can be due to the splitting being too small to resolve or that the stresses are approximately hydrostatic. Another possible explanation for this is that the non-hydrostatic stresses are randomly distributed.

4.7 Advantages and Limitations of Raman Spectroscopy

The advantages of Raman spectroscopy are four-fold:

- (a) The optical method is superior to other techniques in terms of spatial resolution (approximately $1\text{ }\mu\text{m}$).
- (b) It is a non-destructive technique and this makes it a very useful technique for industry.
- (c) The Raman spectrum includes contributions from overtone processes. Phonon energies may thus be determined directly from the Raman spectrum.
- (d) With Raman spectroscopy there is minimum sample preparation required [37].

Some of the main limitations of the Raman spectroscopy technique are that:

- (a) Not all materials are Raman active. This is because for a material to show Raman bands, a change in polarization is required, which is not possible in some materials such as metals.
- (b) In a highly deformed material, broadening of the peak and a lower signal to noise ratio introduces inaccuracies in the peak position measurement [37].
- (c) Fluorescence can swamp the Raman signal. This problem can be minimized by the correct choice of laser excitation wavelength.
- (d) The Raman effect is inherently weak. This can however be overcome by intense sources (lasers) and efficient detectors (PMT/CCD).
- (e) One can only probe the sub-surface properties of materials which are transparent to the incident laser wavelength since the penetration depth is dependent on wavelength and the absorption coefficient of the material. Typical in PCD materials this is confined to the first $20\text{ }\mu\text{m}$ from the measuring surface.

4.8 Typical Raman Spectra for Diamond

In Raman spectroscopy, a small portion of the photons in the laser beam interacts with the material under investigation and are then scattered inelastically. The inelastically scattered photons have a frequency shifted from the incident photons by the frequency of the mode which is characteristic of the sample material [80]. An unstressed large good quality single crystal diamond has a single, triply degenerate Raman peak at 1332.5 cm^{-1} (see Figure 4.8.1). This provides an appropriate standard reference peak since it is the respective stresses within the polycrystalline diamond components of the PCD that are being measured by the Raman technique. The additional phases within the PCD do not affect or influence this fixed reference position [78].

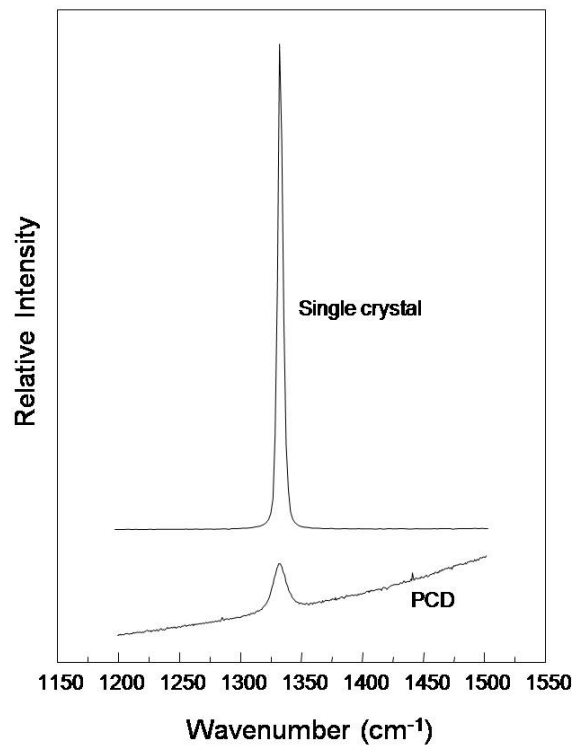


Figure 4.8.1: Typical Raman spectra for a single crystal diamond and for polycrystalline diamond.

Since micro-Raman spectroscopy is essentially a back scattering technique the volume that scatters is very important. This explains why in Figure 4.8.1 the Raman peak for the single crystal has a higher intensity as compared to that of PCD. The Raman peak for PCD has some broadening which is possibly a result of some plastic deformation taking place especially in the small diamond grains during the sintering process.

Chapter 5

Methods and Results: Unleached PCD

Diamond tools have been used for a long time and in most of their applications, the general problem of brittleness, reflected as the inability to sustain tensile stresses in a reliable and predictable manner, has persisted [51]. Two types of PCD tool bits are generally used for these applications, namely the leached PCD and the unleached PCD. The two types are synthesised in virtually the same way except that with the leached PCD some of the metallic phase (cobalt) is leached out through the use of powerful acids. More on the synthesis process of leached PCD is covered in detail in chapter 6. The leached PCD, whilst exhibiting slightly less fracture toughness [89] as compared to the unleached PCD, exhibits better thermal stability. This chapter focuses on the results from conducting the fatigue experiments and stress measurements on a batch of unleached PCD cylindrical tool bits. Results of investigations of leached PCD samples are discussed in chapter 6. The sample dimensions and the respective settings for the different measurements are explained in detail. All measurements were conducted under room temperature conditions.

5.1 Sample Dimensions and Preparation

The PCD cylindrical tool-bits used in the present work were manufactured by Element Six (Pty) Ltd (E6). They consist of a PCD layer sintered onto a tungsten carbide substrate as shown in Figure 5.1.1. The synthesis procedure was described in sections 2.3 to 2.5. They are typical of cylindrical tool-bits with a PCD layer of 19 mm in diameter and 2 mm in thickness. In the synthesis of the PCD blends of different diamond powder grain sizes are used ranging from $2\text{ }\mu\text{m}$ – $20\text{ }\mu\text{m}$ in size. In this work only the PCD layer was used and these were delivered already removed from the tungsten carbide substrate using Electrical Discharge Machining (EDM) cutting. The surface of the cutting side was slightly polished. They had the dimensions shown in Figure 5.1.1. For the fatigue experiments, the mapped sample surface was in direct contact with the three balls of the ball on three balls arrangement shown in Figure 5.1.2. Sections 5.2 and 5.3 discusses the fatigue measurements method in detail. Before each fatiguing run, the samples were loaded randomly into the fatigue jig, i.e. the contact points were different between different runs. It is thus not possible to visualize any localised damage in the 2D maps that may be related to the contact points.

As mentioned in section 2.5, due to the different thermal expansion coefficients between the diamond layer and the tungsten carbide substrate, differential cooling results in compressive residual stresses in the PCD layer. One would expect these stresses to be released during the removal of the PCD from the substrate, however the detached PCD layers still exhibited average compressive residual stress on the cutting surface. Catledge *et al.* [52] in their work on PCD suggested that these residual stresses are primarily due to the large mismatch in the thermal expansion coefficient between the diamond and the WC-Co substrate.

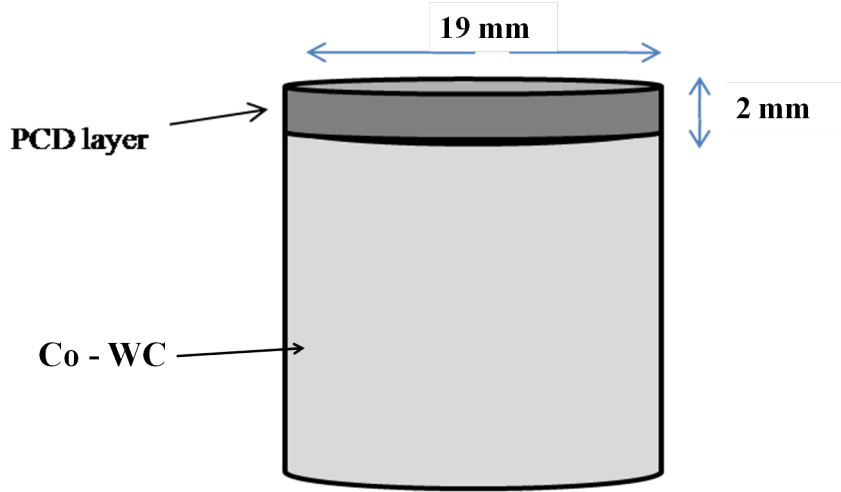


Figure 5.1.1: Showing the schematic of a typical cylindrical cutter with dimensions of the PCD layer.

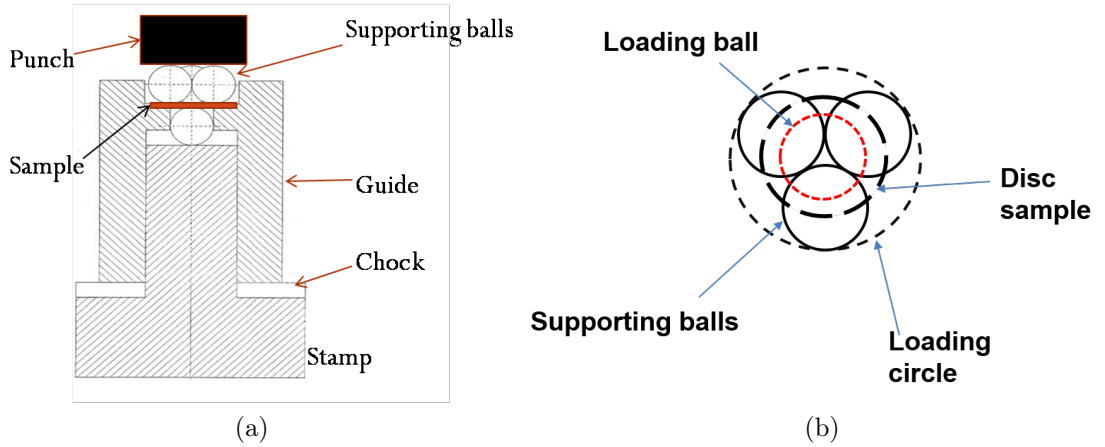


Figure 5.1.2: (a) showing the ball on three ball setup and the configuration of the sample and the balls for the fatigue experiments. For the actual cyclic loading the chock is removed and this allows the guide to slide down and the result is the sample being held only by the spherical balls and a small vertical cavity is ensured so that the sample can flex vertically. The flexing distance in the experiment was 0.1 mm . (b) shows the isometric view of the positioning of the balls relative to the sample. Marked on the sample are the contact points of the support balls [90].

5.2 Quasi-Static Loading Test Procedure

In order to do fatigue experiments the maximum strength of the sample material had to be determined. For this, the Transverse Rupture Strength (TRS)

measurements were made using the ball on three balls setup in a 5500R Instron machine, (see Figure 5.2.1). The sample is placed and supported as shown in Figure 5.1.2 then loaded centrally until fracture occurs. The Instron machine is interfaced with a computer which displays the maximum load at which the sample fails using the embedded software. Three samples were used in the test and the average load calculated to be 3470 ± 276 N. This was applied as the fracture load for the sample material. The results are shown in Figure 5.2.2 and Table 5.1.



Figure 5.2.1: The 5500R Instron machine in the Element Six laboratory, used for the quasi-static loading test.

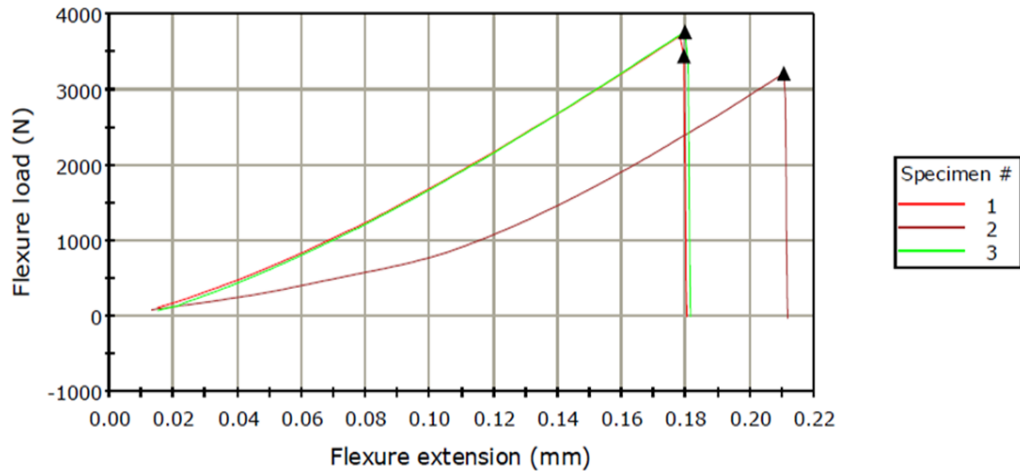


Figure 5.2.2: Results of quasi - static loading test. (*Curves for specimen 1 and 3 are almost superimposed one on top of the other*).

Whilst the specimen used for the transverse rupture strength tests were taken from the same manufacturing batch, the results exhibited by the third sample were interestingly different. From figure 5.2.2 it is evident that specimen 3 exhibited a huge fluctuation and greater flexure extension. It is important to note that the flexure strength of a ceramic samples vary from one specimen to the another. Inherently statistical scatter in the results will exist. At the present the reasons behind this fluctuation are not clear.

5.3 Fatigue Test

Cyclic loading which results in fatigue can be classified roughly into two categories, namely constant amplitude loading and random cyclic loading. In the present work constant amplitude fatigue testing was carried out under load control at a frequency of 10 Hz. The load used for these experiments was 3100 N, which is approximately 89% of the fracture load obtained and noted in section 5.2. This value was arrived at after several samples had been subjected to loads at different percentages of the fracture load. The aim was to identify the percentage of the fracture load at which the samples could be

Table 5.1: Quasi - static loading test results.

	Thickness (mm)	Fracture Load (N)	Displacement (mm)
1	2.00	-3440	0.18
2	2.00	-3210	0.21
3	2.00	-3760	0.18
Mean		-3470	0.19
Standard Deviation		276	0.02

cyclically loaded for a substantial number of loading cycles without fracturing in order to be able to do Raman measurements. An Instron SYN 179 servo-hydraulic test machine (see Figure 5.3.1) was used for all the fatigue experiments. The disc specimens were loaded and held as shown previously in Figure 5.1.2 and the repeatedly subjected to a predetermined number of cycles. The instrument makes use of the Instron MAX software to control the servo-hydraulic machine and to collect the test data. The fatigue experiments were done under standard room temperature and pressure conditions. Due to the fatigue loading it is possible that there would be temperature changes on the surface of the sample during the fatigue experiments. However due to the arrangement of the three support balls which were in contact with the cutting surface of the disc sample it was not possible to track these temperature shifts. It is also our firm belief that no significant temperature shifts would occur because diamond is a good heat conductor and as such it is possible that the fatigue jig acted as a heat sink thus helping to maintain the temperature

relative unchanged.

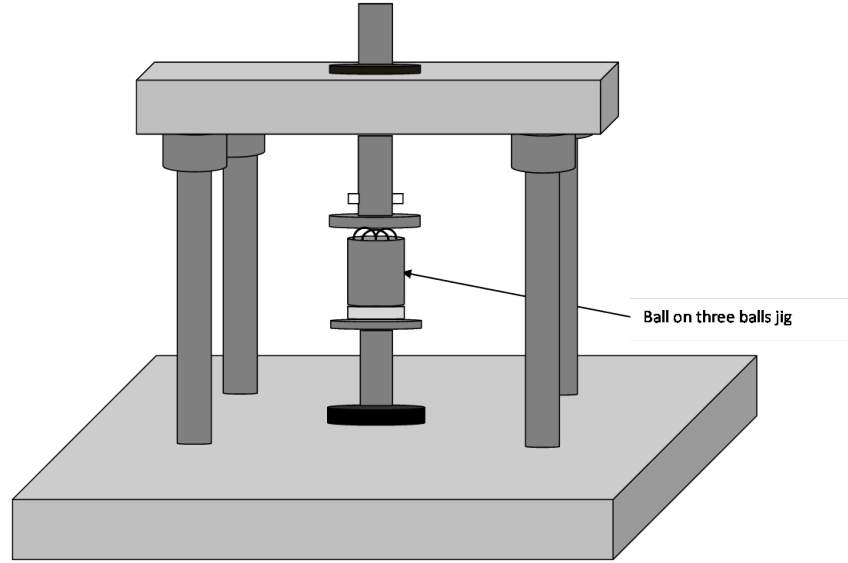


Figure 5.3.1: Schematic of the Instron SYN 179 servo-hydraulic test machine.

For successful fatigue tests three important quantities had to be determined. These are namely mean stress, stress range, and stress amplitude. These are shown in Figure 5.3.2 and explained below:

Mean stress σ_m is the algebraic mean of the maximum stress σ_{max} and the minimum stress σ_{min} , see Figure 5.3.2.

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2}.$$

Stress Range σ_r is the algebraic difference between the maximum stress σ_{max} and minimum stress σ_{min} , see Figure 5.3.2.

$$\sigma_r = \sigma_{max} - \sigma_{min}.$$

The alternating stress or stress amplitude σ_a is half the stress range in a cycle see Figure 5.3.2.

$$\sigma_a = \frac{\sigma_r}{2} = \frac{\sigma_{max} - \sigma_{min}}{2}.$$

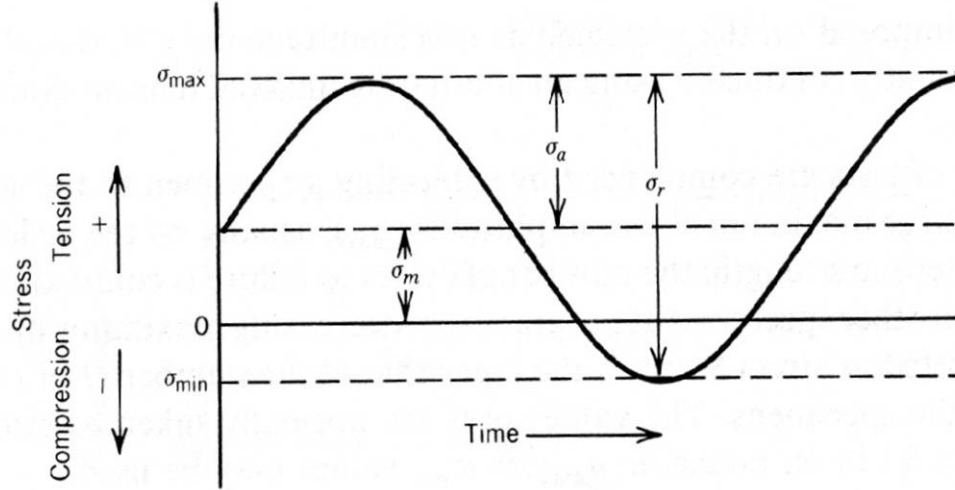


Figure 5.3.2: Constant amplitude cyclic loading characteristics as described as in the text [44].

Table 5.2 shows the settings used for the fatigue measurements.

Table 5.2: Fatigue loading settings used for the unleached samples

Maximum Load (89% UTS)	3100 N
Minimum (10% UTS)	310 N
Amplitude	1390 N
Set-point	1700 N
Frequency	10 Hz

5.4 Raman Experimental Arrangement

The potential of Raman scattering as a major research tool was noted in the early stages of its inception but the challenge was the weak signal and the subsequent need for sensitive measuring equipment. With the availability of lasers and the much improved high sensitivity detectors, Raman spectroscopy has become one of the most important tools in material science research.

5.5 Laser

A laser is a source of intense, coherent monochromatic radiation. Radiant emission and absorption take place within the atomic or molecular structure of materials. If atoms (or molecules) are in their ground state, they will stay there until they are excited by external forces. If light energy is given to these atoms (or molecules) of the lasing material, then some of the atoms will attain an excited state. Figure 5.5.1 is a schematic energy diagram showing the atomic energy levels and the pumping action of sufficient intensity which results in most of the atoms occupying the higher energy level. This phenomenon is known as a population inversion. This is an unstable condition for these atoms and as such they will reside in this excited state for a short time and then decay back to their ground energy state. The decay can occur in one of two ways: (i) spontaneous decay or (ii) stimulated decay. In spontaneous decay the atoms will revert to their original energy state while emitting randomly directed photons; with stimulated decay the photons from the decaying atoms strike other excited atoms causing them to revert to their ground state. These stimulated transitions emit photons that travel in phase at the same wavelength and in the same direction as the incident photon. In a typical gas laser, the excited medium is within an optical cavity fitted with a totally reflecting mirror and a partially transmitting mirror at each end. The stimulated photons that are reflected back and forth within the cavity are thus amplified, such that the laser light emerging from the partially transmitting mirror has considerable intensity.

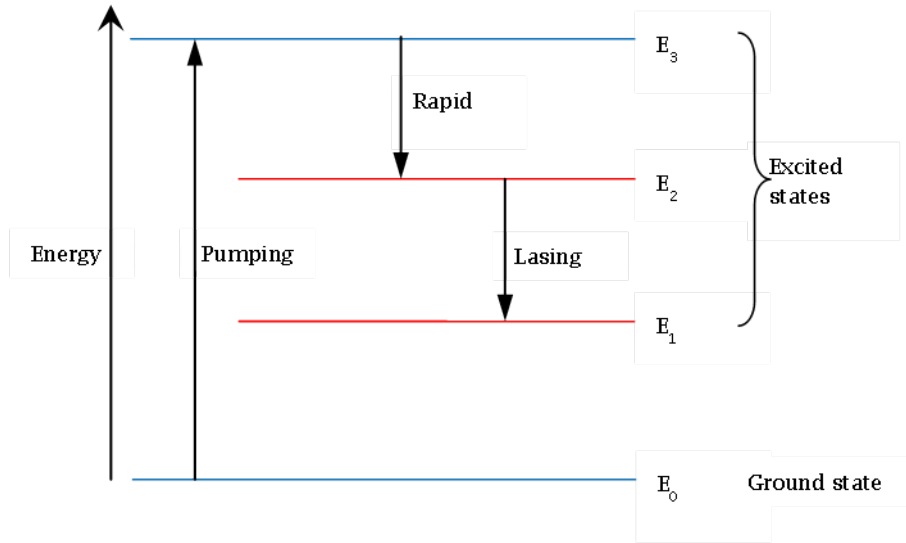


Figure 5.5.1: Schematic representation of a four-level laser transition scheme [91].

The argon-ion laser's properties are particularly well understood amongst ionized gas laser media. It principally works in the following way; Ar^+ atoms are ionized by electron collisions in a high current electrical discharge. This is followed up by further multiple collisions with electrons which excites the argon ion, Ar^+ , to a group of $4p$ energy levels. A population inversion forms between the $4p$ levels and the $4s$ level which is about 33.5 eV above the Ar atom ground level. Consequently the stimulated radiation from the $4p$ level down to the $4s$ level contains a series of wavelengths ranging from 351.1 nm to 528.7 nm but most of the power is concentrated in the 488 nm to 514.5 nm emission lines. The Ar^+ ion at the lower level ($4s$) returns to its neutral atomic ground state by radiative decay followed by recombination with an electron to form a neutral atom and after this the atom is ready for pumping again. Laser action thus takes place between these levels. Figure 5.5.2 illustrates the energy level diagram of the argon ion laser.

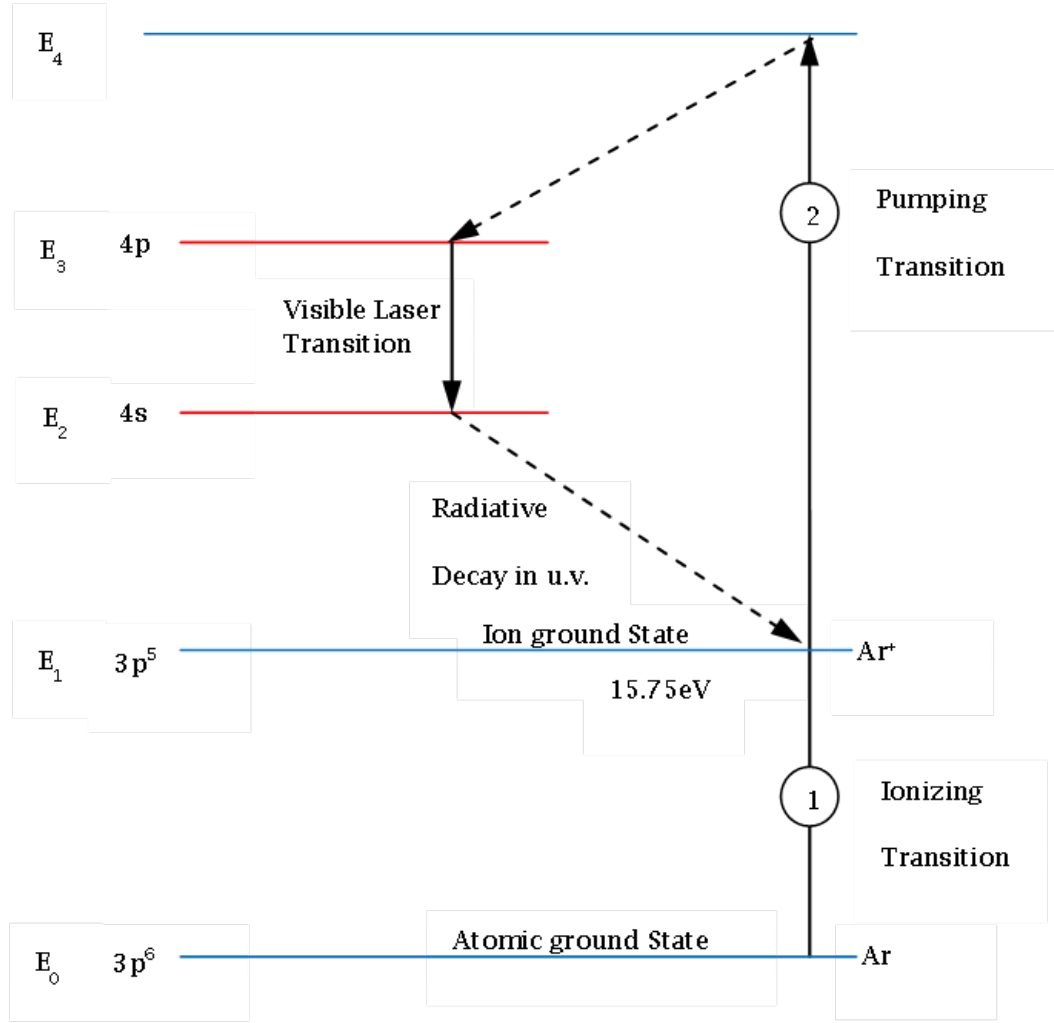


Figure 5.5.2: The Ar-ion laser energy diagram [91].

5.6 The Raman Spectrograph

The emerging light from the laser passes through a laser filter monochromator before being directed onto the sample and from there into the spectrograph. The light goes through shutters which protects the microscope camera and the CCD detector. Figure 5.6.1 shows a schematic diagram of the Jobin-Yvon T64000 Raman spectrograph used in the measurement presented in this work. Laser light is directed into the spectrograph by optical mirrors.

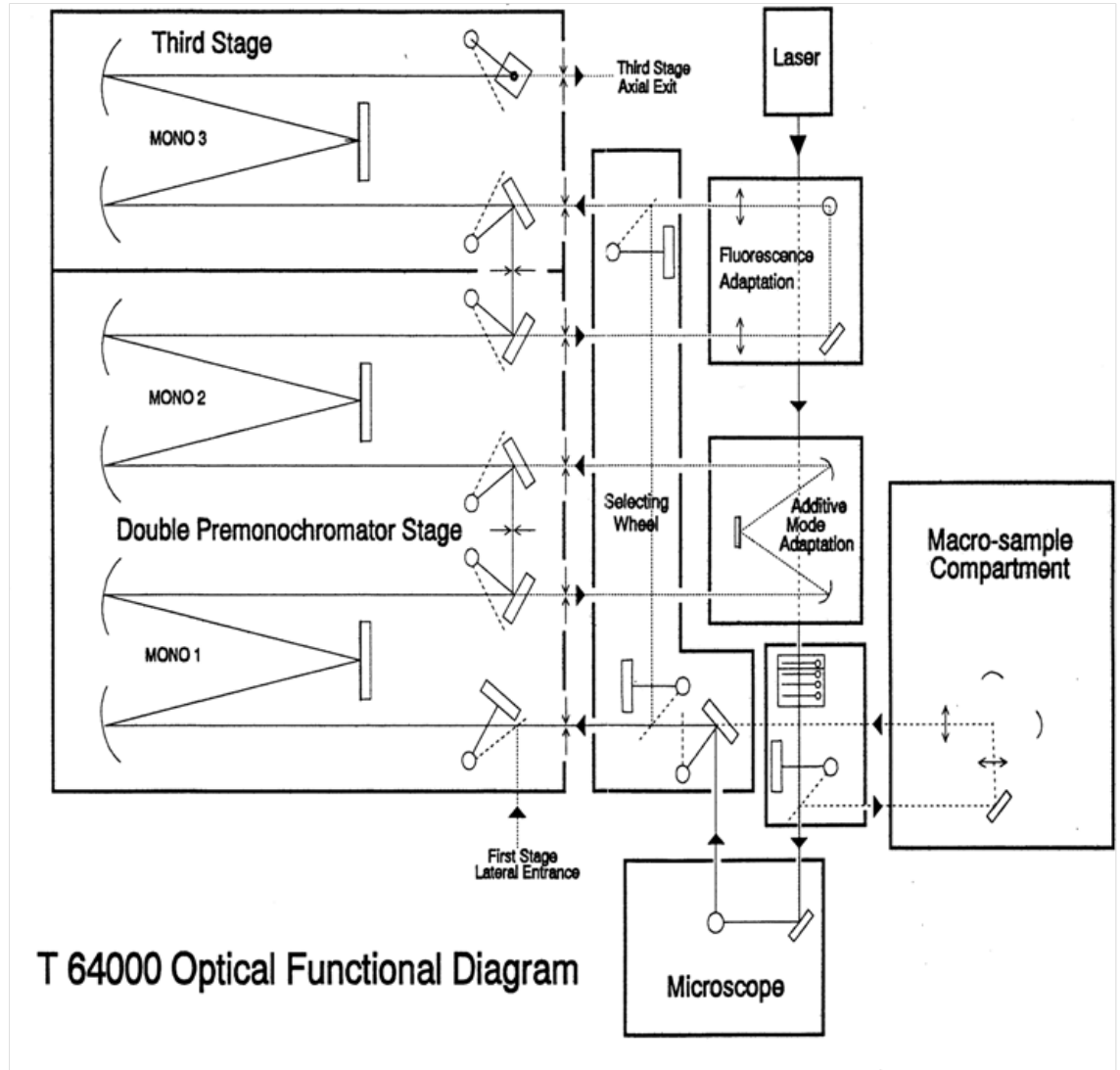


Figure 5.6.1: Schematic diagram of the Raman spectrograph showing the beam path [92].

5.6.1 Single Spectrograph Mode

The spectrograph is capable of being used in various modes. It can be operated as a single monochromator or a triple monochromator in either additive or subtractive mode. In single spectrograph mode, the light is directed to a holographic notch filter which strongly suppresses the elastically scattered light but allows the Raman scattered light to pass through. After passing through the notch filter the light passes through the entrance slit and into

the monochromator. The light entering the monochromator is then incident on a grating before finally reaching the detector. Two types of grating are available with the spectrometer and can be used interchangeably using the software. The choice of grating is influenced by the spectral range and resolution required. The 600 grooves/mm grating offers a wide spectral range but resolution is reduced, whereas the 1800 grooves/mm grating has a narrow spectral range but improved resolution. For all the present work the 1800 grooves/mm grating was used. This mode was employed because it gave good resolution with a faster cycle time, since the optical throughput is significantly greater than that for the triple spectrograph modes discussed below. An entrance slit width of 50 μm was used.

5.6.2 Triple Spectrograph Modes

In the triple subtractive mode, the pre-monochromators work as a filtering device, by dispersing the scattered light and recombining part of it, before it is re-dispersed by the spectrograph. It is very efficient in removing stray light resulting from the laser excitation line making analysis at low wavenumbers possible. The throughput is evidently weaker than that obtained using the single mode. The triple additive mode is useful when extremely high resolution is needed. All three monochromators act as dispersers, and this results in a narrow range of wavelengths being spread across the detector.

5.6.3 Charge Coupled Device (CCD) Detector

The light dispersed by the grating falls on the charge coupled device (CCD) detector cooled to $-130\text{ }^{\circ}\text{C}$ by liquid nitrogen, which detects the scattered light. The CCD detector is a rectangular chip consisting of 1024×256 pixels and the detector works in such a way that it measures the amount of light

on each pixel. The CCD converts the scattered light to a digital signal which is manipulated by the computer software to produce observable spectra. The spectra obtained are a plot of intensity (measured in arbitrary units) (y- axis) against wavenumbers relative to the exciting laser line (x-axis).

5.6.4 Raman Microscope

A modified Olympus BX40 microscope was used in this work. This has a beam splitter which enables it to be used with the laser beam or conventional light sources. Objective lenses with magnification factors of $20\times$, $50\times$ and $100\times$ were available but only the $20\times$ lens was used throughout the present work. It had the largest spot size on the sample of $\sim 2\text{ }\mu\text{m}$. The confocal pinhole varies from 0.1 mm to 2 mm and in this work the pinhole was set at 2 mm as this gave the best signal. The opaque nature of the samples meant it was not necessary to use the improved axial resolution offered by the smaller pinhole sizes. The beam is focused using the beam splitter and the microscope camera/monitor set-up. Scattered light from the sample returns through the microscope into the spectrometer where it is processed in any one of the three configurations of the spectrograph.

5.7 Raman 2D Mapping Details

The Raman experimental spectrometer system is interfaced to a computer and is software controlled. The spectrometer can be operated in a macro-Raman mode, where measurements are done in the macro-sample chamber, normally for a large or irregular sample specimen, or in the micro-Raman mode, where the measurements are done on the microscope stage. In the present work the spectrometer was operated in the 2-D micro-Raman mapping mode where the

computer controlled measurements are done using a motorized X-Y microscope stage. Before each set of daily measurements, spectral calibration of the spectrograph was done using the 546.074 nm emission line of a mercury discharge lamp as a reference value.

All Raman measurements were done at room temperature and standard pressure conditions. The 514.5 nm line of an Ar⁺ ion laser was used as excitation source at a beam power of 300 mW at the laser and ~ 2 mW at the sample. The 2-D mapping was done over a square plot of 6×6 points by sequential translation of the X-Y stage under the objective lens of the microscope. As mentioned in the previous section the $20\times$ objective was used with a spot size of $2\text{ }\mu\text{m}$. For the reasons described below three maps of small, medium and large size with the associated mapping points were made for each sample, see Figure 5.7.1. The spot separation for the different map sizes was $\sim 1000\text{ }\mu\text{m}$ for the small map, $\sim 1500\text{ }\mu\text{m}$ for the medium map and $\sim 2500\text{ }\mu\text{m}$ for the large map. The map areas were $\sim 36\text{ mm}^2$ for the smaller map, $\sim 100\text{ mm}^2$ for the medium map and $\sim 225\text{ mm}^2$ for the large map. The diamond grains size ranged from $2\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$ whilst the largest spot size achieved was $2\text{ }\mu\text{m}$. As a result on average the spot size was smaller than the average grain size.

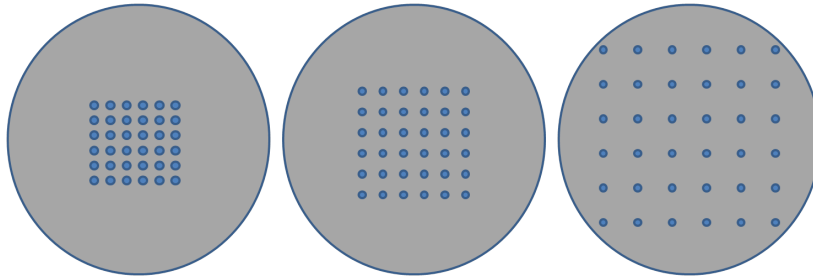


Figure 5.7.1: The three different map sizes used in this work; the distributions of the mapping points are illustrated.

Three map sizes were used in the initial Raman measurements with the set-up employed for the fatigue experiments in mind. The set-up is such that the

ball underneath the disc sample (see Figure 5.1.2) applies the maximum load at its centre.

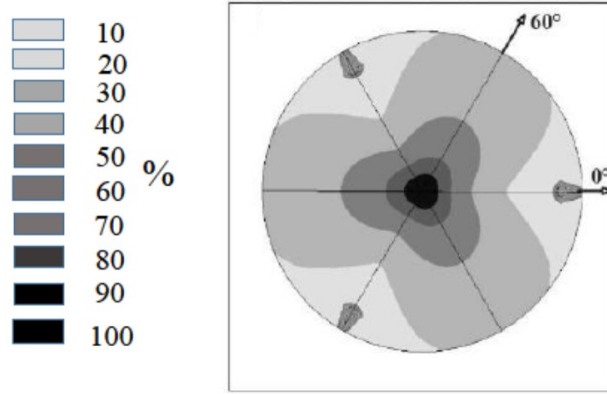


Figure 5.7.2: The expected stress field for the ball on three balls test [90], where the percentage of the maximum tensile stress component is plotted. The view is of the tensile stress surface of the disc showing the positive (tensile) first principal stresses.

Börger et al. [90], have performed finite element modelling for the three balls on ball arrangement and the expected stress field according to their calculations is given in figure 5.7.2. The percentage of the maximum tensile stress component in the disc (0–100%) is plotted, illustrating that the maximum tensile stress can be expected at the centre of the disc. The maximum stress calculated using this model, the dimensions of our test rig and the material properties of PCD is found to be 7.68 GPa. According to the model if measurements are done moving further away from the centre area of the sample, the effect of the applied load would gradually decrease. Thus the three map sizes used were aimed at investigating this possible range of damage or deformation. This would also give an indication of the degree of homogeneity of residual stresses within the samples.

5.8 Results and Discussion

This section gives the Raman scattering results as a function of the numbers of loading cycles to which the samples were subjected. Initial measurements were taken over 6×6 square maps of three varying sizes from a small map around the centre of the sample to a medium map and lastly a large map that covered as much of the sample as possible (see Figure 5.7.1). All the measurements were done on the cutting surface which is the surface that the three support balls were in contact with during the fatigue measurements. Nine samples were used for these Raman scattering measurements. Figure 5.8.1 shows Raman spectra recorded for the three maps on sample A and the results are shown in Table 5.3. It was observed from the Raman measured results similar to those shown in Figure 5.8.1 that the samples exhibited good agreement of the average surface stress. Several unfatigued samples were used to see if any variation would be observed as a function of map size and results as shown in Figure 5.8.1 show little variation. A comparison of the Raman spectra obtained from the use of different map sizes show negligible shifts in the peak position of the diamond Raman band and the measured full width at half maximum. As a result further Raman measurements of only the large map size are employed in the present work, with the spectra being averaged over the respective 36 mapping points for each sample using the Origin 8 software. These are the spectra plotted in this chapter.

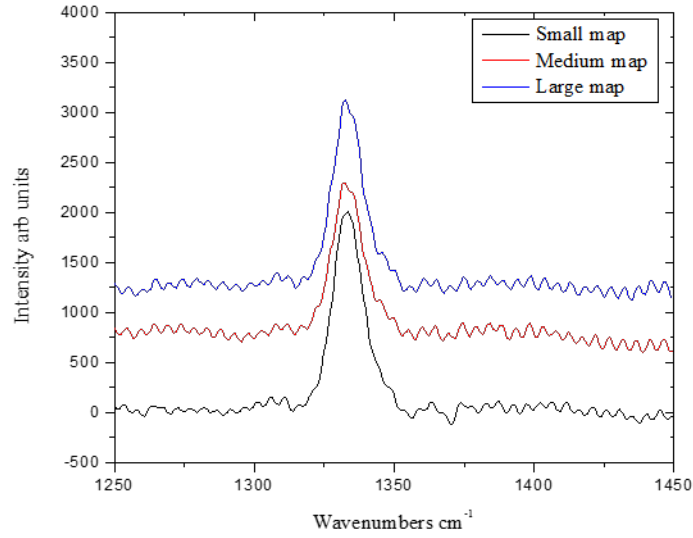


Figure 5.8.1: Raman spectra centred on the 1330 diamond Raman line for the three different map sizes for one of the PCD samples (sample A). The spectra have been vertically displaced and stacked for comparison purposes. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

5.9 Raman Spectra of Diamond

Diamond has a single, triply degenerate Raman peak at 1332.5 R.cm^{-1} (units are in wavenumbers relative to the incident laser beam wavenumber) [80]. The peak position conveys information on the nature and structure of the material under investigation. In an ideal diamond crystal, the sample would be stress free and the Raman peak would be measured at its theoretical position but as soon as it is subjected to stresses, be it externally imposed or due to internal imperfections, the frequency of the lattice phonons is subtly affected and the position of the Raman peak changes as discussed in section 4.5 [80].

Additional information is contained in the full width at half maximum of the peak. The Raman line-width of natural diamond is related to the average lifetime of the phonons created in the Raman process. In imperfect crystals the

phonons created in the Raman process can decay (scatter) at grain boundaries and at defect sites, thereby reducing the average lifetime and broadening the Raman line [81]. The theory of homogeneous spectral line width predicts that the line-width is inversely proportional to the average phonon lifetime and that the line shape is expected to be Lorentzian [82].

5.10 Average Spectra for all the Samples

As mentioned in section 5.2, the samples used in this work were taken from the same batch processed under the same conditions. With this in mind it was expected that if the samples were to be fatigued with the same load but to different numbers of cycles then some noticeable trend would be observed using the Raman technique.

The depth resolution, i.e. calculated length of focal barrel, for the objective used and the pinhole employed was approximately 20 μm . The actual sampling depth depends on the transparency of the sample and thus depends on the amount of cobalt in the sampling volume as well as the size of the diamond grain being sampled. The sampling depth thus varies from as little as 1 μm to a possible 20 μm for the largest grains. The measured stresses are thus limited to a region of the sample close to the surface. These average surface stresses for the samples would then be calculated and then plotted as a function of the number of cycles. The corresponding stress errors are calculated as the standard deviation of the average of the stress values measured in the respective map. Samples fatigued to relatively lower numbers of loading cycles were expected to exhibit less disorder and plastic damage and associated stress changes, with those fatigued to higher numbers of loading cycles exhibiting an increased degree of disorder. With an increase in the degree of disorder the measured spectra would exhibit some broadening as well as

significant peak shifts due to stress changes.

Table 5.3 shows a comparison of the position of the measured peak and the FWHM. A quick glance at the Table 5.3 shows that we have variation from one sample to the next with no trend with respect to the increase in the number of cycles. A plot of this variation is shown in Figure 5.10.1 where the measured spectra are stacked for comparison.

Table 5.3: Showing the respective average Raman peak positions and full width measured at half maximum for the samples. The errors in the Table are calculated from the standard deviation from the average.

Sample	Number of cycles	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error
Sample A	0	1335.34	0.09	12.29	0.31
Sample B	250000	1333.58	0.07	14.01	0.27
Sample C	300000	1333.81	0.06	12.62	0.22
Sample D	350000	1331.01	0.08	16.94	0.30
Sample E	400000	1333.23	0.07	13.55	0.26
Sample F	500000	1332.56	0.06	13.82	0.21
Sample G	600000	1333.28	0.08	13.41	0.27
Sample H	700000	1333.42	0.01	12.41	0.57
Sample I	750000	1332.71	0.08	12.05	0.32

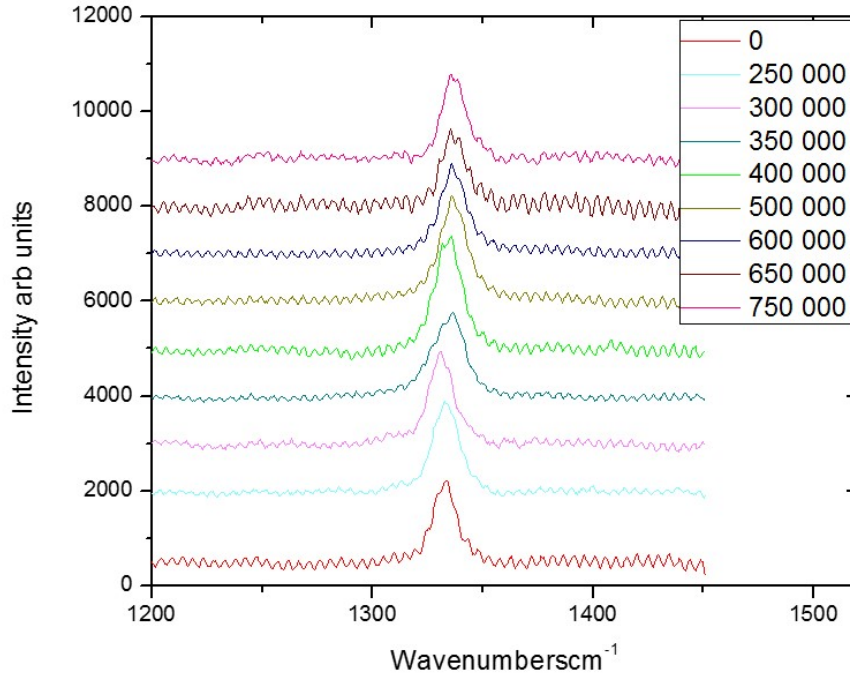


Figure 5.10.1: Comparison of the average Raman surface spectra for the samples A to I as a function of number of cycles. The spectra are taken as an average over all the mapping spots for the large map of each sample. The spectra have been stacked for comparison. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

It was expected that a gradual shift towards lower wavenumbers as the number of cycles increased because the degree of localized damage or deformation induced is expected to increase with number of cycles. As the degree of damage increases, the residual compressive stresses would decrease. Thus a shift in the peak position to lower frequencies was anticipated. Examination of the calculated stress indicates for the measurements performed that the shift to lower wavenumbers for the diamond peak position and an increase in the broadening of the FWHM was not observed, see Table 5.3. Figure 5.10.2 shows the variation in the peak position for the samples and the variation in the average surface stress is shown in 5.10.3. Negative stress values indicate compressive stress and positive stress values indicate tensile stress.

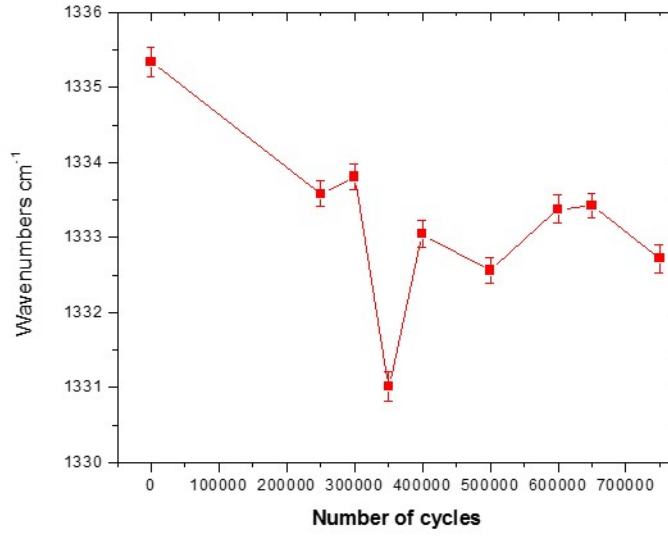


Figure 5.10.2: Variation of Raman peak position as a function of number of cycles for the nine samples used (*sample A through to sample I*).

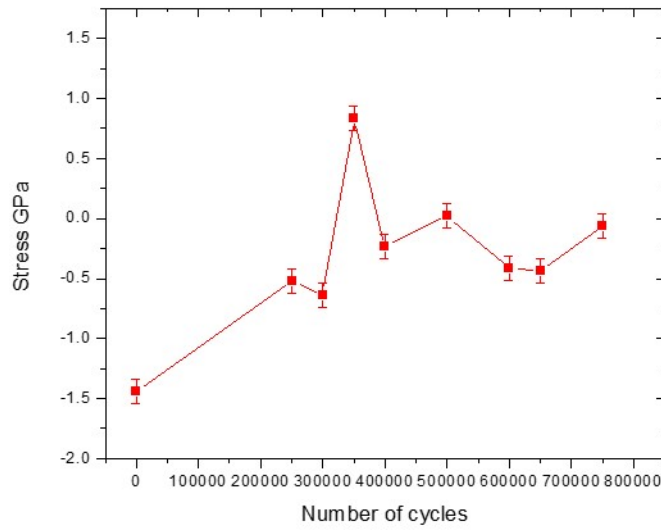


Figure 5.10.3: Variation of stress as function of number of cycles for the nine sample used (*sample A through to sample I*). The reported stress values were calculated using equation 4.6.3 and piezo-Raman coefficient $\alpha = 1.92 \text{ cm}^{-1}/\text{GPa}$. The unstressed diamond peak position used is 1332.5 cm^{-1} .

There is a trend in figures 5.10.2 and 5.10.3 but it is not as clear as at first thought. Despite the fact that all samples were obtained from the same

batch the results suggested that the samples were not entirely the same and as such, the results would vary from one sample to the next. Sample D is good example of this as it is obviously an outlier from the results shown in figures 5.10.2 and 5.10.3. Further alternating fatigue and Raman measurements were thus required to refine the initial measurements with the anticipation of clearer trends in the results.

5.11 Further Raman Measurements

Having noticed the variation across the samples an attempt to investigate the possibility of getting a noticeable trend for each individual sample was done. Hence the individual samples were subjected to alternating fatigue and Raman measurements, with the measurements being taken at different numbers of cycles to establish the trend. The brittleness of the sample material resulted in several of the samples fracturing before reaching the desired number of cycles. Of the nine samples listed in Table 5.3 only five survived a series of alternating fatigue experiments and Raman experiments with the number of cycles increasing each time. These were sample A, sample B, sample E, sample F, and sample G. For the remainder of this chapter these five samples will be discussed in detail. The average stresses reported here were calculated from the 2D maps by first determining the peak position measured at each grid point and then taking the average of these 36 peak position values.

5.12 Sample A

This sample was not subjected to any loading and was kept for comparison purposes. Raman measurements were done and Figure 5.12.1 shows the spectra obtained for the three different map sizes.

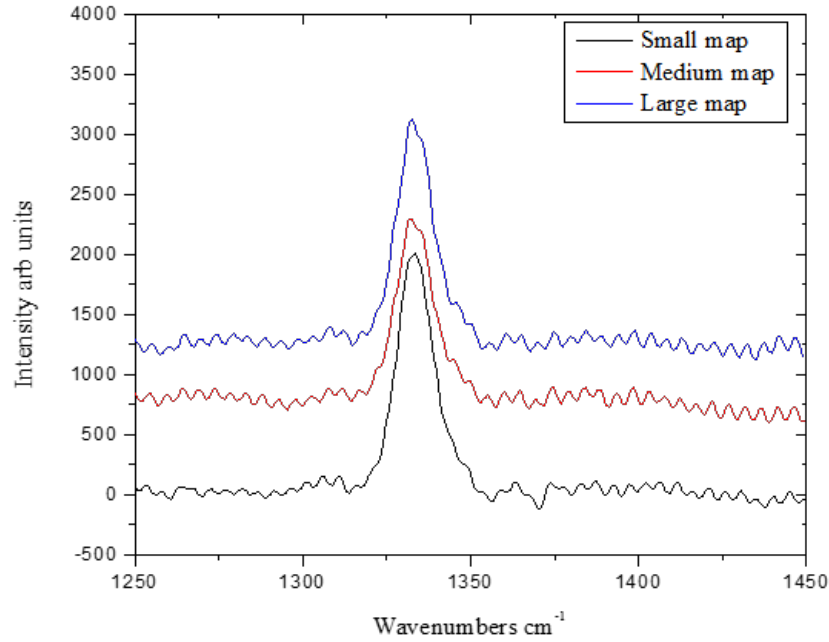


Figure 5.12.1: Comparison of the measured Raman spectra for sample A as a function of map size. The spectra have been displaced and stacked for comparison. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

5.13 Sample B

The sample had been fatigued to 250000 cycles initially. Subsequent measurements were conducted with incremental sets of 50000 cycles each time, with the exception of the last set which was set at 25000 to ensure the sample would not fracture before the stress mapping measurement. Table 5.4 shows the follow up number of cycles of loading to which the sample was subjected, the respective Raman peak positions, full width measured at half maximum and the calculated stress. The stress was calculated using equation 4.6.3. Figure 5.13.1 shows the different spectra obtained at the different number of cycles and the spectra indicate a progressive shift of the frequency to lower

wavenumbers and subsequently a change in the nature of the calculated residual stress.

Table 5.4: Table indicating Raman peak position and full width measured at half maximum for sample B.

Cycles	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error	Stress (GPa)
250000	1333.58	0.07	14.01	0.27	-0.53
300000	1333.74	0.02	12.29	0.08	-0.60
350000	1333.55	0.03	12.51	0.11	-0.50
400000	1333.63	0.02	12.64	0.09	-0.36
450000	1333.35	0.02	12.89	0.10	-0.42
500000	1332.93	0.02	12.64	0.09	-0.17
550000	1332.45	0.02	12.89	0.10	0.08
575000	1332.34	0.05	13.76	0.22	0.14

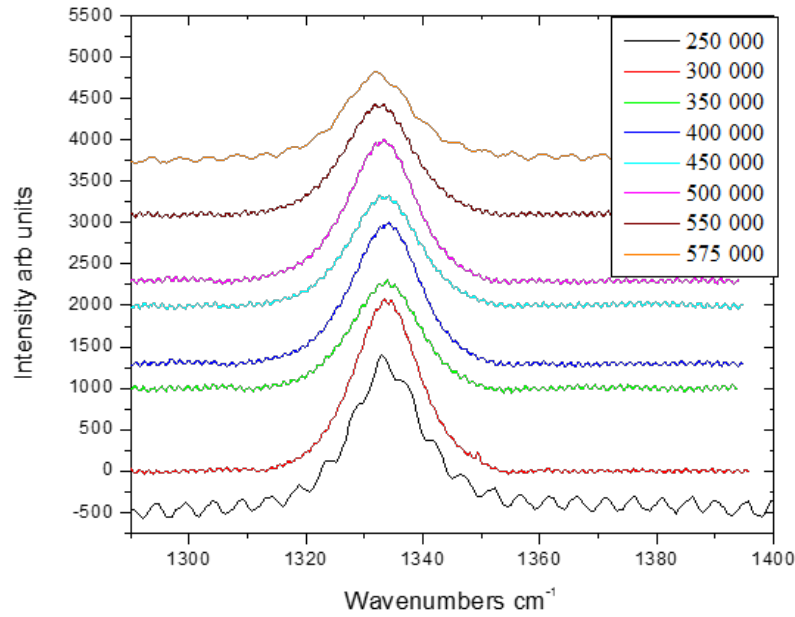


Figure 5.13.1: The measured Raman spectra as a function of number of cycles for sample B. The spectra have been displaced and stacked for comparison. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

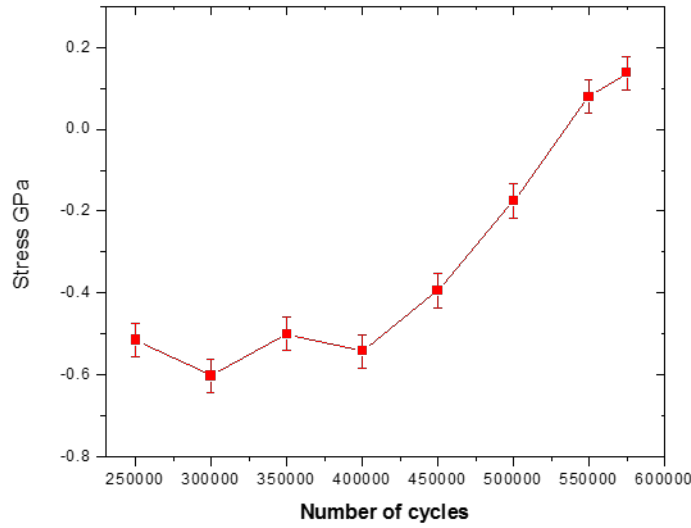
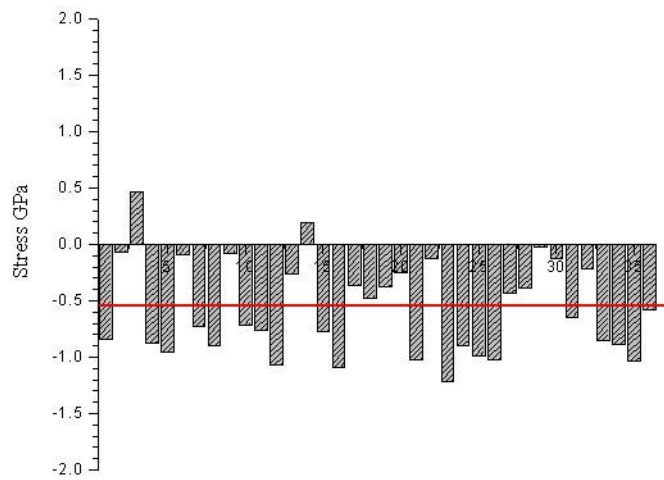


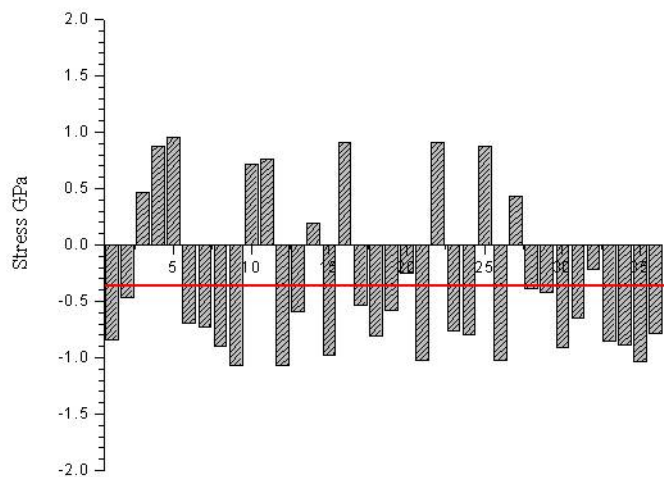
Figure 5.13.2: Stress variation as a function of the number of cycles for sample B.

The calculated stress as indicated in Figure 5.13.2 clearly illustrates the shift in the nature of the residual stresses from being compressive to being tensile in nature. The calculated stress from Table 5.4 changed from -0.53 GPa to 0.14 GPa. These stresses are calculated as the average of the 36 individual mapping points, however a consideration of the point to point stress measured shows some variation.

The histogram diagrams in Figure 5.13.3 and Figure 5.13.4 following indicate the point to point stress variation within the respective samples after being subjected to the respective number of loading cycles. Since the samples were randomly loaded for the fatigue experiments, the mapping points in the respective histograms related to the different number of loading cycles are random. The graphs clearly show the number of tensile points within the mapped area increasing with the increase in the number of loading cycles.



Point to point stress variation in the 6×6 square mapping
for sample B after 250 000 cycles



Point to point stress variation in the 6×6 square mapping
for sample B after 400 000 cycles

Figure 5.13.3: Point to point stress variation as a function of the number of cycles for Sample B after 250000 cycles and 400000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

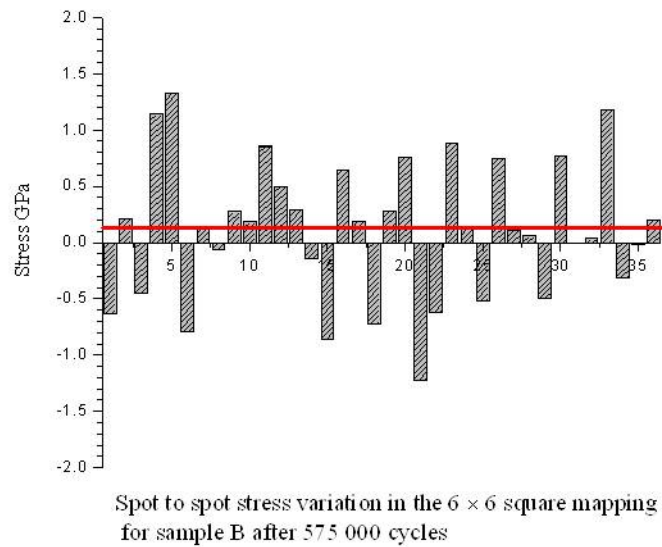
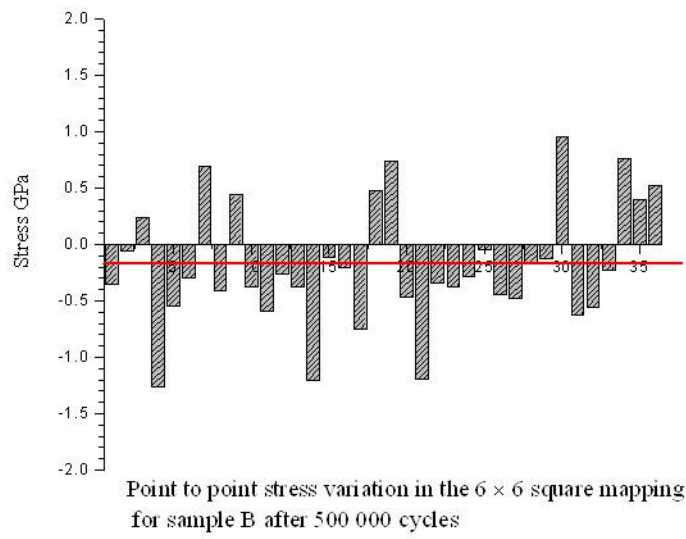


Figure 5.13.4: Point to point stress variation as a function of the number of cycles for Sample B after 500000 cycles and 575000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

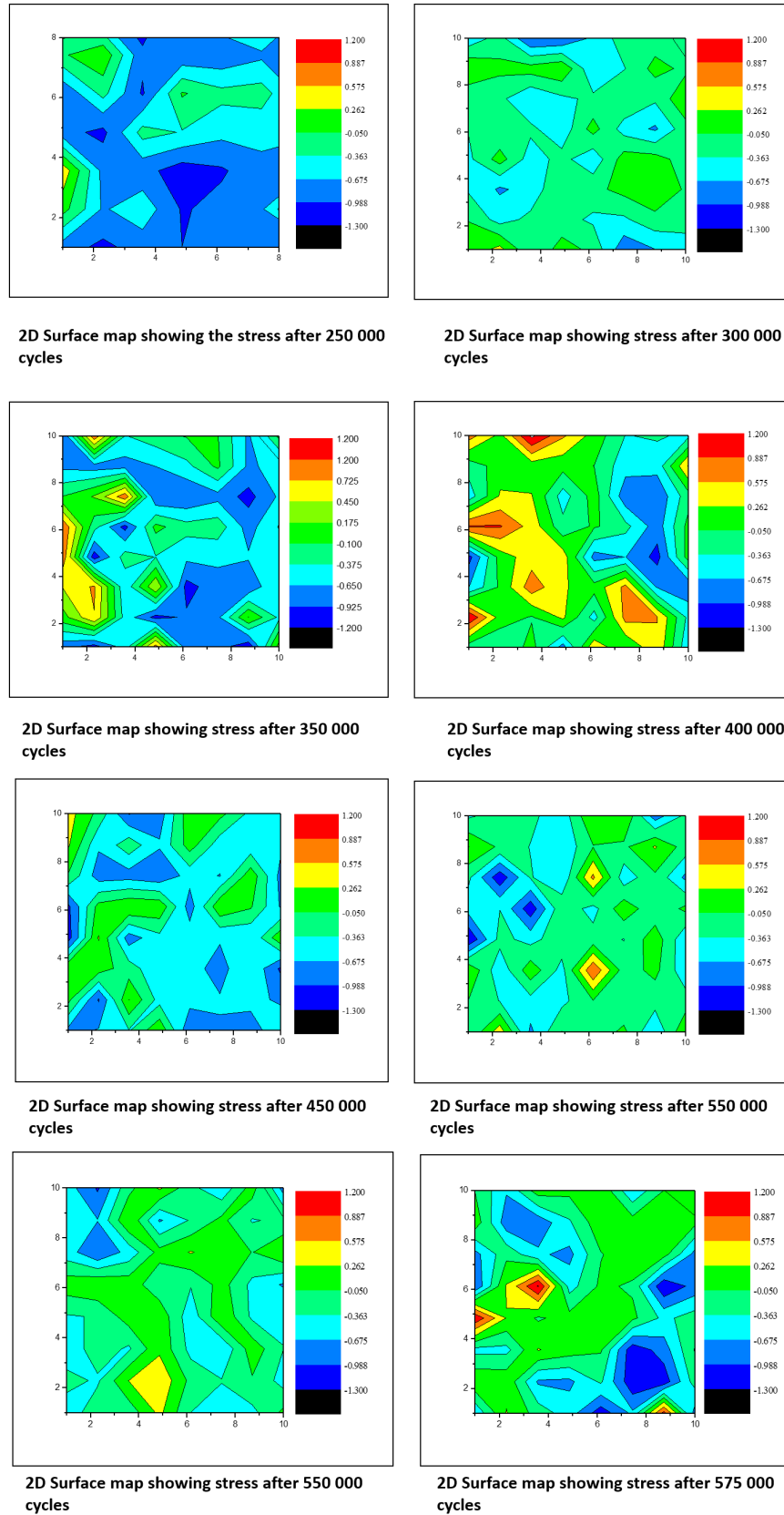


Figure 5.13.5: 2D Surface maps showing the nature and distribution of stress as a function of the number of cycles for sample B. Compressive stresses are shown by the colours black - deep green; and tensile stresses are indicated by the colour range yellow-red. The stresses are reported in GPa.

2D surface maps were plotted to show the nature of the stresses and their distribution in the mapped area and are shown in Figure 5.13.5. These maps were generated via the “2D Contour Plot” feature of Origin 8 software. Each of the 36 points of the 6×6 matrix is assigned a colour based on its associated value. The number of colours is chosen by the user, and the software then interpolates between adjacent points so that the change in colour represents the gradient between the values of the points. Thus similar values will have the same or adjacent colours, while values with larger differences will have more contours between the points. The 2D surface maps clearly show the changes that are taking place within the sample.

Table 5.5: Comparison of the number of mapping points exhibiting tensile stresses as a function of the number of loading cycles for sample B.

Number of cycles	Number of points
250000	2
300000	0
350000	1
400000	10
450000	10
500000	9
550000	13
575000	22

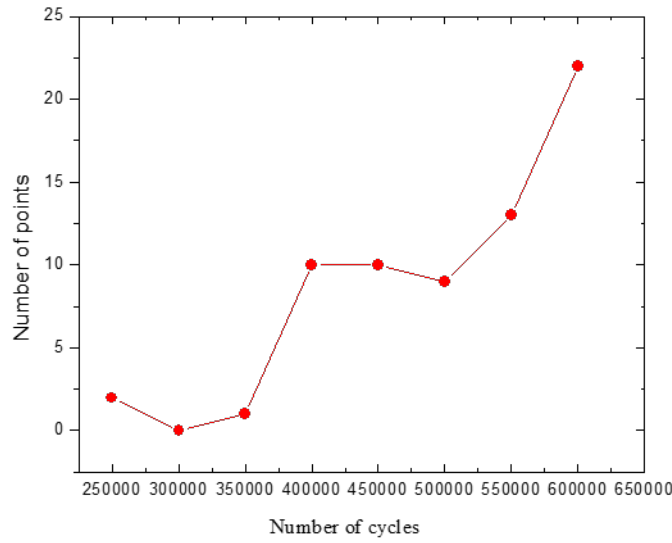


Figure 5.13.6: A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample B.

Figure 5.13.6 and Table 5.5 shows the number of mapping points within the mapped area that were exhibiting tensile residual stresses at the different number of cycles. Even though the sample was showing average surface residual stresses compressive in nature for the first six levels of the number of cycles, there existed some spots which had stresses tensile in nature. From Table 5.5 it is evident that these spots were not enough in the first six readings to significantly alter the nature of the average residual stresses. A notable trend however is observed which indicates an increase of the number of spots in the tensile regime as the number of cycles increase. It is possibly due to the inter-grain bridges formed during sintering which give rise to the diamond to diamond bonding in the PCD that start breaking during the fatigue experiments and as a result the grains become loosely connected. This then gives rise to the observed tensile residual stress in these spots. Eventually in the last two Raman measurement a transition from average compressive residual stresses to average tensile residual stresses is seen.

5.14 Sample E

The sample had been fatigued to 400000 cycles before being fatigued to higher number of cycles as shown in Table 5.6. Again the respective spectra were measured and the subsequent peak position, the full width measured at half maximum as well as the calculated stress are shown in Table 5.6. A comparison of the spectra obtained at the different number of cycles to which the sample was subjected, was done and the spectra obtained are shown in Figure 5.14.1.

Table 5.6: Showing the Raman peak position and full width measured at half maximum as a function of number of cycles for sample E.

Cycles	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error	Stress (GPa)
400000	1333.23	0.07	13.55	0.26	-0.21
450000	1333.33	0.09	14.76	0.33	-0.25
500000	1332.57	0.09	14.84	0.32	0.22
525000	1332.40	0.09	15.05	0.32	0.23
550000	1332.19	0.09	15.80	0.35	0.37

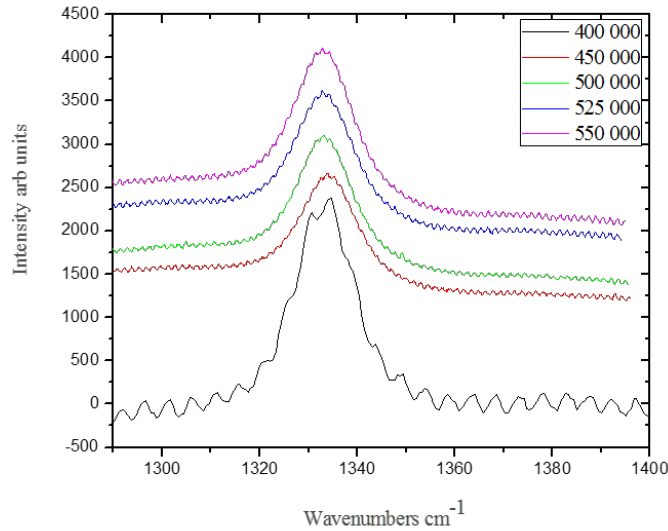


Figure 5.14.1: The measured Raman spectra as a function of number of cycles for sample E. The spectra have been displaced and stacked for comparison. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

The calculated stress again indicates a shift in the nature of the stresses from being compressive to being tensile. A plot of the stresses as a function of number of cycles is shown in Figure 5.14.2. The calculated stress ranged from -0.21 GPa to 0.37 GPa. The subsequent 2D surface maps were plotted to indicate the distribution of the stresses. Clear changes in the nature of the stresses are observed, as shown in Figure 5.14.5.

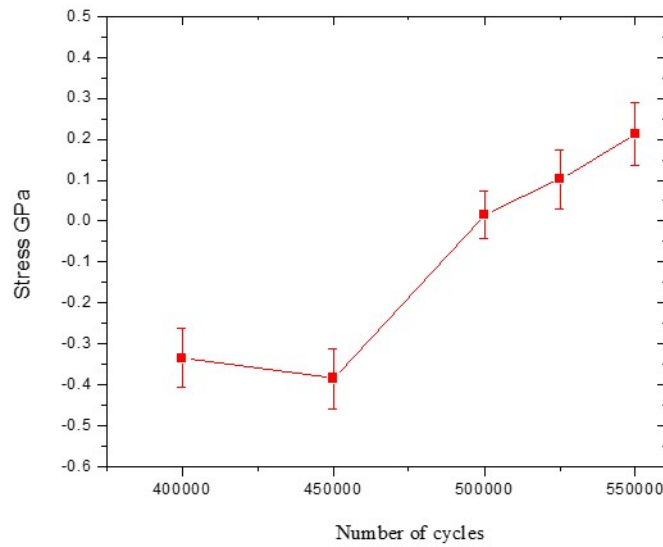


Figure 5.14.2: Stress variation as a function of number of cycles for sample E.

The histogram diagrams in Figure 5.14.3 and Figure 5.14.4 indicate the point to point stress variation within Sample E. Again the sample was randomly loaded for the fatigue experiments, thus the mapping points in the respective histograms related to the different number of loading cycles are random. The graphs clearly indicated the number of tensile points within the mapped area increasing with the increase in the number of loading cycles.

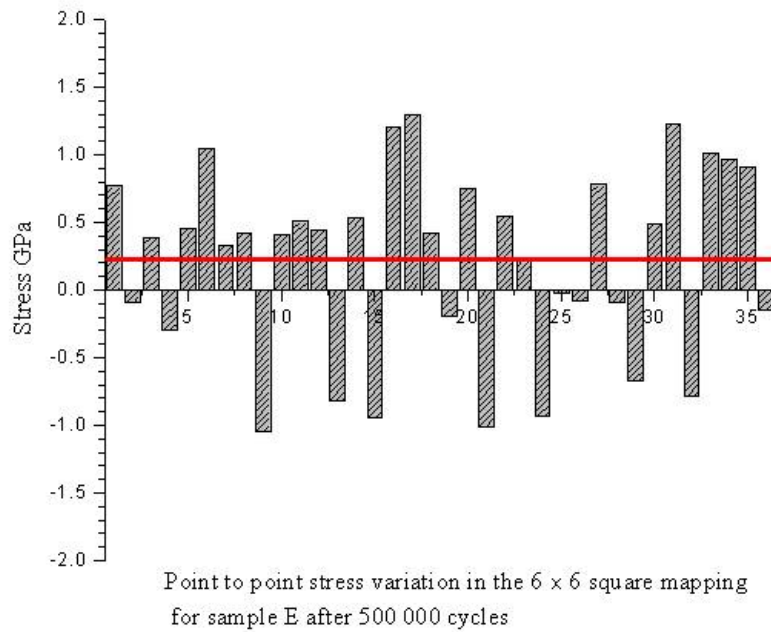
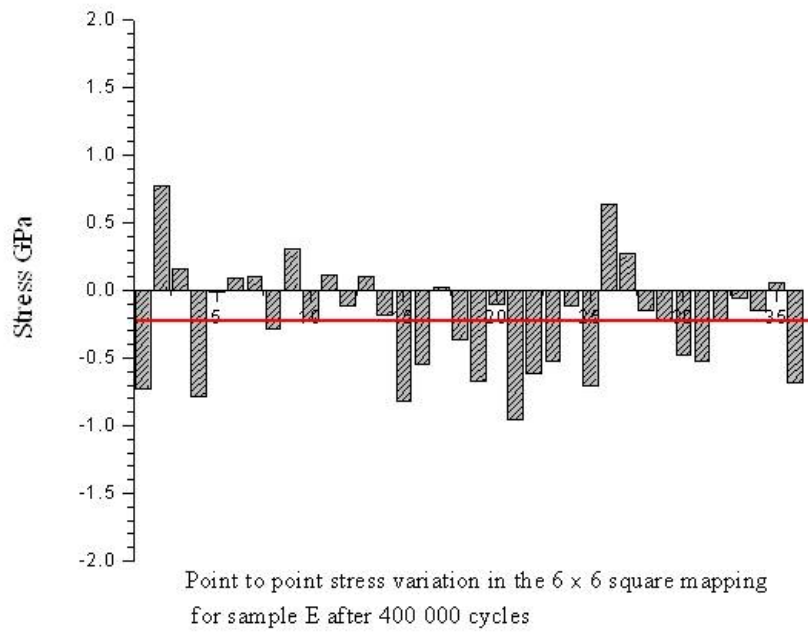


Figure 5.14.3: Point to point stress variation as a function of the number of cycles for Sample E after 400000 cycles and 500000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

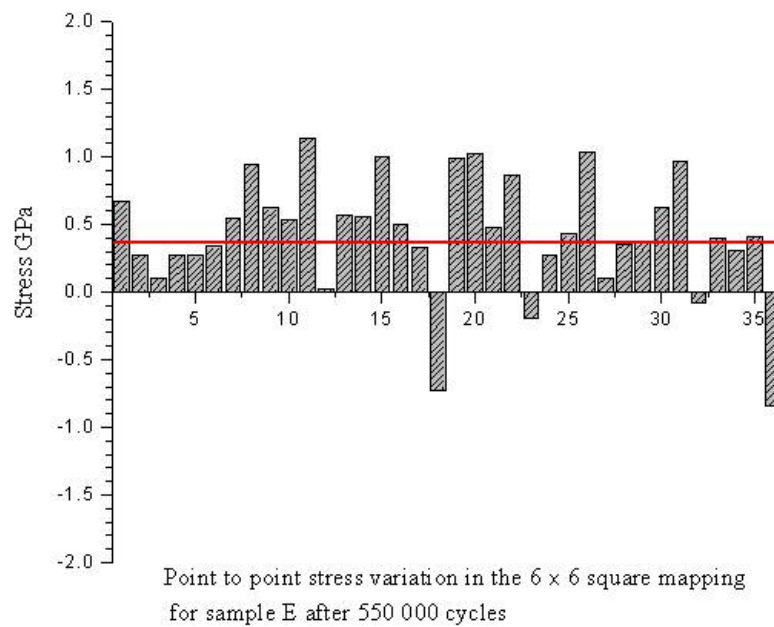
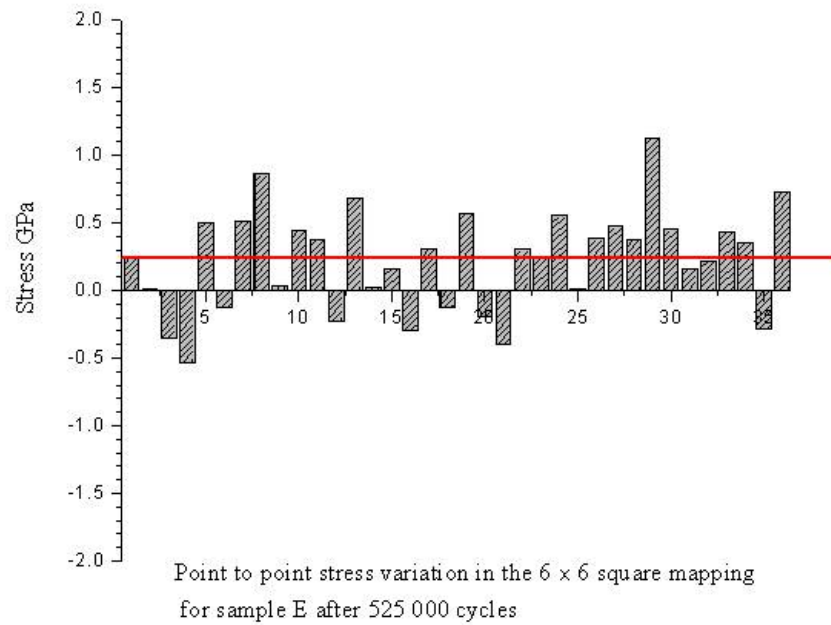


Figure 5.14.4: Point to point stress variation as a function of the number of cycles for Sample E after 525000 cycles and 550000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

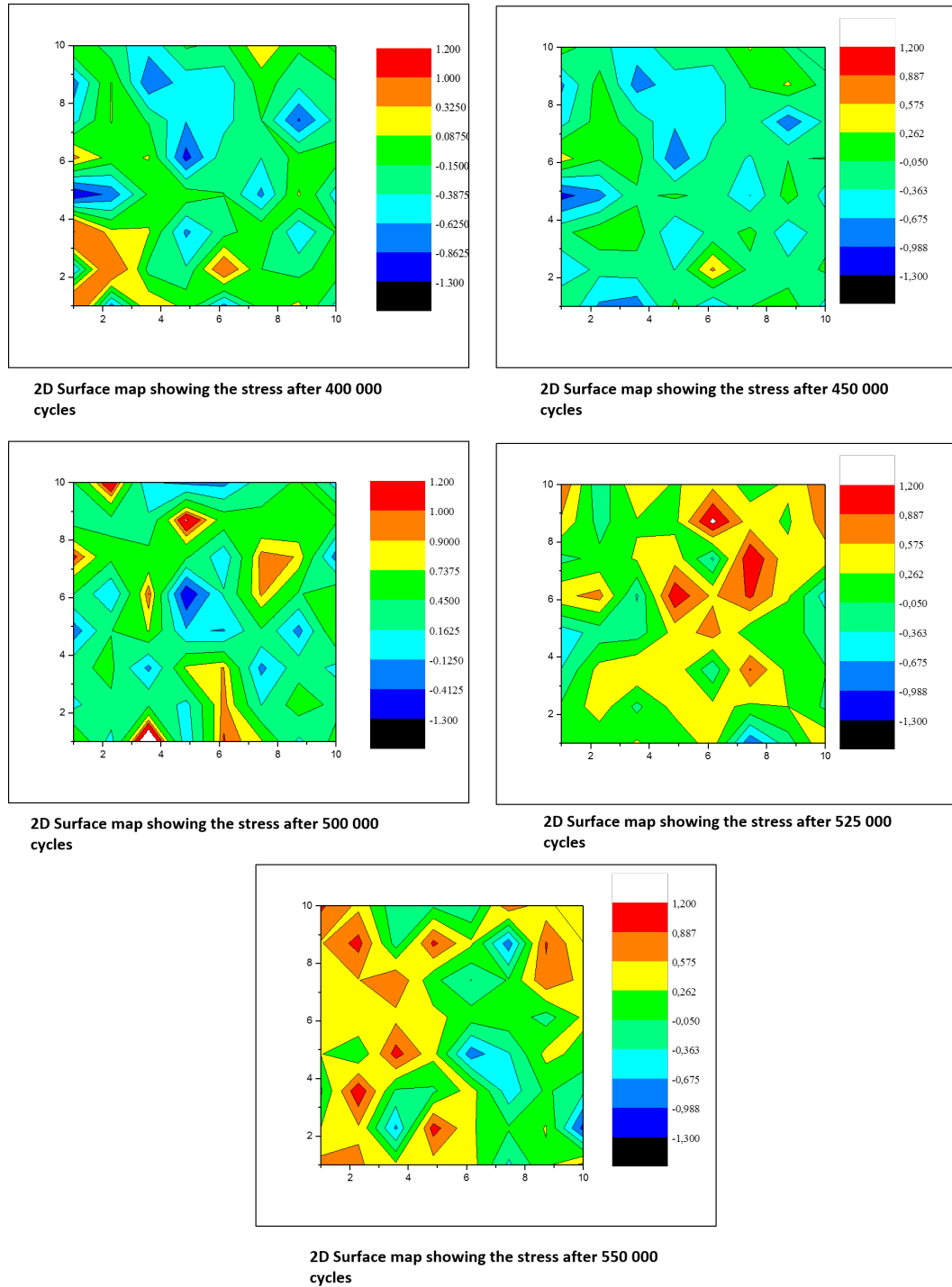


Figure 5.14.5: 2D Surface maps showing the nature and distribution of stress as a function of the number of cycles for Sample E. Colour range black - light green show compressive stresses and the range deep green - red indicate tensile stresses. The stresses are reported in GPa.

Table 5.7: Comparison of the number of mapping points exhibiting tensile stresses as a function of the number of loading cycles for sample E.

Number of cycles	Number of points
400000	11
450000	25
500000	22
525000	27
550000	32

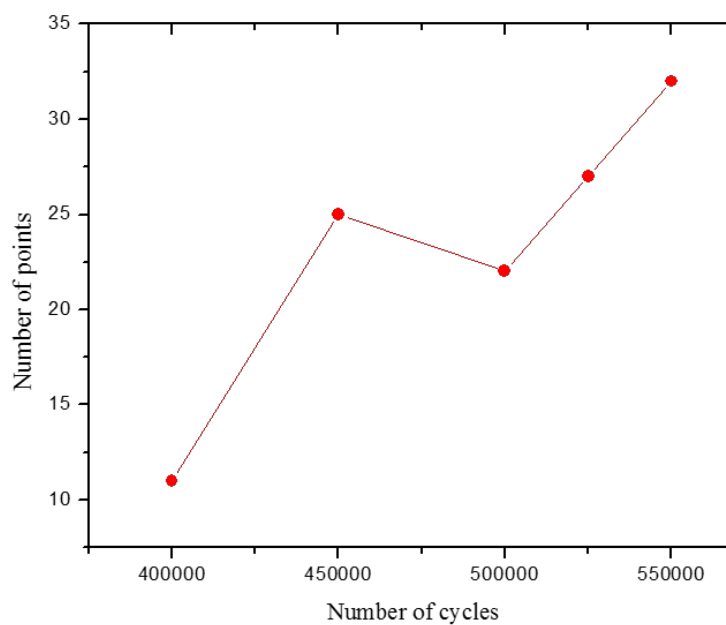


Figure 5.14.6: A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample E.

Five Raman measurements were carried out on sample E. The first two measurements indicated that the sample was exhibiting compressive residual stress but for the rest of the measurements the sample exhibited average tensile stress (see Table 5.6). Table 5.7 and Figure 5.14.6 show the number of mapping points exhibiting tensile residual stresses against number of cycles and a trend is observed. As the number of cycles increases so does the number of spots showing tensile residual stresses. Because the residual stresses have to

be globally balanced, it is plausible that the interior is compressive. Unfortunately, the interior was not measured to track for stress changes.

5.15 Sample F

The sample had been fatigued to 500000 cycles initially. Alternating fatigue and Raman measurements were done for the different number of cycles that followed and the results obtained are shown in Table 5.8. The sample exhibited an average tensile residual stress after 550000 cycles and the highest stress calculated was found to be 0.41 *GPa*.

Table 5.8: Showing the Raman peak position and the full width measured at half maximum for the different number of cycles for sample F.

Cycles	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error	Stress (GPa)
500000	1332.56	0.06	13.82	0.22	-0.02
550000	1332.23	0.11	14.75	0.40	0.14
600000	1332.19	0.09	14.88	0.33	0.16
625000	1332.49	0.12	16.75	0.46	0.01
675000	1331.08	0.08	15.06	0.29	0.74

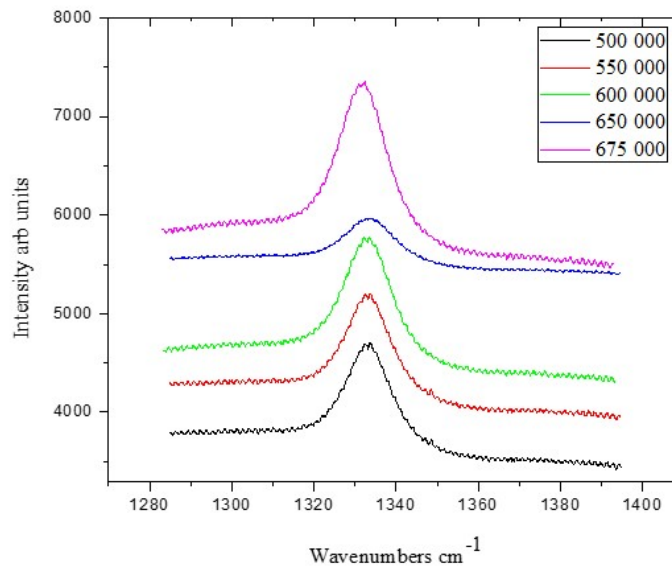


Figure 5.15.1: Raman peak position and the full width measured at half maximum for sample F. The spectra have been displaced and stacked for comparison. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

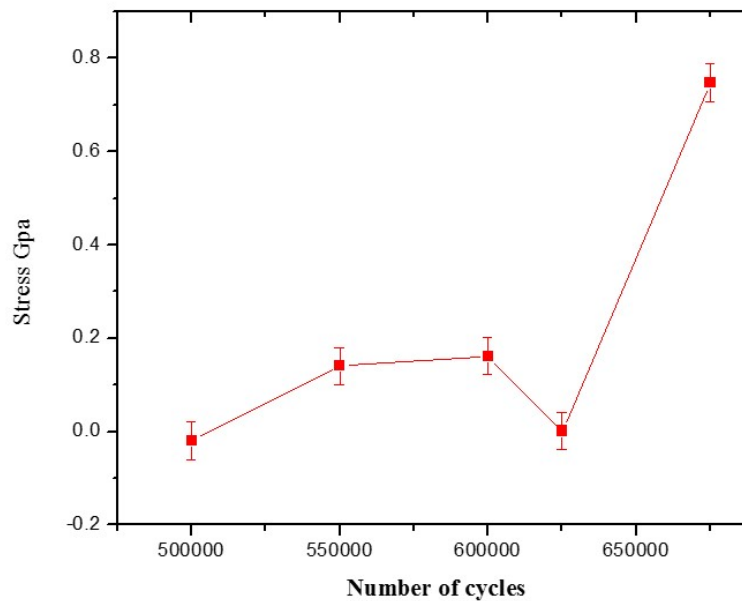


Figure 5.15.2: Stress variation as a function of number of cycles for sample F.

The histogram diagrams in Figure 5.15.3 and Figure 5.15.4 indicate the point to point stress variation within Sample F. Again the sample was randomly loaded for the fatigue experiments, thus the mapping points in the respective histograms are random. The graphs clearly indicated the number of tensile point within the mapped area increasing with the increase in the number of loading cycles.

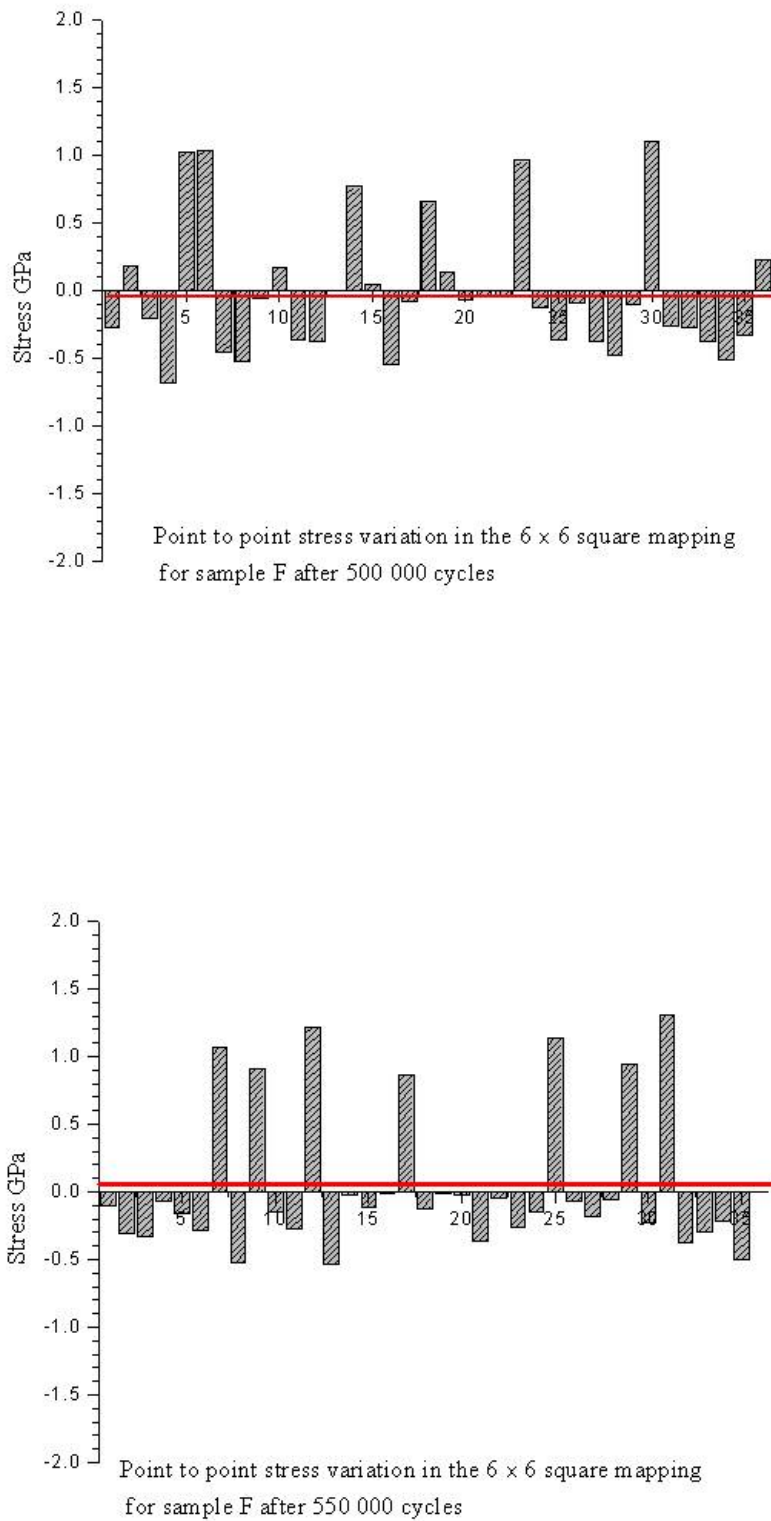


Figure 5.15.3: Point to point stress variation as a function of the number of cycles for Sample F after 500000 cycles and 550000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

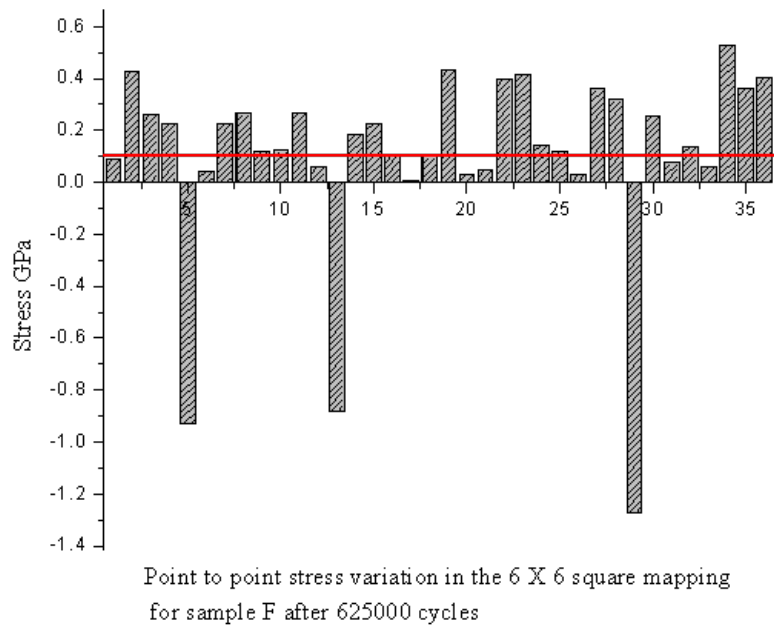
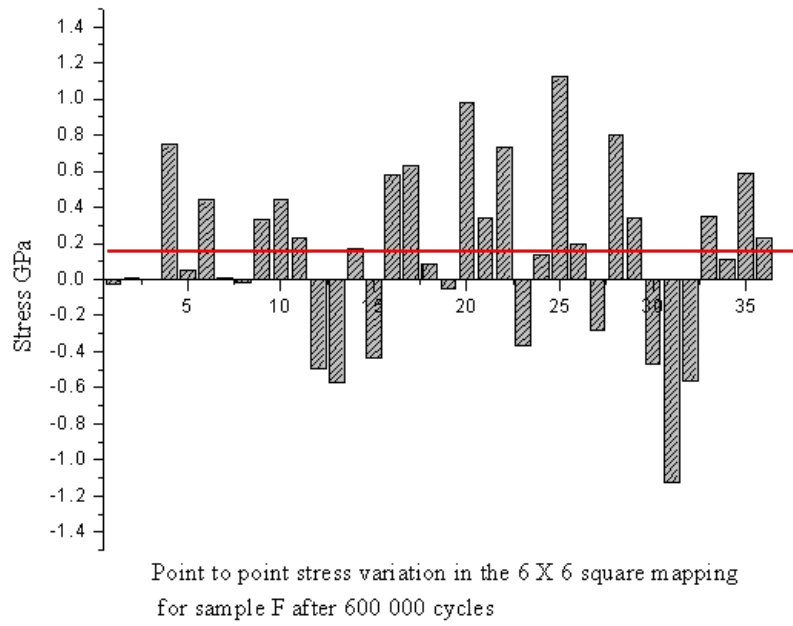


Figure 5.15.4: Point to point stress variation as a function of the number of cycles for Sample F after 600000 cycles and 625000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

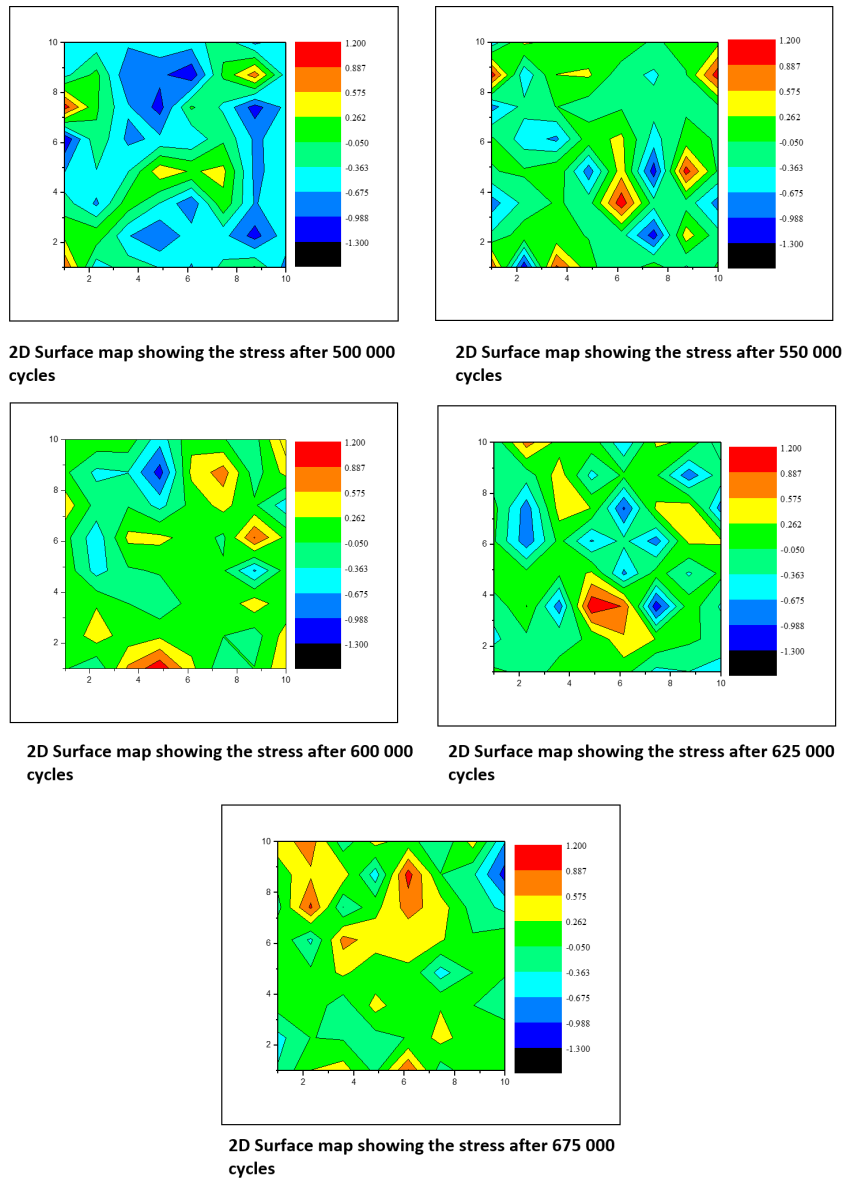


Figure 5.15.5: . 2D maps showing the nature and distribution of stresses as a function of number of cycles for sample F. Colour range black - light green indicate compressive stresses and deep green - red show tensile stresses. The stresses are reported in GPa.

Table 5.9: Comparison of the number of mapping points exhibiting tensile stresses as a function of the number of loading cycles for sample F.

Number of cycles	Number of cycles
500000	11
550000	6
600000	24
625000	33
675000	34

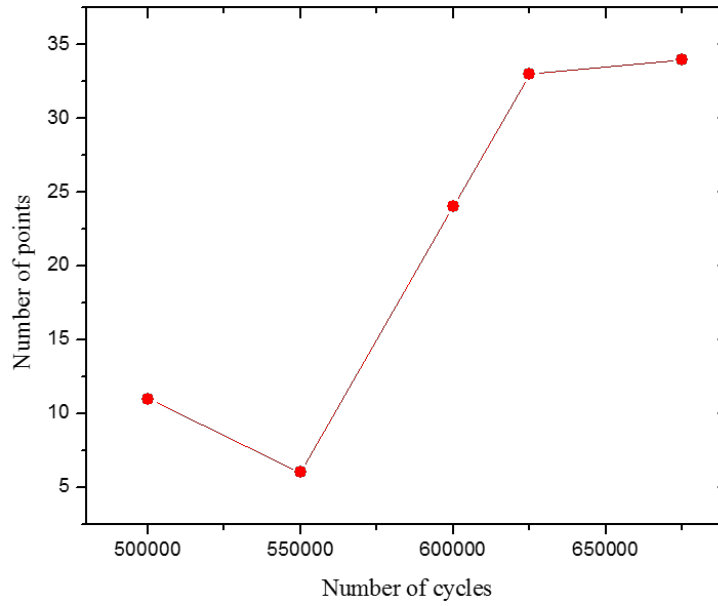


Figure 5.15.6: A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample F.

This sample exhibited tensile residual stresses in all its measured Raman spectra as shown in Table 5.8. A quick look at Table 5.9 and Figure 5.15.6 shows a general gradual increase in the number of spots exhibiting tensile stresses. Again this can be attributed to the inter-grain bridges breaking mentioned in section 5.13. The dip at 550000 cycles can be attributed to incomplete crack closure which happens at times in the micro-cracks present in the samples.

5.16 Sample G

Sample G was initially subjected to 600000 cycles of loading and as with the other samples, further alternating fatigue and Raman experiments were carried out and the results obtained are shown in Figure 5.16.1 as well as Table 5.10. The peak position values, the full width measured at half maximum and the calculated stress are shown as well. Again there is a notable trend showing

a definite shift in the nature of the residual stresses from being compressive in nature to being tensile (see Figure 5.16.2). The full width measured at half maximum values also indicate some broadening at the highest number of cycles indicating an increasing degree of plastic deformation in the diamond crystals.

Table 5.10: Showing the Raman peak position and the full width measured at half maximum and the calculated stress for sample G.

Cycles	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error	Stress (GPa)
600000	1333.28	0.08	13.41	0.27	-0.38
650000	1333.57	0.03	12.39	0.10	-0.61
675000	1333.08	0.03	13.48	0.11	-0.20
700000	1332.69	0.02	13.49	0.08	-0.05
725000	1331.76	0.07	17.14	0.25	0.36

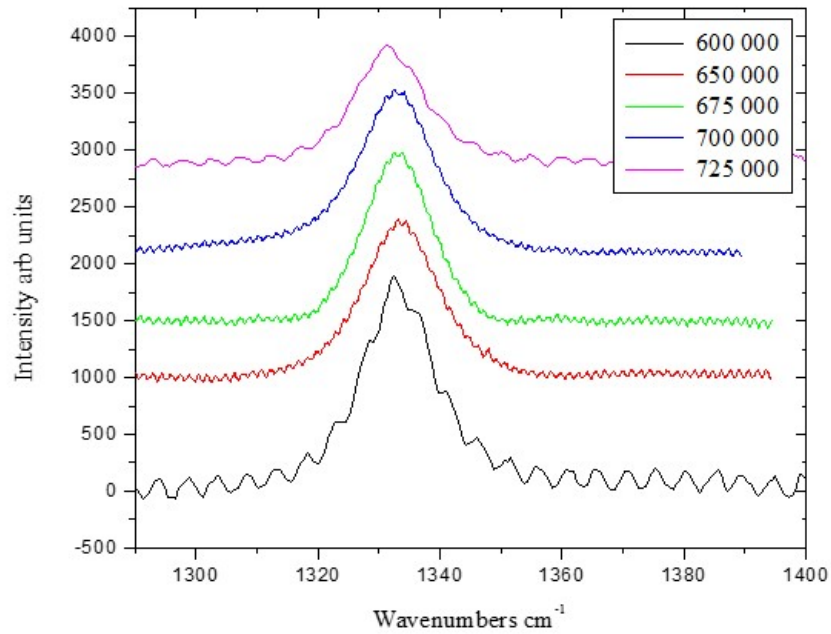


Figure 5.16.1: Measured Raman spectra showing peak position as a function of number of cycles for sample G. The apparent periodicity in the background in some of the spectra is a result of instrumental effect and does not affect the peak position or peak width being studied.

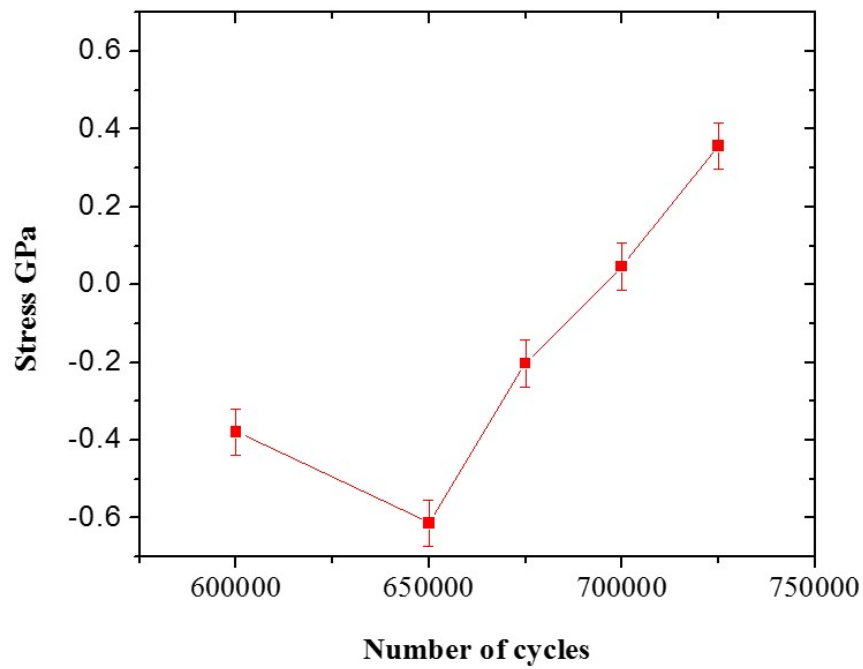


Figure 5.16.2: Stress variation as a function of number of cycles for Sample G.

The histogram diagrams in Figure 5.16.3 and Figure 5.16.4 indicate the point to point stress variation within Sample G. Again the sample was randomly loaded for the fatigue experiments, thus the mapping points in the respective histograms are random. The graphs clearly indicated the number of tensile points within the mapped area increasing with the increase in the number of loading cycles.

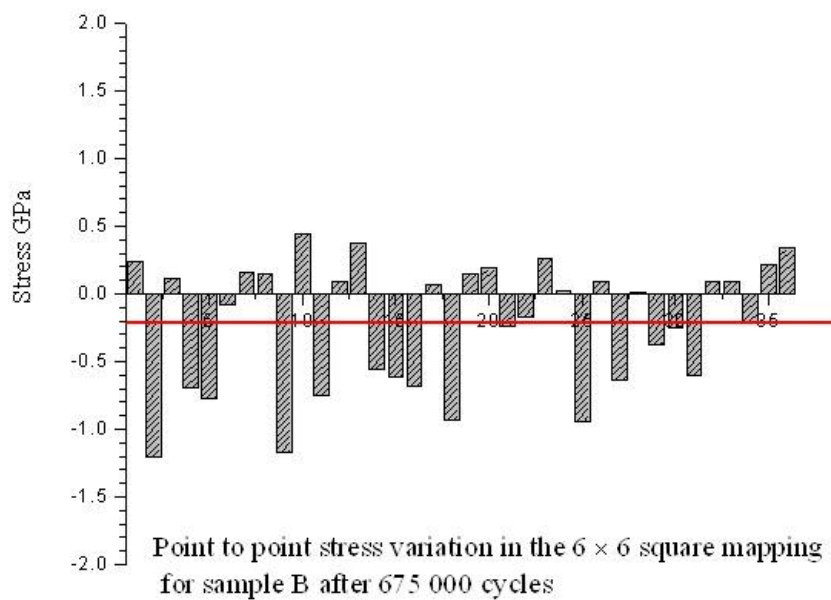
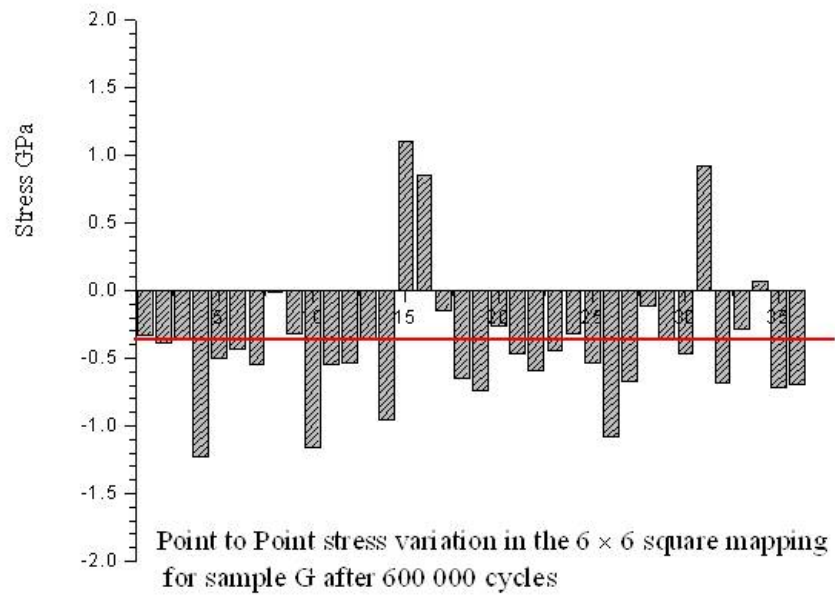


Figure 5.16.3: Point to point stress variation as a function of the number of cycles for Sample G after 600000 cycles and 675000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

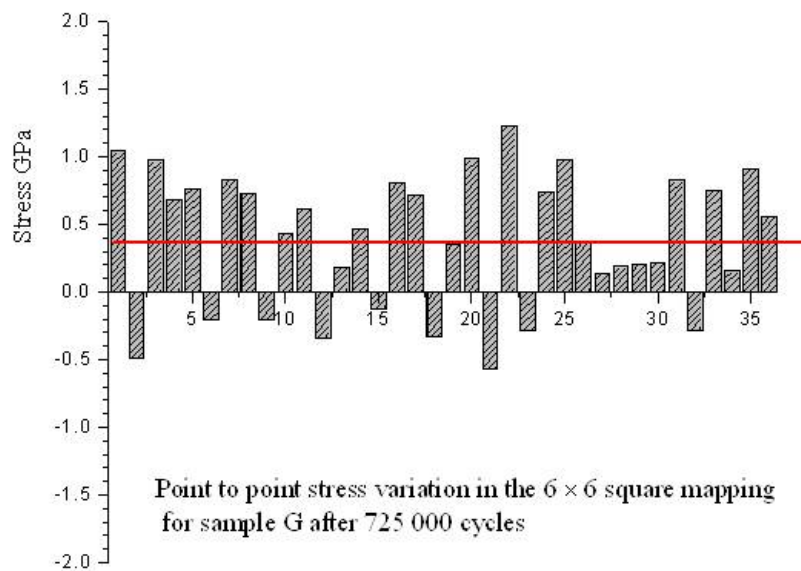
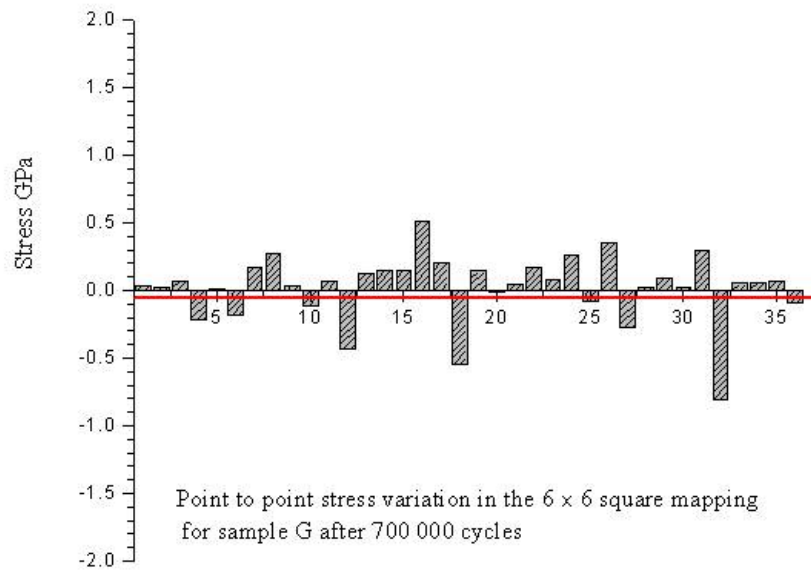


Figure 5.16.4: Point to point stress variation as a function of the number of cycles for Sample G after 700000 cycles and 725000 cycles respectively. The red line indicates the average surface stress value after the respective number of cycles. The order of these mapping points as seen in the graphs is random since the sample was loaded randomly after each run.

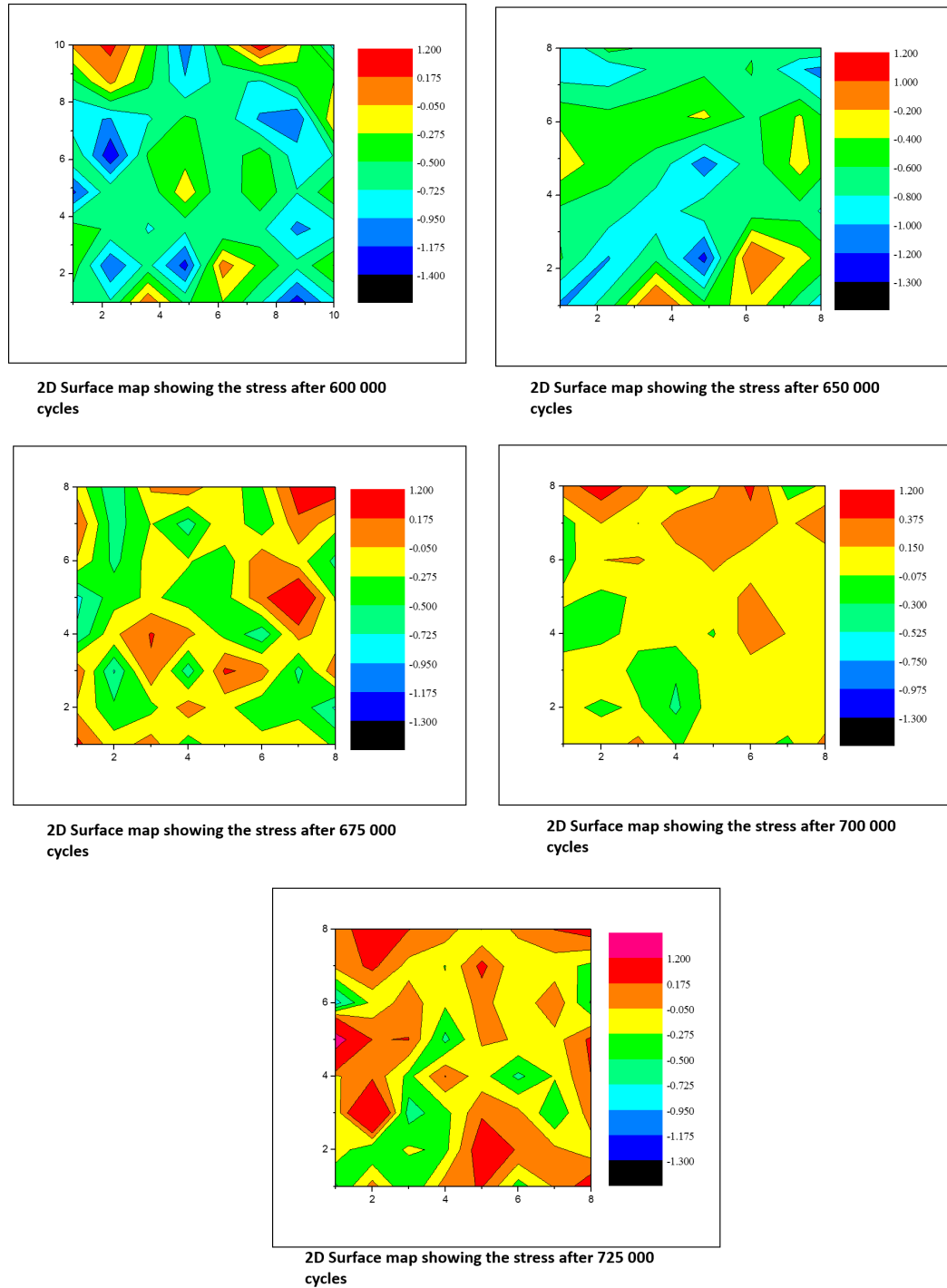


Figure 5.16.5: 2D surface maps showing the distribution of the stress as a function of number of cycles for sample G. Colour range black - deep green indicate compressive stresses and yellow - pink show tensile stresses. The stresses are reported in GPa.

Table 5.11: Comparison of the number of mapping points exhibiting tensile stresses as a function of the number of loading cycles for sample G.

Number of cycles	Number of points
600000	4
650000	7
675000	18
700000	26
725000	27

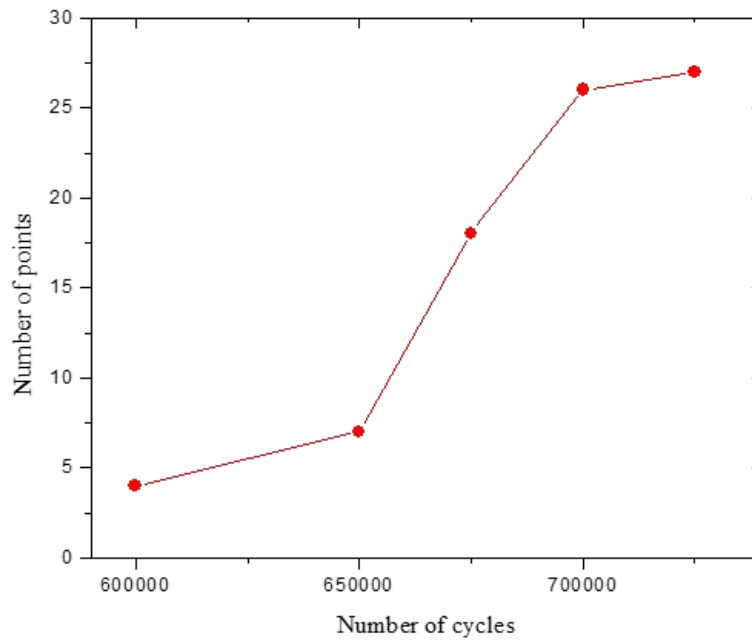


Figure 5.16.6: A plot of the number of mapping points exhibiting tensile stresses against number of loading cycles for sample G.

Table 5.11 and Figure 5.16.6 show the number of mapping points which are experiencing tensile residual stresses at the different levels of loading cycles. The sample showed average tensile residual stresses for most of its measurements and the mapping points with this type of stresses increased with number of cycles.

In the fatigue experiments, the mapped sample surface was in direct contact with the three balls of the ball on three balls arrangement shown in Figure

5.2. Before each fatiguing run, the samples were loaded randomly into the fatigue jig, i.e. the contact points were different between different runs. It is thus not possible to visualize any localised damage in the 2D maps that may be related to the contact points.

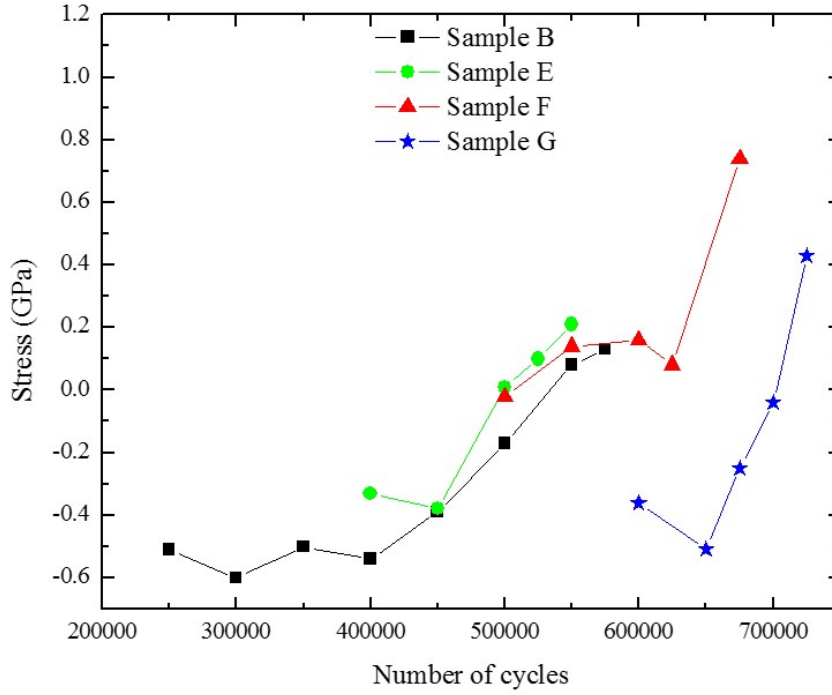


Figure 5.16.7: Average surface stress variations as a function of the number of cycles for samples B, E, F and G.

For comparison purposes, Figures 5.16.7 and 5.16.8 illustrate the respective effects of the multiple fatigue cycles for the samples B, E, F and G. The average stress variations for the samples are shown in Figure 5.16.7 while in Figure 5.16.8, the number of mapping points exhibiting tensile stress is indicated. Although there are obvious variations in detail in the results for the various samples there are also common trends. In particular the average surface stress is compressive during the earlier phase in which the number of fatigue cycles remains relatively limited while in the later phase of a large

number of cycles the average surface stress becomes tensile in nature for all the samples. A comparison of the data for the mapping points shows that for the earlier phase of limited fatigue cycles there are relatively few points in which the local stress is tensile and that the number increases substantially when the samples have been subjected to a large number of cycles. These measurements confirm the differing nature of the mapping points and hence indicate that the fatigue cycles produce localised damage.

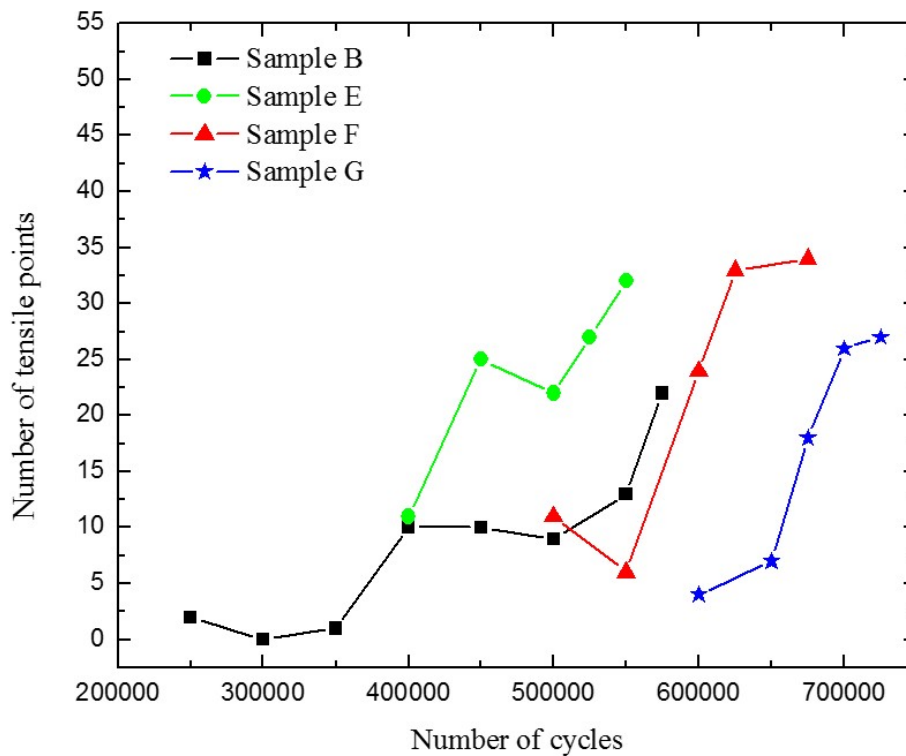


Figure 5.16.8: The number of mapping points exhibiting tensile stress as a function of the number of fatigue cycles for samples B, E, F and G.

5.17 Scanning Electron Microscope and Energy Dispersive Spectroscopy Measurements

The observed trend of a general increase of the number of mapping points exhibiting average tensile residual stress with increase in number of loading cycles can possibly be explained using the cracking on the inter-grain bridges within the samples. It is therefore reasonable to expect some observable evidence of cracking on the surface of the fatigued tool-bits. To substantiate this notion scanning electron microscope pictures were taken to establish if there was visible evidence of damage due to fatigue. This was done with the understanding that fatigue is defined as being the accumulation of localized damaged due to cyclic loading, the critical word here being localized. Hence it was anticipated that areas showing signs of fracture would be observed.

A JEOL JSM7500F field emission scanning electron microscope was employed for this part of the work operating at 15 keV in a vacuum of 5.1×10^{-4} Pa. The results obtained are shown in the subsections that follow. Energy dispersion spectroscopy measurements were also done using the same equipment.

5.17.1 Sample B

The SEM pictures obtained for this particular sample showed no signs of damage. Large pools of cobalt were however noted. See Figure 5.17.1 for results. Figure 5.17.2 and Table 5.12 show the Energy Dispersive Spectroscopy (EDS) results giving an elementary analysis of the composition of the sample. The EDS results show an acceptable atomic percentage of the sample being 91.82 % carbon which is primarily arising from diamond.

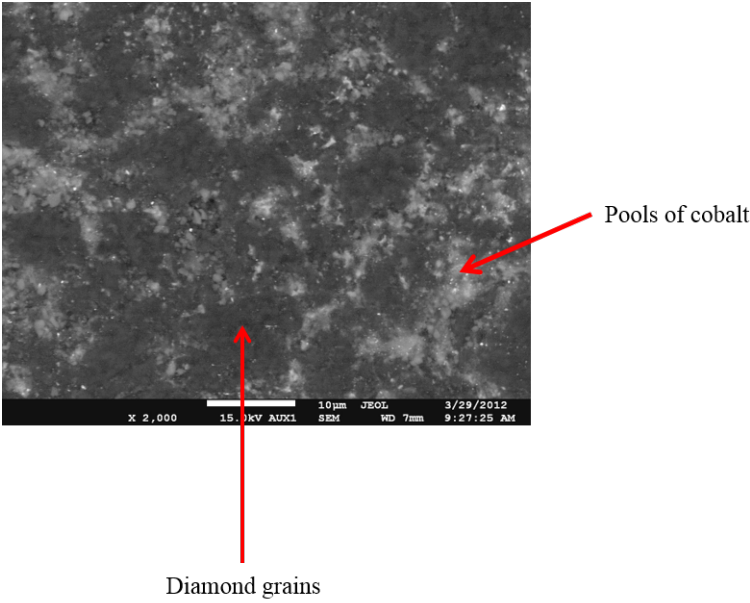


Figure 5.17.1: SEM images showing the cobalt pools and the diamond grains for sample B. The cobalt pools are the bright areas in the images and the dark regions are the diamond grains.

Table 5.12: EDS results for sample B.

Element	Weight %	Atomic %
C	82.71	91.82
Co	7.79	6.49
O	6.50	1.47
W	3.00	0.22
Total	100.00	

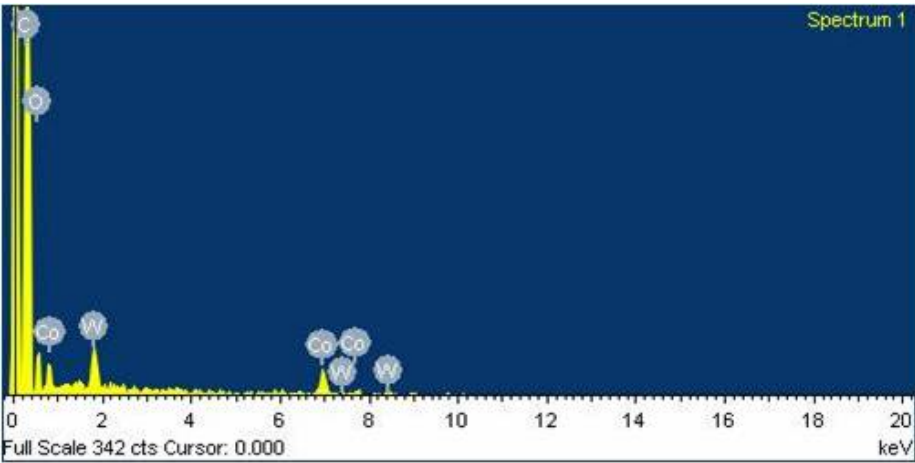


Figure 5.17.2: Energy dispersion spectra for sample B.

5.17.2 Sample E

The SEM pictures obtained did not show signs of any damage as shown in Figure 5.17.3. EDS results are shown in Figure 5.17.4 and Table 5.13. The EDS results indicate a 92.65 % atomic percentage of the sample as diamond being in the expected range. Some traces of oxygen were also noted.

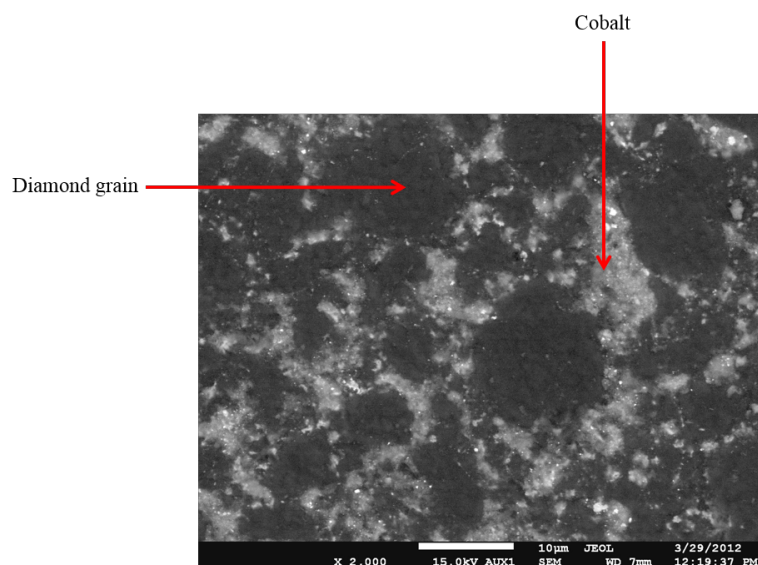


Figure 5.17.3: SEM images showing the cobalt pools and the diamond grains for sample E. The cobalt pools are the bright areas in the images and the dark regions are the diamond grains.

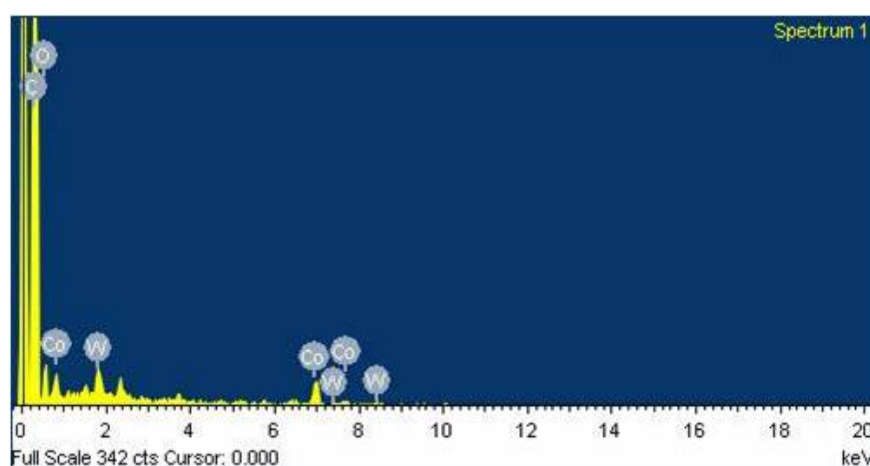


Figure 5.17.4: Energy dispersion spectra for sample E.

Table 5.13: EDS results for sample E.

Element	Weight %	Atomic %
C	84.98	92.65
Co	7.21	5.90
O	5.90	1.31
W	1.91	0.14
Total	100.00	

5.17.3 Sample F

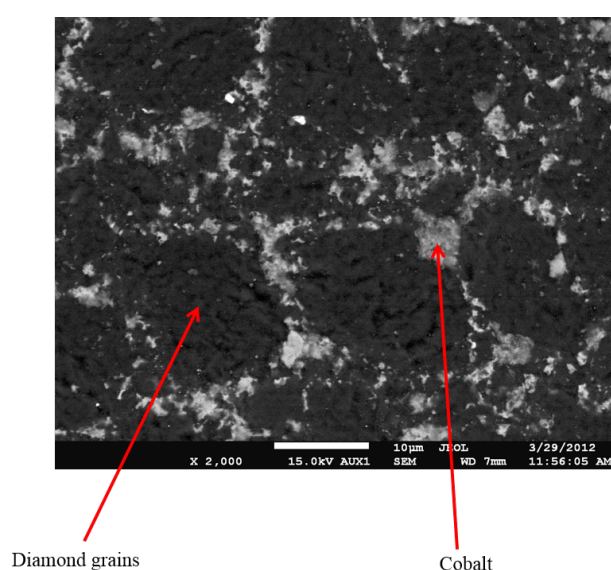


Figure 5.17.5: SEM images showing the cobalt pools and the diamond grains for sample F. The cobalt pools are the bright areas in the images and the dark regions are the diamond grains.

SEM pictures obtained again did not give any indications of damage or areas with localized damage. The results are shown in Figure 5.17.5. Figure 5.17.6 and Table 5.14 show an atomic percentage of 89.94 % for carbon which is slightly below what is expected and some traces of oxygen are noted as well.

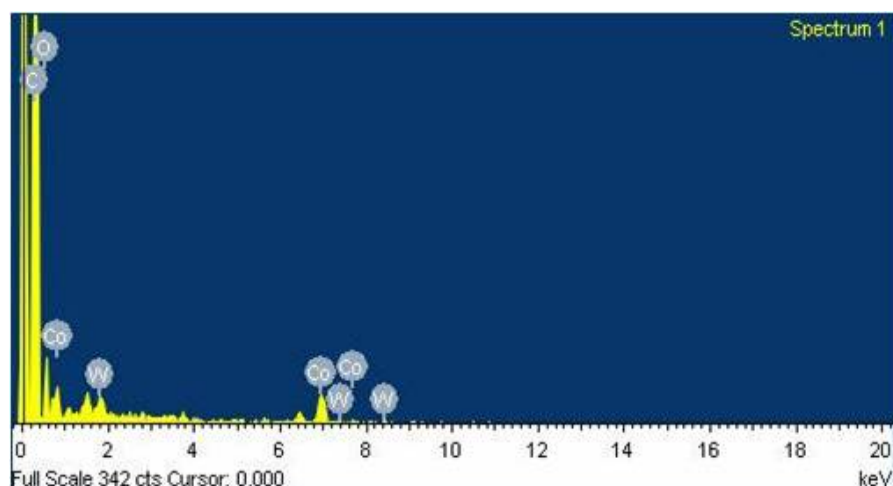


Figure 5.17.6: Energy dispersion spectra for sample F.

Table 5.14: EDS results for sample F.

Element	Weight %	Atomic %
C	81.46	89.94
Co	10.02	8.30
O	7.48	1.68
W	1.03	0.07
Total	100.00	

5.17.4 Sample G

SEM pictures obtained had several areas exhibiting possible localized damage. Unlike the traditional cracks running through the sample the defects in the picture are characteristic of diamond grains flaking off the surface possibly due to the fatigue loading experiments. The possible areas exhibiting localized damage are shown in Figure 5.17.7. Sample G was subjected to the highest number of cycles and this is probably the reason why damage is observed in this sample. EDS results are shown in Figure 5.17.8 and Table 5.15 and indicate a 92.65 % atomic percentage to be diamond.

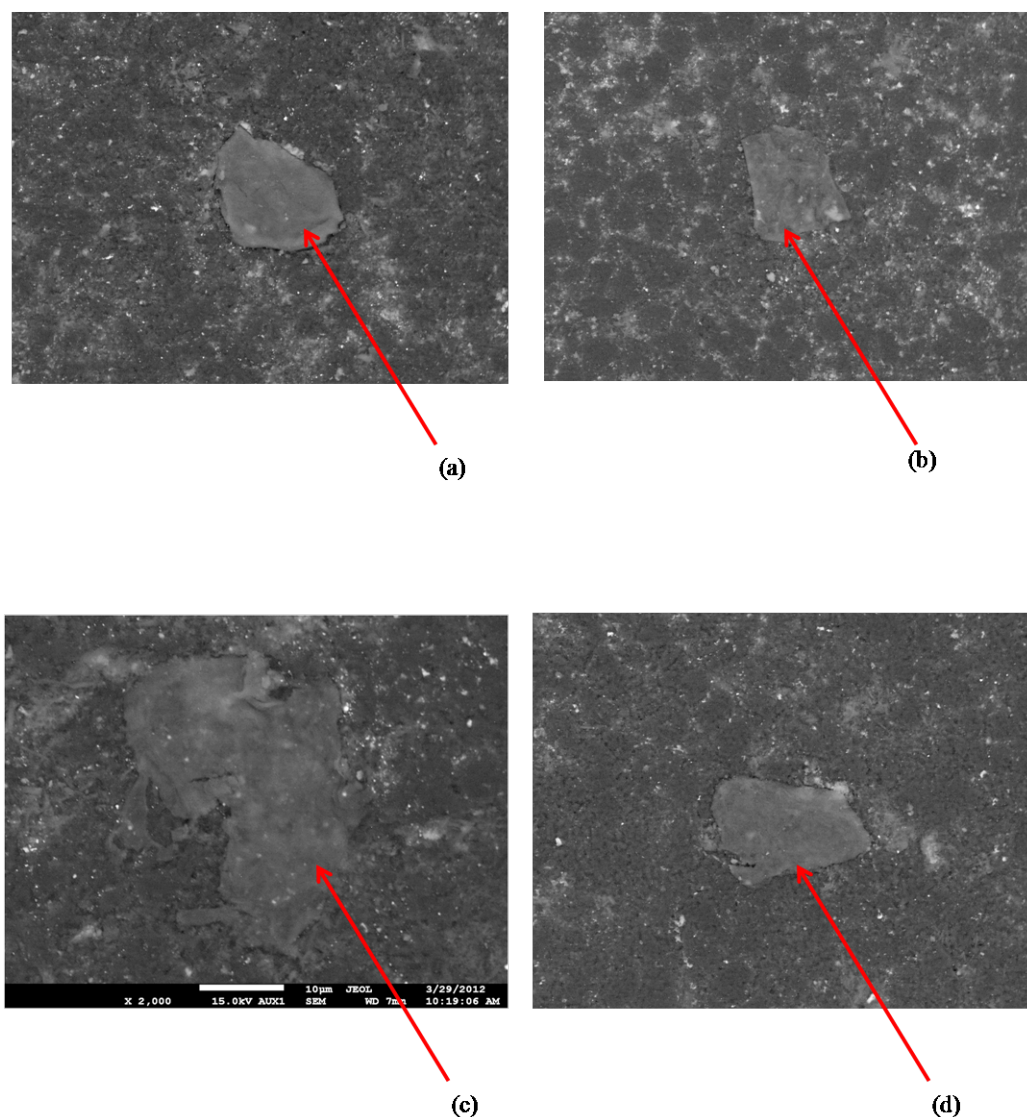


Figure 5.17.7: SEM images showing the cobalt pools (bright areas) and the diamond grains (dark areas) for sample G. The arrows in the images are showing the areas of damage on the surface of the sample.

Table 5.15: EDS results for sample G.

Element	Weight %	Atomic %
C	89.04	92.65
Co	8.97	7.01
O	1.46	0.31
W	0.54	0.04
Total	100.00	

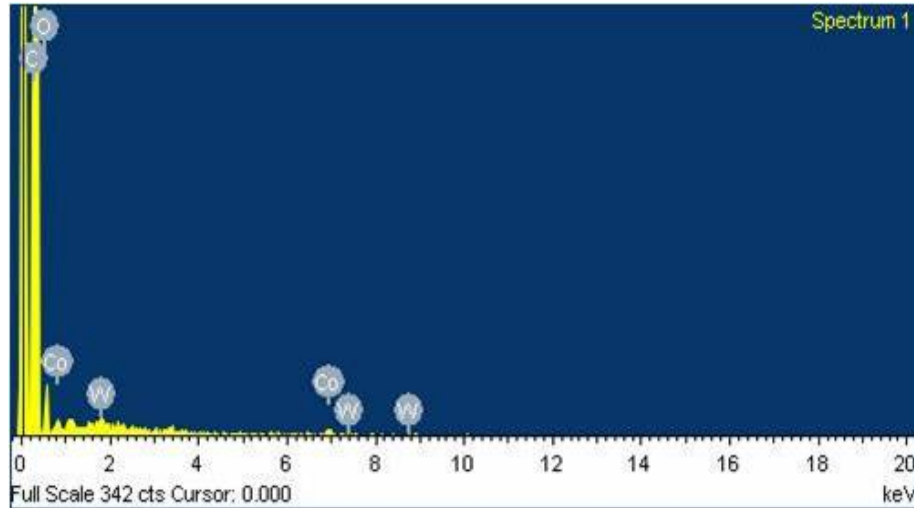


Figure 5.17.8: Energy dispersion spectra for sample G.

5.18 Summary of Results

- To our knowledge this is the first report of the successful application of Raman spectroscopy to characterise fatigue-type processes in PCD materials. The main findings were published in [93].
- The Raman results showed that for all the samples there was very little variation of the average stress with map size, however point to point variation of the residual stresses for the mapping points in the mapped area were observed. The number of the mapping points under tensile residual stresses were clearly shown to increase as a function of the increase in the number of the loading cycles. Whilst the samples were loaded into the jig randomly and the mapped points are random the trend observed is nevertheless clear; as the number of the loading cycles increased, the number of mapping points under tensile stress increased. This trend is possibly as a result of the inter-grain bridges giving rise to the diamond to diamond bonding being broken during the fatigue cycling and thus exhibiting tensile stress as the fatigue loading progresses.

- A comparison of the average surface stresses across all the samples after the initial Raman measurements indicated that there is considerable variation from one sample to the next. Some samples with lesser numbers of cycles exhibited tensile residual stresses as compared to some with higher numbers of cycles. According to A. Lammer this can be attributed to the fact that the hardness of the diamond grains is highly dependent on grain size and orientation [94]. Therefore variable sizes, shape and orientations of the diamond grains in the samples are the likely sources of the variation observed. The observation can also be explained from a synthesis point of view. In as much as the samples were manufactured in the same batch it is possible that slight temperature gradients within the manufacturing press at the time of sintering can result in a sample exhibiting slightly different residual stresses and inevitably different strength.
- All samples exhibited overall compressive residual stresses which progressively shifted towards being tensile in nature with increase in the number of cycles.
- SEM images taken for sample B, sample E, and sample F did not show any evidence of damage taking place. It is possible that damage is present but not visible at the level of magnification that could be attained with the instrument. It is possible that micro-cracks are present though none were observed.
- For sample G, the majority of the Raman measurements exhibited compressive residual stresses. The stresses ranged from -0.38 GPa to 0.36 GPa. The FWHM for the measurement after 750000 cycles showed a significant increase. The increase is significant enough for one to expect localized areas with evidence for damage.

Chapter 6

Methods and Results: Leached PCD

6.1 Introduction

The invention of the cobalt sintered polycrystalline diamond was first reported by Katzman and Libby [95], in 1971 and it provided a new material for use in the drilling industry. Prior to the advent of the polycrystalline diamond tool bits the main tool used in the drilling industry was the roller cone which works by impact excavation and possesses a convenient wear resistance suitable for use in hard rock formations [96]. Equipped with primary hardness, strength and elastic modulus similar to that of diamond, polycrystalline diamond has increasingly found applications in harsh and demanding environments. Wear resistance in PCD cutters is a function of both abrasion resistance and thermal stability. Generally speaking abrasion resistance improves with smaller diamond grain size and thermal stability improves with larger diamond grain sizes, so increasing overall wear resistance is a significant challenge [97].

As shown in Section 2.5, when polycrystalline diamond is sintered in a high

temperature, high pressure manufacturing process, the cobalt functions primarily as a solvent-catalyst aiding diamond to diamond bonding thus creating a cohesive network of interconnected diamond particles [98]. In most cases the diamond constitutes 90% to 97% by volume with the binding-catalyzing material constituting the remainder. Due to the fact that the thermal expansion of diamond is relatively low compared to that of cobalt, a subsequent result of the sintering process is that mutual interfacial constraints and internal equilibrium result in the diamond phase being in compression and the cobalt phase in tension [99]. It is this same cobalt which, during the drilling operations, expands and breaks apart the diamond bonds that it helped to form in the first place [100] typically limiting the operation temperatures to about 750 °C [89]. Because the PCD is virtually a two phase material comprising of a cobalt alloy and diamond, it is possible to remove a significant volume of the cobalt phase through a chemical leaching process and still maintain some level of cohesive structure which would be dominantly diamond [100]. To enable the cobalt removal, the PCD is chemically leached in a pressure vessel containing (usually) 1 : 1 : 1 ratio of reagent nitric acid, reagent grade hydrochloric acid and water maintained at 160 °C for approximately two weeks [96]. According to literature this leaching process typically results in an observable increase in the thermal stability of the PCD to about 1200 °C , with the consequence of the overall toughness of the cutter being dramatically reduced [100]. It is therefore interesting to investigate how leached polycrystalline diamond samples would perform in comparison to unleached samples if subjected to similar fatigue measurements. It is reasonable to assume that after the content of the cobalt has been significantly reduced, the resultant PCD cutters would exhibit less strength. The next few sections detail how the leached samples were subjected to fatigue measurements similar to those outlined in Chapter 5 conducted on a batch of unleached samples.

6.2 Methodology

Similar to the cylindrical tool-bits used in measurements described in Chapter 5, the leached samples used in this work were manufactured by Element Six (Pty) Ltd (E6). The leached PCD samples had slightly different dimensions of 16 mm in diameter and 2 mm in thickness, see Figure 6.2.1. Unlike with the previous measurements, care was taken before each fatiguing run to make sure the samples were loaded with exactly the same orientation into the jig, making sure the support balls were located in more or less the same contact points for every set of fatigue measurements.

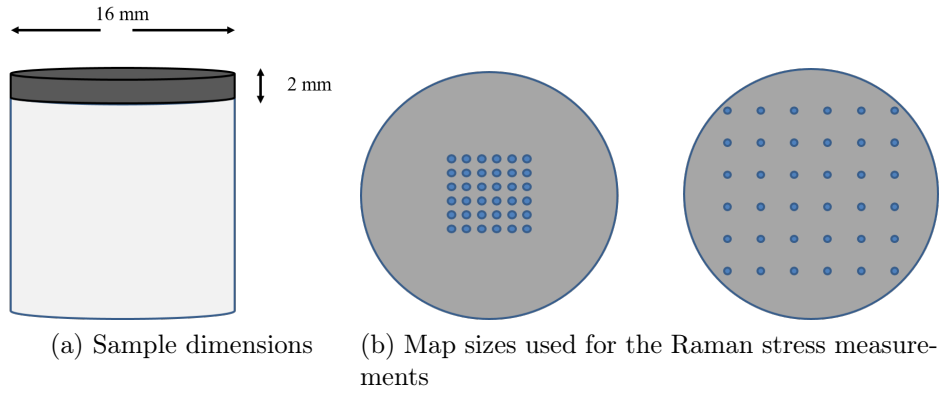


Figure 6.2.1: Sample dimensions of the PCD layer used for the experiments and the map sizes employed for the Raman stress measurements.

6.2.1 Fatigue Experiments - Methodology

Quasi-static loading of a few of the samples in transverse rupture strength tests were conducted so as to identify the strength of the materials. The leaching was done on one side (to be known as the leached side) of the PCD and this was the surface in contact with the three support balls in the ball on three balls set up, with the EDM cut side (to be known as the underside) in contact with the single ball on the centre of the disc samples. There after similar procedures as outlined in Chapter 5, Sections 5.2 and 5.3, were employed in conducting the fatigue measurements. The transverse rupture strength tests

showed that the leached samples exhibited high average strength compared to the unleached samples. This is due to the slight difference in the diameter of the samples with the unleached samples being 19 mm and the leached samples having a diameter of 16 mm. The difference inherently influences the flexure distance which results in the different strength. Table 6.1 shows the quasi-static loading for the leached samples.

Table 6.1: Quasi - static loading test results for the leached samples.

Sample	Thickness (mm)	Fracture Load (N)	Displacement (mm)
1	2.00	-3938	0.18
2	2.00	-3955	0.16
3	2.00	-3704	0.16
Mean		-3866	0.17
Standard Deviation		0.140	0.01

The careful loading of the samples mentioned earlier was done so as to help observe whether there would be noticeable deformation or cracks at these respective contact points. All measurements were conducted at room temperature, under constant amplitude loading with the settings as indicated in Table 6.2. A maximum load of 2900 N was used and this was approximately 75% of the average fracture load obtained from the transverse rupture strength tests. The samples were then subjected to a series of cumulative sets of 50000 cycles at a time. Due to instrument limitation of the new equipment employed for this phase of measurements, the frequency was changed from 10 Hz to 4 Hz. This was the maximum attainable frequency on the new equipment.

Table 6.2: Fatigue loading settings used for the leached samples.

Maximum Load (75% UTS)	2900 N
Minimum (10% UTS)	2900 N
Amplitude	1305 N
Setpoint	1595 kN
Frequency	4.0 Hz

6.3 X-Ray diffraction stress measurements

Both X-ray diffraction and Raman spectroscopy were used to characterise the fatigued samples. Raman spectroscopy is discussed in section 6.4. The X-ray diffraction measurements were conducted at NECSA. Prior to the experiment, the alignment of the diffractometer was verified by measuring the laboratory prepared tungsten sample of known stress value as a reference. The repeatability of a measurement on a standard sample can give an indication of the likely uncertainty in a stress measurement. The following factors were considered in selecting the appropriate peak for stress investigation:

6.3.1 The highest Bragg Peak

When measuring residual stress, the highest peak on the powder diffraction pattern is always chosen since it is possible to pick up the small changes in the d-spacing at high angles. At high 2θ angles, small changes in the d-spacing will give measurable changes in 2θ , although the peak shifts are still only a few increments of a degree. At low angles the difference would be too small to be measured with any degree of precision [101]. The strain induced changes in the d-spacings are generally very small, typically in the third decimal place. The resultant peak position shift of the diffraction peak, $\Delta\theta$ when there is a change in d-spacing Δd is obtained by differentiating Bragg's law, which gives

$$\frac{\Delta d}{d} = \frac{\Delta \lambda}{\lambda} = -\Delta\theta \cot\theta \quad (6.3.1)$$

Equation 6.3.1 implies that when θ is close to 180° , the the fractional error given by $\Delta d/d$ $\frac{\Delta d}{d}$ goes to zero, hence the use of the highest diffraction peak closest to $2\theta = 180^\circ$ [102].

6.3.2 Peak with the highest Intensity

The highest intensity peak at $2\theta = 136.5^\circ$, (see table 6.3) was selected for the measurements. The advantage of using the peak with the highest intensity is to get the improvement in statistics while keeping the measurement time minimal. The statistics will be improved such that the error bars are minimal and hence the behaviour of the residual stress can be determined.

6.3.3 Experimental Procedure

The laser video camera on the Bruker D8 Discover instrument was used to align the sample height by ensuring that the sample height coincides with the centre of the goniometer. It was important to adjust the z-axis value to ensure that the sample height coincides with the centre of the goniometer.

The primary side of the equipment consists of a graphite monochromator, a collimator and *Cu* X-ray tube of wavelength of $1.544 \text{ \AA}$. In this particular investigation a 0,8 mm collimator was used. Since *Cu* was used, the generator was operated at a voltage of 40 kV and a current of 40 mA. The diffraction data was collected using an area detector *Vantec* – 500.

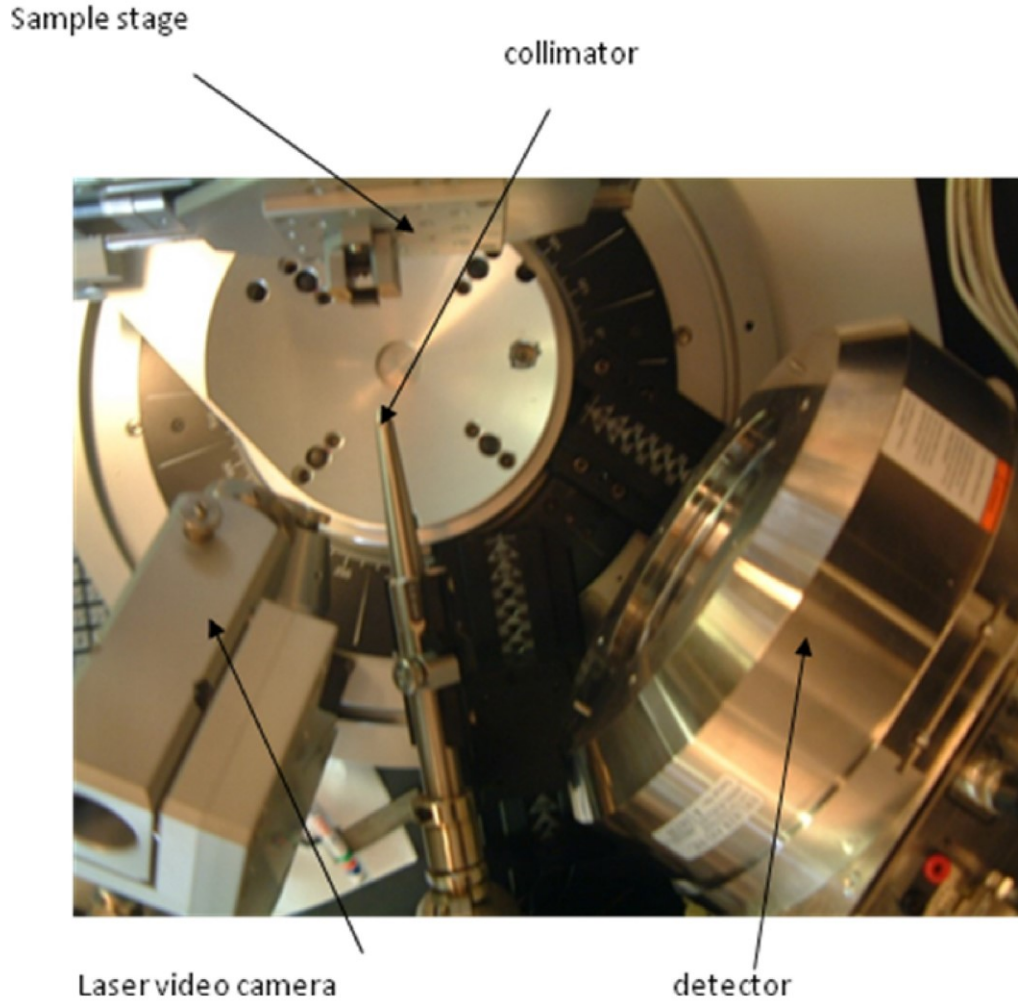


Figure 6.3.1: X-ray diffraction instrument at NECSA showing the laser video camera that is used to locate the sample height.

The instrument was then aligned to the specifications of the highest possible Bragg Peak which in this case was 136.5° . Once the detector was well aligned, it was important to prepare the instruction file on the General Area Detector Diffraction System (GADDS) system to put all the values required for the measurement namely set 2θ , the angle between the incident (transmitted) and diffracted X-ray beams and ω , the angle between the incident X-ray beam and the sample surface. To determine the full stress tensor, samples were measured at 6 different azimuth angles $\phi = 0^\circ, 180^\circ, 90^\circ, 270^\circ, 45^\circ$, and 225° with each azimuth measured at 8 different tilt angles ψ ranging from 0° to 70° in steps of 10° . Measurements were done in side-inclination mode.

Table 6.3 summarises the measurement parameters employed.

Table 6.3: : Parameters settings on D8 GADDS diffractometer.

Parameters	Value
hkl reflection	311
2θ	136.5
Tilt angle	0 – 70
Frame width $\Delta\psi$	10
Azimuth Orientation Φ	0, 45, 90, 180, 225, 270
Sample - Detector distance (cm)	20

6.4 Raman stress measurements

Raman spectroscopy has been proven to be a competent technique for stress measurements. In this work the Raman stress measurements were conducted in the Raman and Luminescence laboratory at the University of the Witwatersrand. Equipped with a $50\times$ Long working distance (LWD) range objective lens, LabRam Horiba instrument was used for these measurements. A detailed procedure of the measurements has been outlined in Chapter 5, Sections 5.6.4 and 5.7.

6.5 Results : Raman Stress Results

This section details the results obtained from the Raman stress measurements on the leached PCD samples. The stress measurement were conducted on both surfaces, i.e the leached side and the unleached underside of the samples. Three samples namely D16_C, D16_D and D16_F survived the 600000 loading cycles conducted in steps of 50000 cycles at a time. Two maps were used in the work, namely the small map and the large map (see Figure 6.2.1). From these measurements 2D colour maps were plotted and the average stresses calculated from these 2D maps by first determining the peak position measured

at each grid point. The related stresses were then calculated and the average of these 36 grid mapping points evaluated.

6.5.1 Sample D16_C

The sample was subjected to 600000 cycles of loading. The results obtained are mainly presented in a plot of the calculated average stresses as a function of the number of loading cycles and 2D colour maps highlighting the distribution of these stresses. No visible cracks were observed on either the leached side or the underside of the sample.

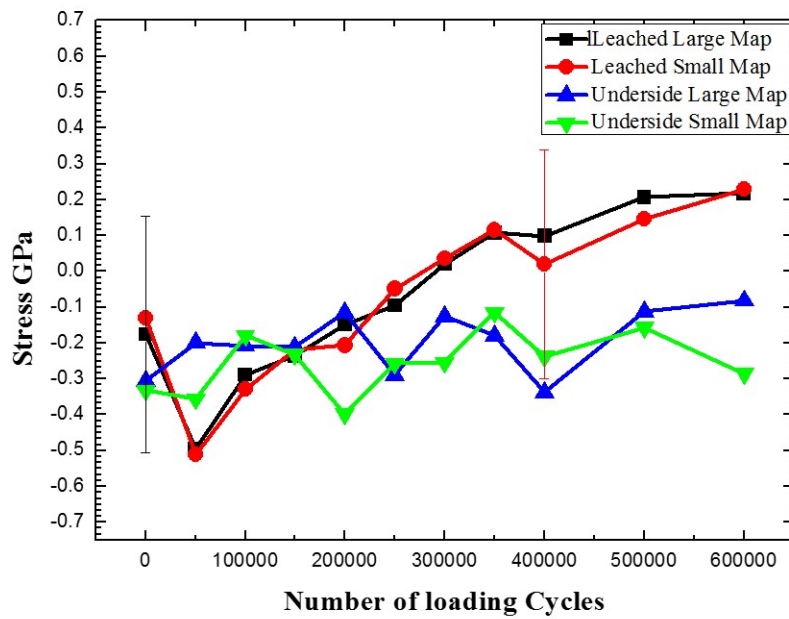


Figure 6.5.1: A comparison of the calculated average stress for the Large and Small maps on both sides of the Sample D16_C, plotted as a function of the number of loading cycles. The error bars indicate the standard deviation in data.

Figure 6.5.1 gives a comparison of the calculated average stress for the large and small maps on both sides of the sample, plotted as a function of the number of loading cycles. Generally on the leached side, for both the large

and small maps, the results show an average compressive residual stress which after the first set of loading cycles gets more compressive before degenerating gradually to an average tensile residual stress with sufficiently large number of cycles. For the leached side both maps yield interestingly similar trends and from the calculated stresses more often that not the small map exhibits less compressive stresses compared to the large map. As indicated by the model developed by Börger et al.[90], this is due to the fact that during the fatigue loading measurements the sample would experiences more tensile stresses around the areas closest to the centre. The fact that the small map has more of the measured grid points covering this area closest to the centre as compared to the large map, means the small map results would be expected to exhibit less compressive stress.

Unlike the leached side, the Raman measurements conducted on the underside seem to yield fluctuating results with little observable trends. This is probably due to the EDM cutting that was performed on this side of the samples. However it was evident that despite the undulating trend, the calculated average stresses on the underside were generally confined to the compressive range throughout the 600000 cycles of loading for both the small and large map. During the sintering process the different thermal expansion coefficients bring about compressive stresses within the diamond matrix. The compressive stresses tend to be more concentrated along the diamond/substrate interface becoming less compressive towards the surface of the PCD. In the current work it is possible that after the samples were EDM cut from their respective substrates, some of the highly compressive stresses remained locked in, in the bulk of the specimen, and this would explain the underside exhibiting compressive stresses even at higher number of loading cycles. Table 6.4 tabulates the calculated stresses for Sample D16_C, on both sides as function of map size and number of loading cycles.

Table 6.4: Showing the calculated average stresses and the full width measured at half maximum for the Sample D16_C. Units for peak position and FWHM are cm^{-1} .

	Leached Large Map		Leached Small Map		Underside Large Map		Underside Small Map	
Cycles	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})
0	-0.176 ± 0.32	11.59	-0.131	15.30	-0.305	15.30	-0.332	13.06
50 000	-0.495	11.56	-0.511	13.98	-0.199	13.10	-0.356	14.26
100 000	-0.289	11.86	-0.329	11.10	-0.208	13.17	-0.179	10.68
150 000	-0.236	12.58	-0.220	11.44	-0.211	12.47	-0.232	11.42
200 000	-0.148	13.01	-0.207	12.75	-0.115	12.99	-0.398	12.60
250 000	-0.096	13.30	-0.049	13.45	-0.289	12.45	-0.257	11.09
300 000	0.020	11.34	0.035	11.85	-0.126	11.81	-0.254	9.68
350 000	0.108	12.26	0.115	12.22	-0.180	12.08	0.115	9.12
400 000	0.099	11.48	0.020	11.63	-0.338	9.85	-0.238	11.52
500 000	0.206	13.23	0.145	12.31	-0.112	14.48	-0.157	13.01
600 000	0.218	11.37	0.228	12.42	-0.082	11.83	-0.285	11.06

In Chapter 5 the reporting of the number of tensile stress points for each mapping grid yielded interesting additional information. It is assumed these represent points in the mapping grids for possible crack initiation sites. Figure 6.5.2 shows this relationship for the leached sample D16_C and the respective variation according to map size and side of measurement. The graphs indicate that as the number of loading cycles gets higher, so does the number of mapping points in the grid exhibiting tensile stresses, increasing proportionally for both maps on the leached side of the sample. For the underside no particular trend was observed.

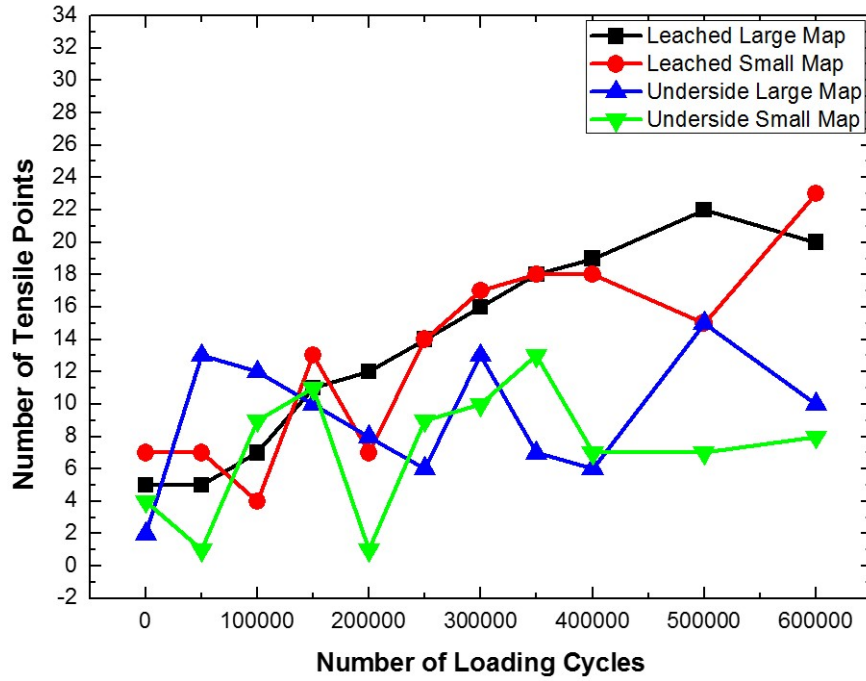


Figure 6.5.2: Shows a plot of the number of mapping points exhibiting tensile stresses as a function of map size and number of loading cycles for the Sample D16_C.

Vhareta et al. [93], highlighted in their work that if a cluster of such points forms, then a surface crack that initiates in that region will quickly grow to critical length prompting catastrophic failure [93]. Histograms were plotted showing the point to point stress variation, see Figure 6.5.3 to Figure 6.5.6. Care was taken to ensure the sample was loaded into the jig exactly in the same way, hence ensuring that the mapping points are more or less in the same vicinity after each set of fatigue loading measurements.

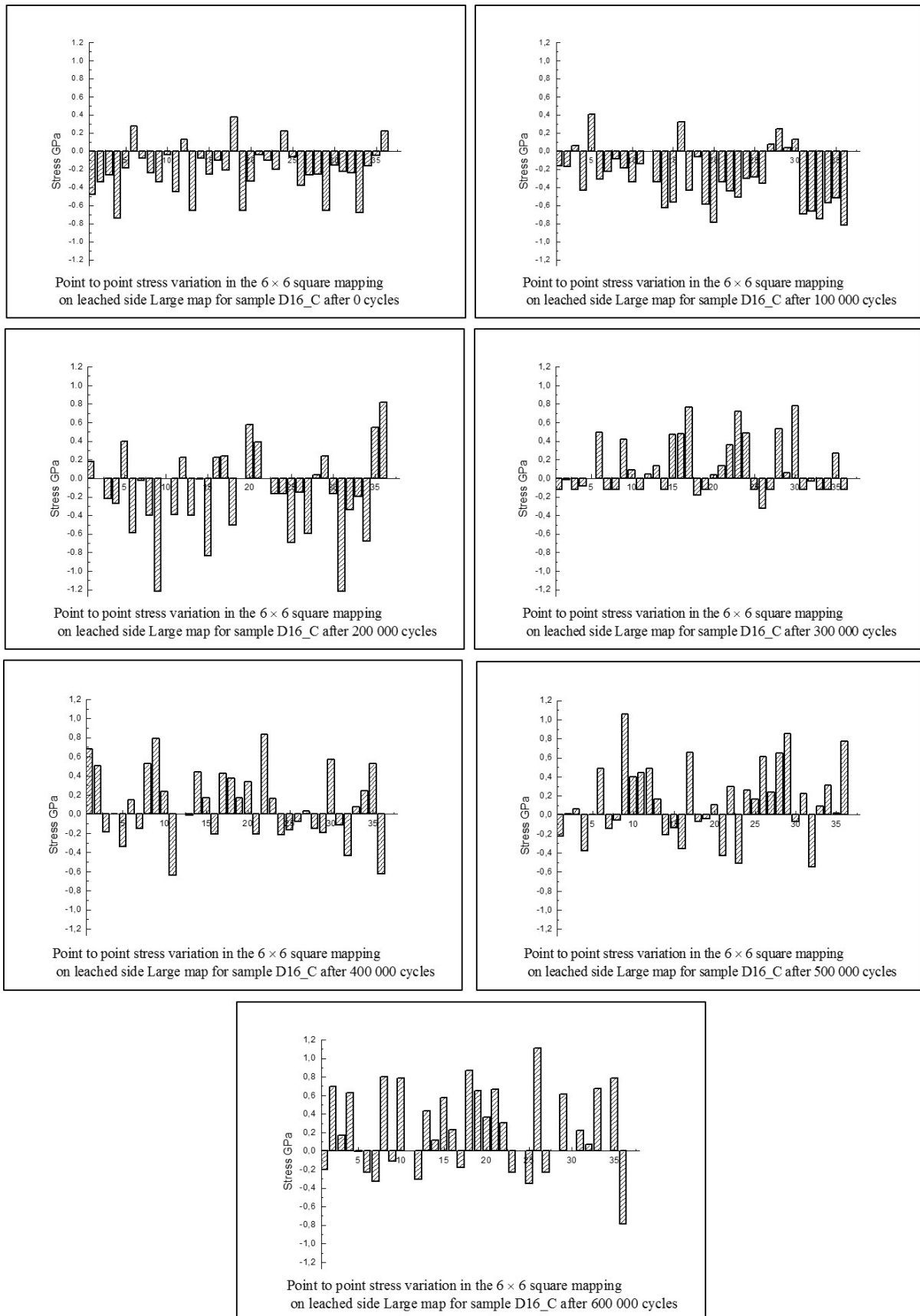


Figure 6.5.3: Point to point stress variation as a function of the number of cycles for Sample D16_C on the leached surface. The histograms represent the stress at each point for the respective number of cycles. Data is for the large map.

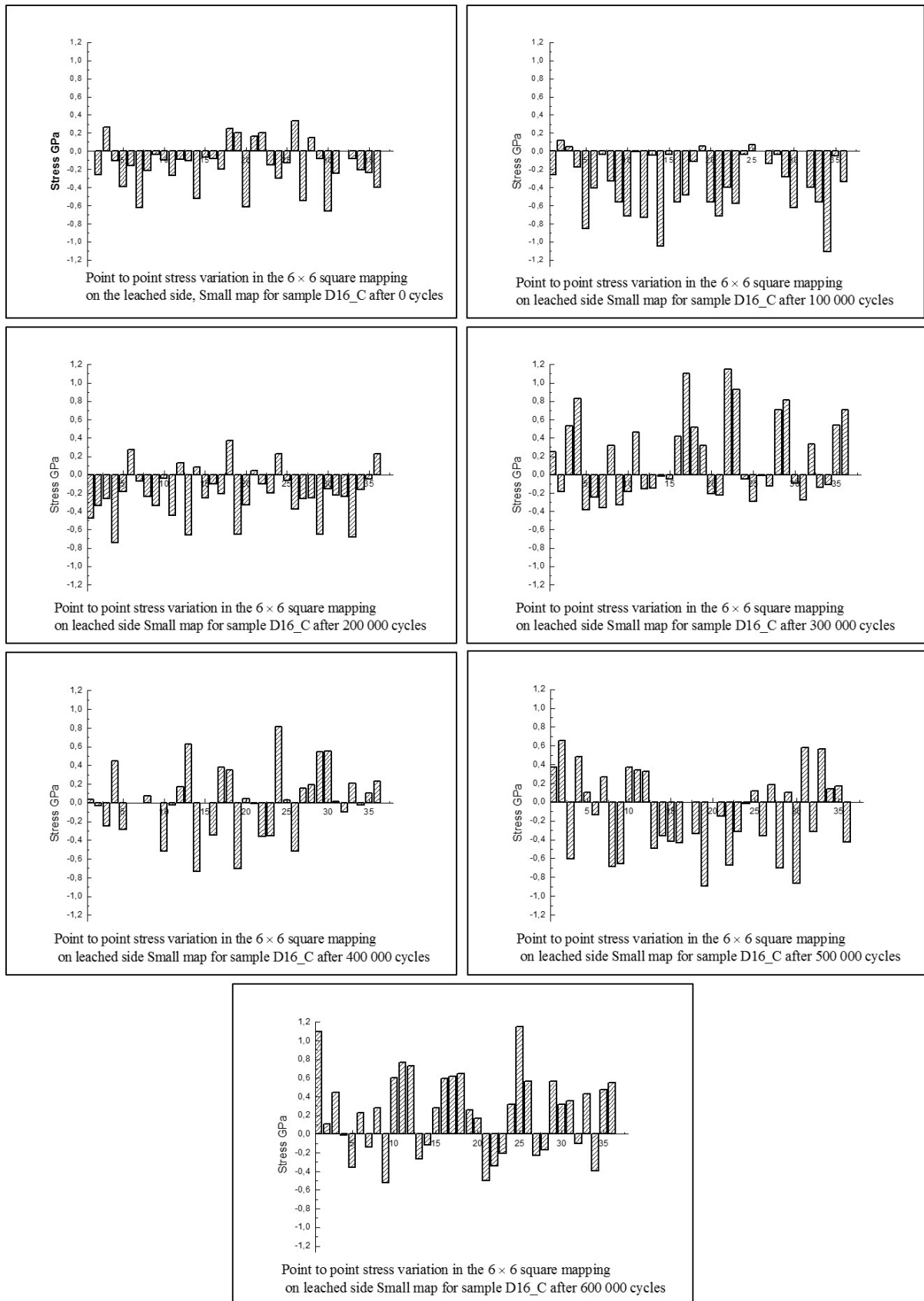


Figure 6.5.4: Point to point stress variation as a function of the number of cycles for Sample D16_C on the leached surface. The histograms represent the stress at each point for the respective number of cycles. Data is for the small map.

It is evident looking at Figures 6.5.3 and 6.5.5 that even before the fatigue measurements were conducted, the sample had a few mapping points already exhibiting tensile stresses within the two square maps on the leached side. The number of tensile points increases as the number of loading cycles increases, with the tensile points dominating the mapped area at the highest number of cycles. Interestingly even before applying any fatigue load the small map had more tensile points compared to the large map. However the same trend as the number of loading cycles increases, is observed as in the results for the large map. The same histograms were plotted for the underside as well and the results are shown in Figure 6.5.5 and Figure 6.5.6.

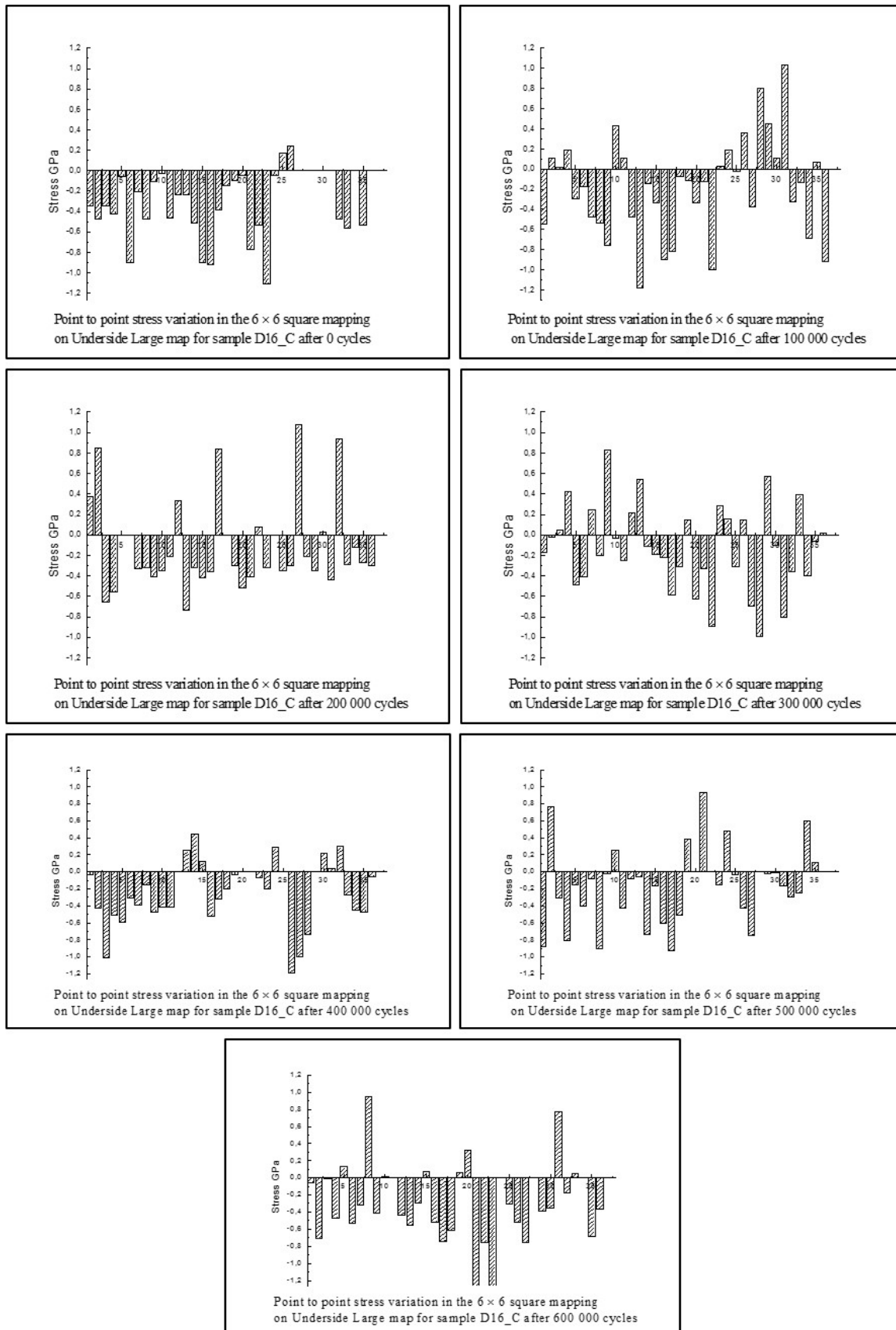


Figure 6.5.5: Point to point stress variation as a function of the number of cycles for Sample D16_C on the underside surface. The histograms represent the stress at each point for the respective number of cycles. Data for the large map.

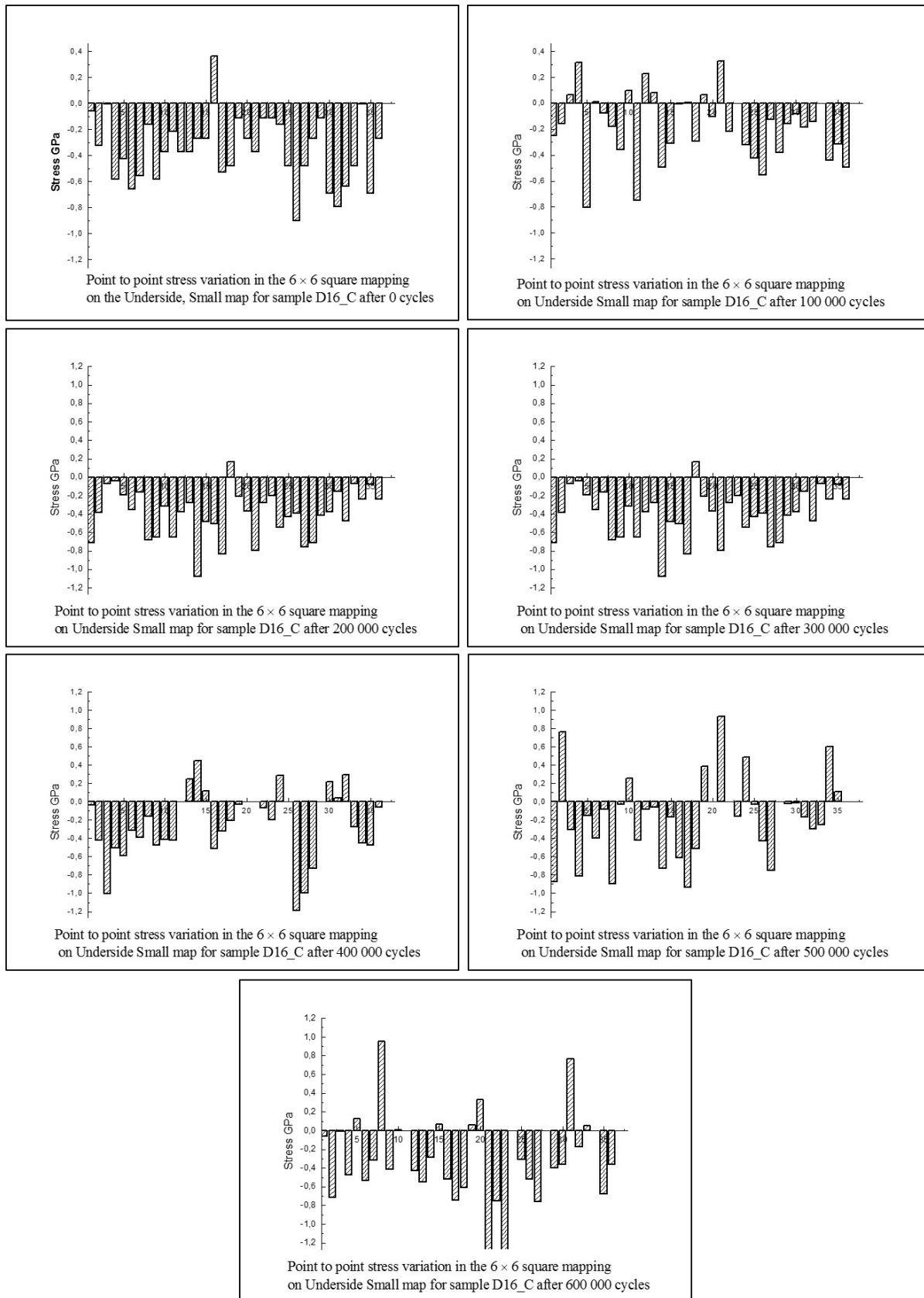
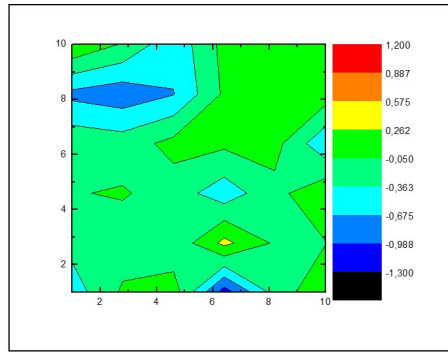


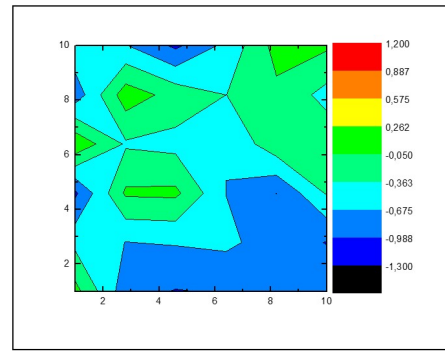
Figure 6.5.6: Point to point stress variation as a function of the number of cycles for Sample D16_C on the underside. The histograms represent the stress at each point for the respective number of cycles. This is for the underside small map.

Unlike with the leached side the histograms on the large map on the underside of the sample shows a varying relationship with the number loading cycles. Again this is thought to be due to the EDM cutting which was performed on this side in the process of detaching the PCD layer from the respective substrate. The same is observed for the small map and this is shown in Figure 6.5.6. It was also observed that the histograms show more compressive points through out with slightly larger magnitudes of the average compressive stresses as compared to the leached side.

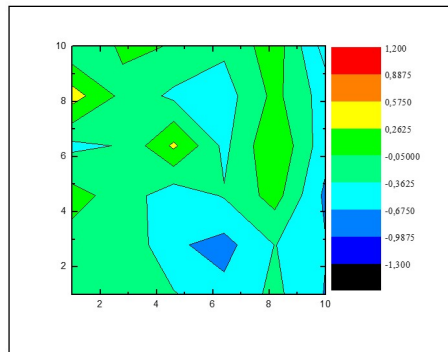
The histogram results were then carefully plotted into 2D colour maps showing the distribution of the calculated stresses on both sides of the sample for both map sizes. Figures 6.5.7 and 6.5.10 shows the 2D plots for the Large map on the leached side. Only a few representative maps are shown here.



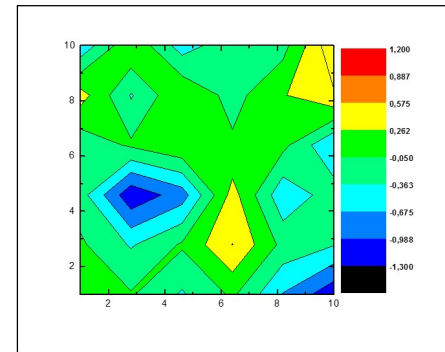
2D Surface map showing the stress after 0 cycles



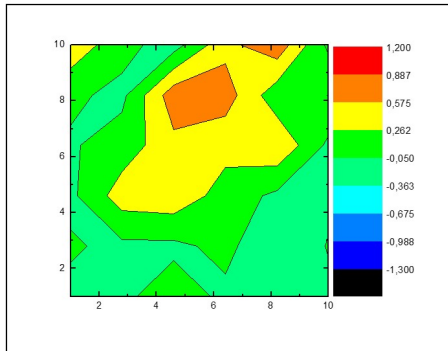
2D Surface map showing the stress after 50 000 cycles



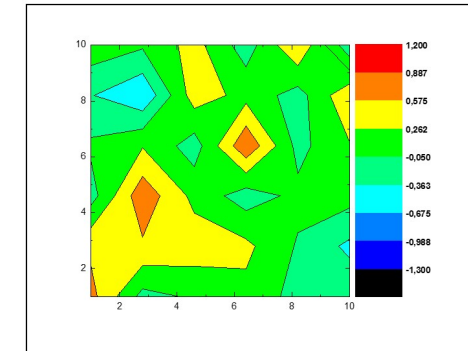
2D Surface map showing the stress after 100 000 cycles



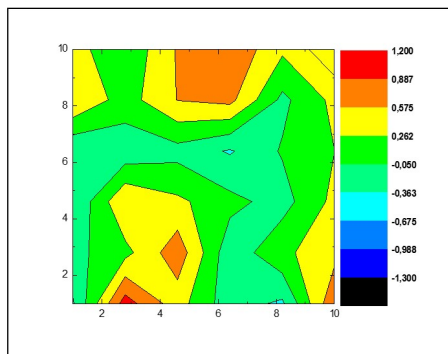
2D Surface map showing the stress after 200 000 cycles



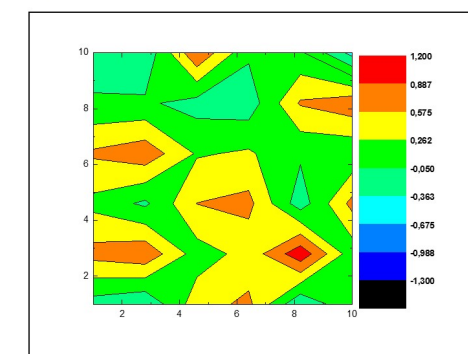
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles

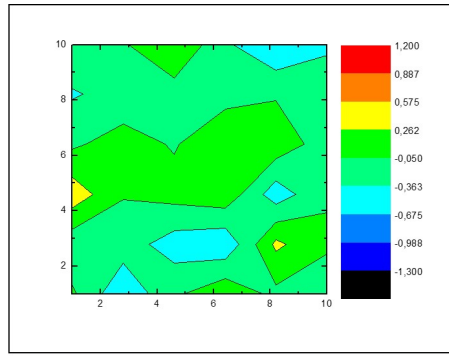


2D Surface map showing the stress after 500 000 cycles

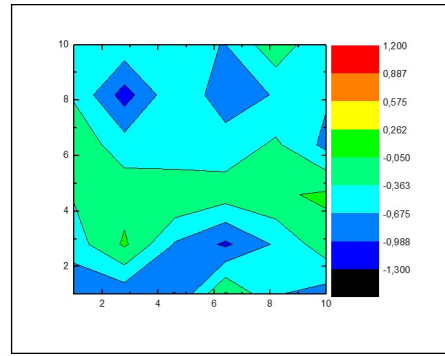


2D Surface map showing the stress after 600 000 cycles

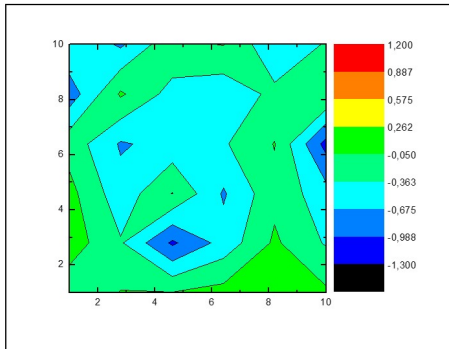
Figure 6.5.7: 2D Surface maps showing the nature and distribution of stress for the large map, as a function of the number of cycles for Sample D16_C. These are results for the leached side. Compressive stresses are shown by the colours black - deep green; and tensile stresses are indicated by the colour range yellow-red. The stresses are reported in GPa.



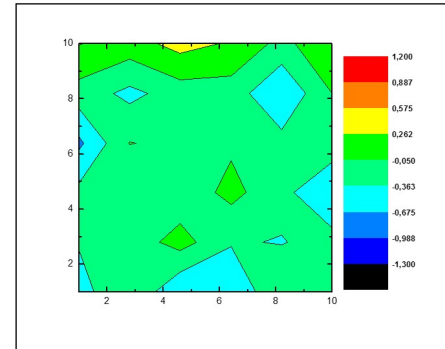
2D Surface map showing the stress after 0 cycles



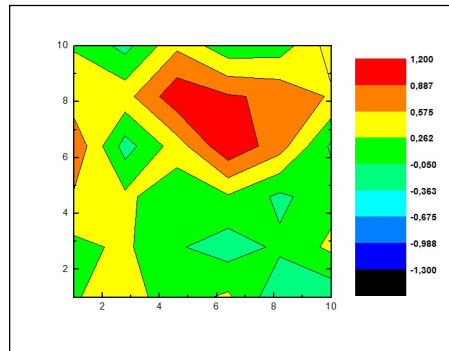
2D Surface map showing the stress after 50 000 cycles



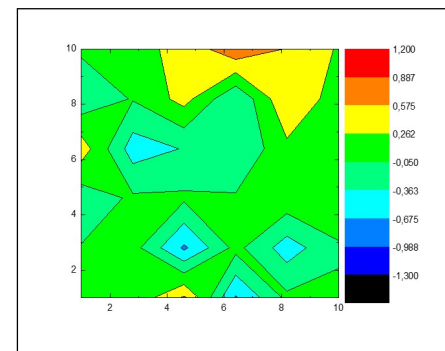
2D Surface map showing the stress after 100 000 cycles



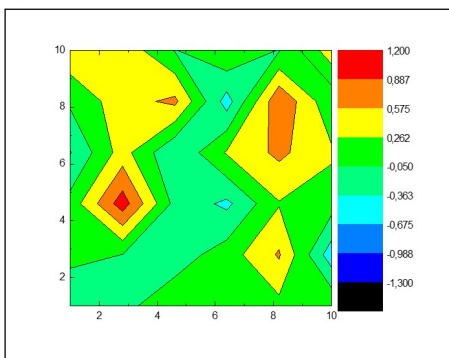
2D Surface map showing the stress after 200 000 cycles



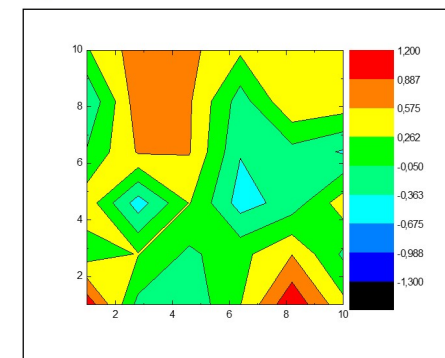
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles



2D Surface map showing the stress after 500 000 cycles



2D Surface map showing the stress after 600 000 cycles

Figure 6.5.8: 2D Surface maps showing the nature and distribution of stress for the small map, as a function of the number of cycles for Sample D16_C. These are results for the leached side. Compressive stresses are shown by the colours black - deep green; and tensile stresses are indicated by the colour range yellow-red. The stresses are reported in GPa.

The 2D maps show residual stresses which are predominantly compressive in nature at lower number of loading cycles, however with sufficiently large number of loading cycles there is a gradual shift towards a tensile stress regime. This is highlighted by the orange to red colours dominating the 2D stress maps after 300000 cycles. There is no evidence of any regions of stress related damage due to the support balls being in contact with the leached side surface. Due to the arrangement of the ball on three balls setup (see Figures 5.1.1 and 5.1.2), the localised areas of damage due to the balls is only a consideration for the large map. Similar trends were noted with the Small map, with the compressive stresses dominant in the early cycles but after 300000 cycles, light green, orange and red colours dominate (see Figure 6.5.7, 6.5.8), indicating an average tensile stress on the surface of the sample. Similar 2D maps plotted for both maps on the Underside of the sample and the results are shown in Figure 6.5.9 and Figure 6.5.10. Unlike with the leached side no clear change is observed around 300 000 cycles.

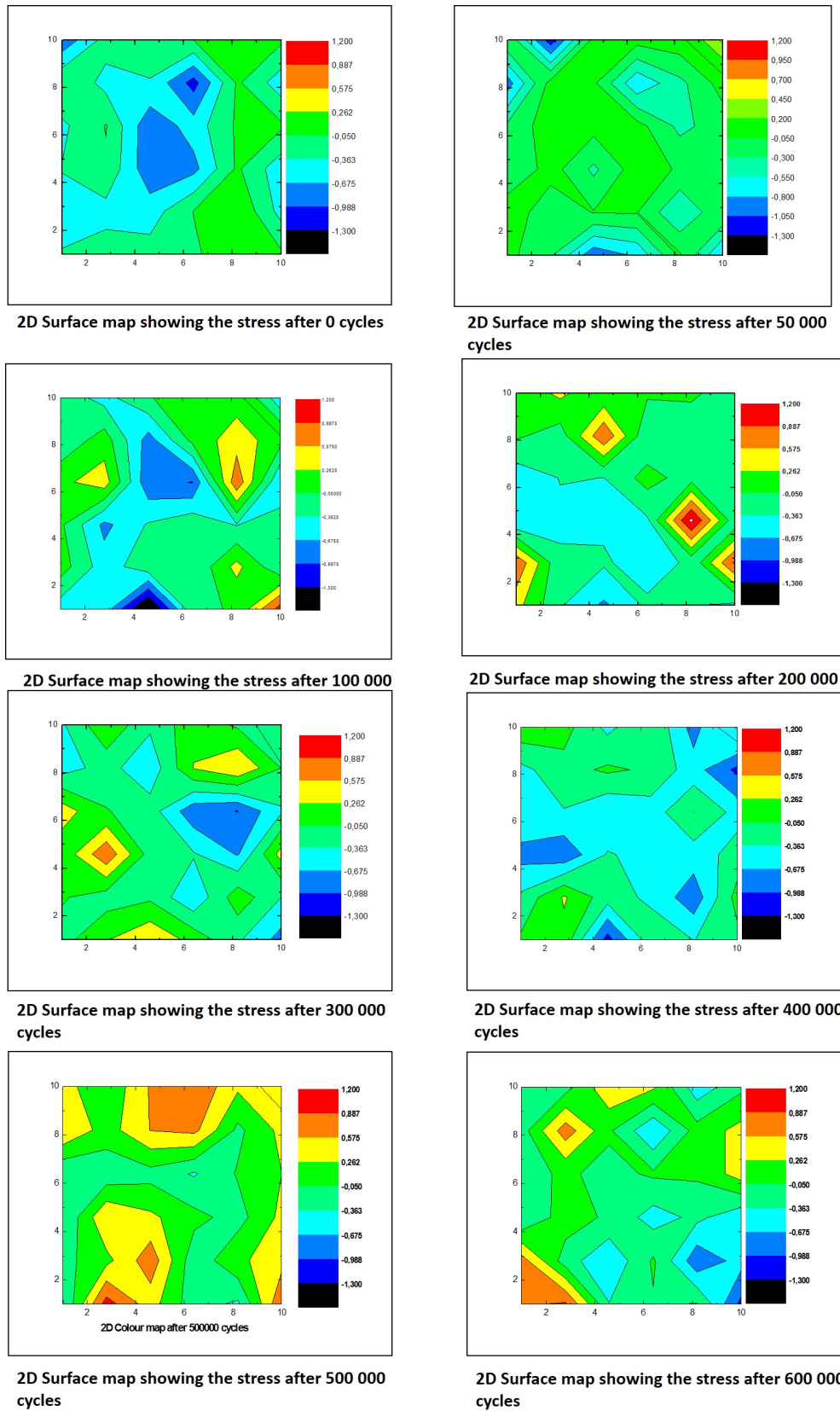


Figure 6.5.9: 2D Surface maps showing the nature and distribution of stress for the large map, as a function of the number of cycles for Sample D16_C. These are results for the underside. Compressive stresses are shown by the colours black - deep green; and tensile stresses are indicated by the colour range yellow-red. The stresses are reported in GPa.

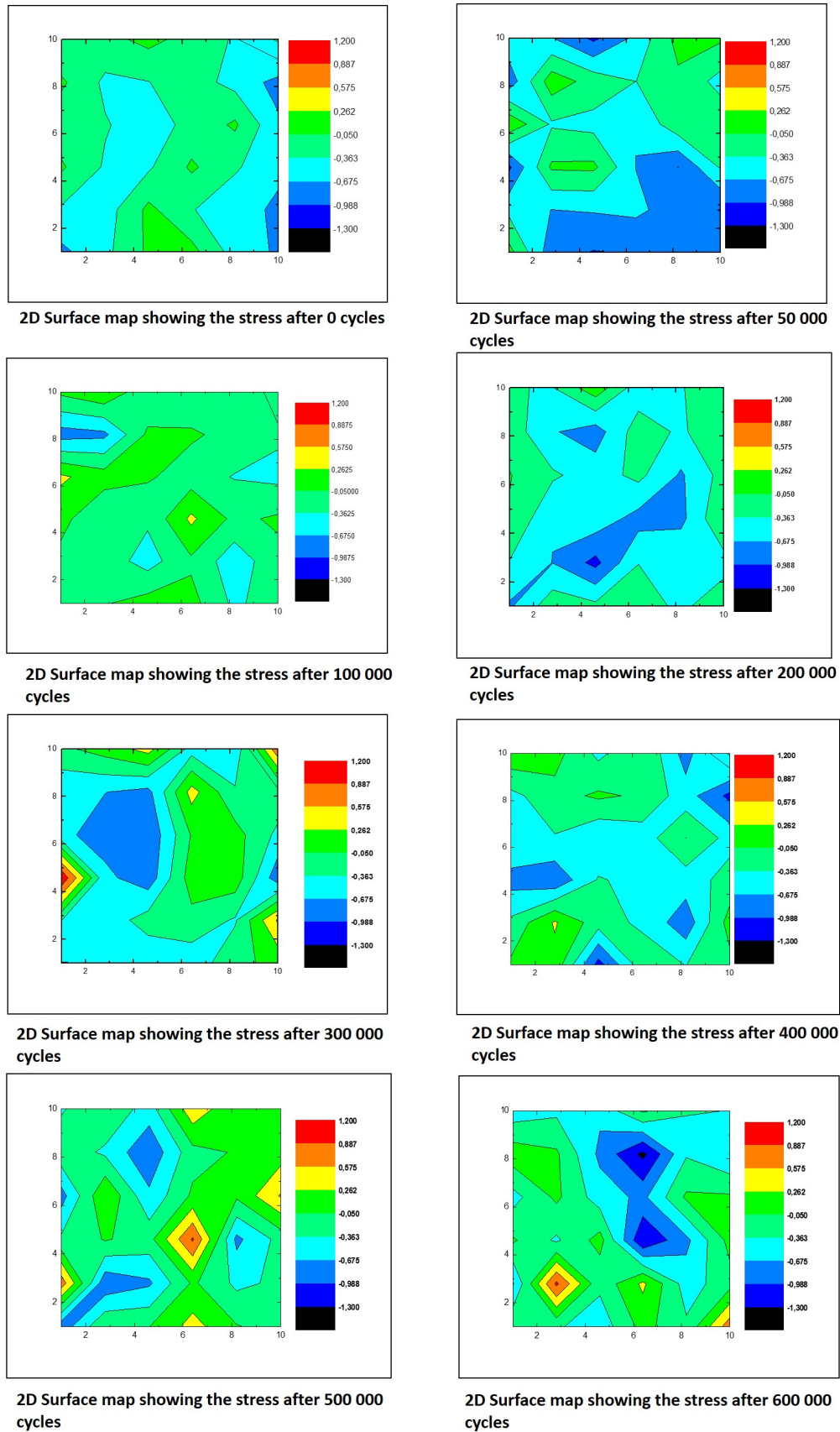


Figure 6.5.10: 2D Surface maps showing the nature and distribution of stress for the small map, as a function of the number of cycles for Sample D16_C. These are results for the underside. Compressive stresses are shown by the colours black - deep green; and tensile stresses are indicated by the colour range yellow-red. The stresses are reported in GPa.

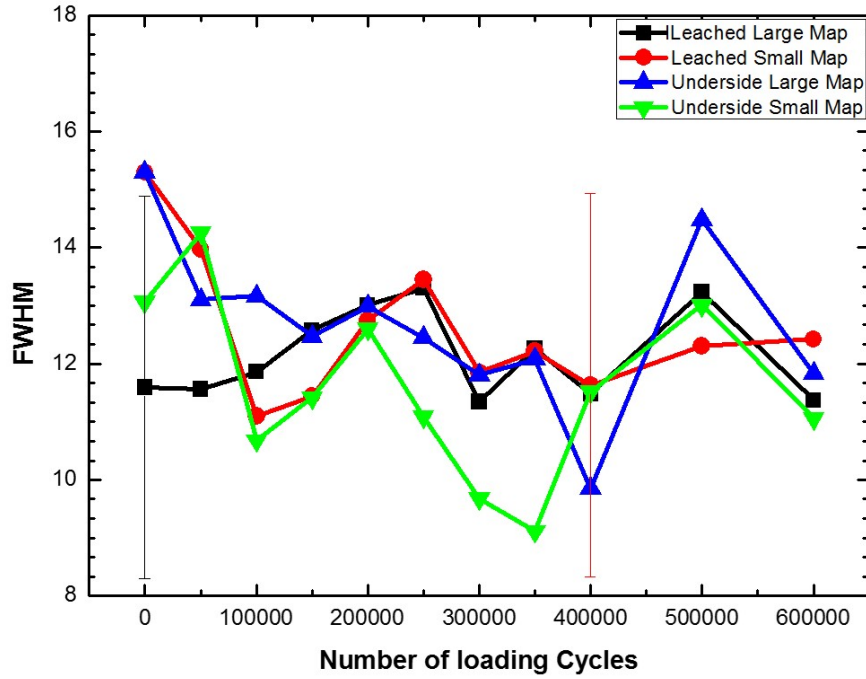


Figure 6.5.11: FWHM of sample D16_C as a function of the number of loading cycles. The data represents the average width value across the surface calculated over 36 mapping points. The error bars indicate the standard deviation in data.

The width of the Raman peak normally measured as the full width at half maximum (FWHM) provides a qualitative measure of the degree of disorder in a crystal and is useful as a ranking indicator [27]. From Table 6.4 the average FWHM as a function of the number of loading cycles does not show any easily identifiable trends. The reported values are calculated averages of the 36 measuring grid points. Even though the calculated FWHM averages do not readily show trends, some of the individual grid points do show broadening of the respective peaks measured at higher number of loading cycles. Figure 6.5.10 shows the FWHM plotted against the number of loading cycles. The results show scattered but a close look indicates that the variations seems to be much wider on the underside as compared to the leached side of the sample.

6.5.2 Sample D16_D

The sample was subjected to 600000 cycles of loading. Again the results obtained are mainly presented in a plot of the calculated average stresses as a function of the number of loading cycles and 2D colour maps highlighting the distribution of these stresses. Visual inspection of the samples did not show any cracks present on either side of the disc sample.

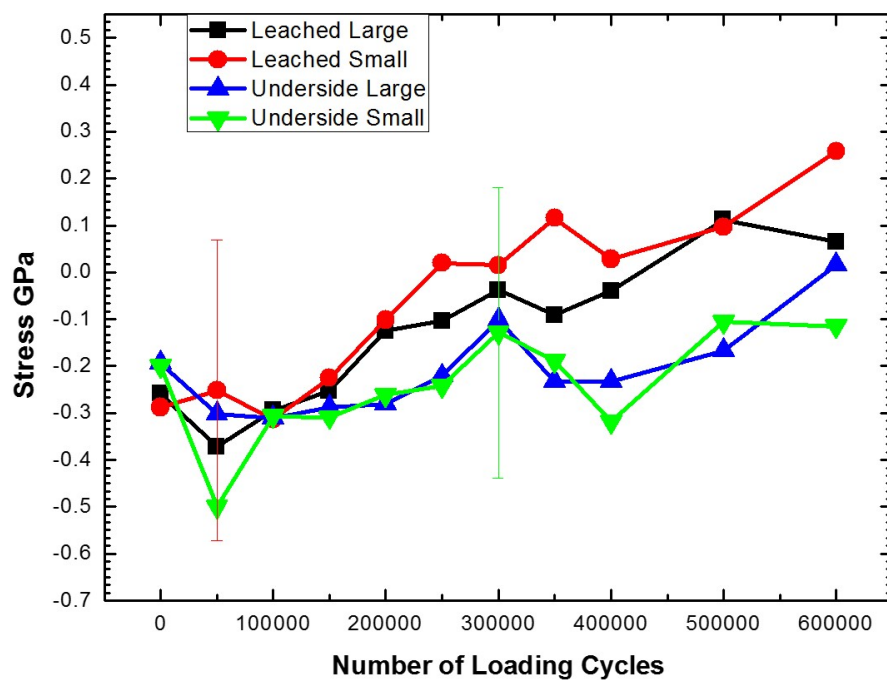


Figure 6.5.12: Shows a plot of the number of mapping points exhibiting tensile stresses as a function of map size and number of loading cycles for Sample D16_D. The error bars indicate the standard deviation in data.

Figure 6.5.12 shows the comparison of the calculated average stress as a function of map size and number of loading cycles for sample D16_D. As was the case with Sample D16_C, the results for the leached side of the sample indicate an average compressive residual stress state which after sufficiently large number of loading cycles begins to degenerate gradually to an average tensile

residual stress. As a function of map size, similar trends to those observed with sample D16_C were recorded (see Figure 6.5.12 and Table 6.5).

Table 6.5: Showing the calculated average stresses and the full width measured at half maximum for the Sample D16_D. Units for peak position and FWHM are cm^{-1} .

	Leached Large Map		Leached Small Map		Underside Large Map		Underside Small Map	
Cycles	Calculated Stress (GPa)	FWHM	Calculated Stress (GPa)	FWHM	Calculated Stress (GPa)	FWHM	Calculated Stress (GPa)	FWHM
0	-0.259	11.10	-0.288	11.32	-0.194	11.96	-0.2	11.59
50 000	-0.373 ± 0.33	12.01	-0.252	12.16	-0.302	12.27	-0.499	11.88
100 000	-0.295	12.11	-0.313	12.21	-0.311	11.48	-0.307	11.52
150 000	-0.253	11.96	-0.225	11.57	-0.288	13.04	-0.309	11.86
200 000	-0.125	12.31	-0.103	12.39	-0.280	12.17	-0.262	11.94
250 000	-0.104	11.81	-0.020	12.36	-0.221	11.79	-0.242	11.82
300 000	-0.038	12.75	0.015	12.49	-0.101	11.44	0.129 ± 0.31	11.89
350 000	-0.092	12.47	0.115	12.75	-0.233	11.95	-0.189	11.75
400 000	-0.04	12.50	0.028	12.62	-0.233	11.87	-0.318	11.75
500 000	0.112	12.46	0.096	12.81	-0.167	12.19	-0.106	12.15
600 000	0.065	12.43	0.258	12.36	0.016	11.89	-0.115	11.48

An evaluation of the number of points in the mapping area showing tensile stresses yields similar trends to those observed with the previous Sample D16_C. In general there is an observable trend of an increase in the number of tensile points with increasing number of loading cycles. Figure 6.5.13 shows this relationship for both the leached and underside of the sample and the variation. The graphs indicate that as the number of loading cycles gets higher, so does the number of mapping points in the grid exhibiting tensile stresses. As a function of map size, it is observed that the small map more often than not, has more number of tensile points as compared to the large map. This is in agreement with the model developed by Börger and his colleagues

(refer to section 5.7 discussion). After 600 000 cycles we believe that due to the number of tensile points covering a sizeable percentage of the surface the samples would be more likely to fail catastrophically.

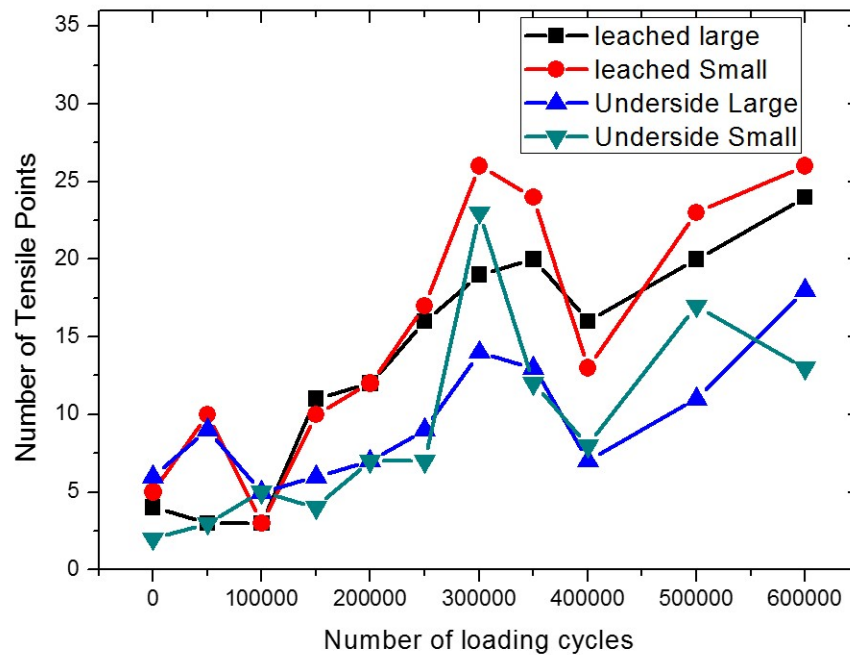


Figure 6.5.13: Shows a plot of the number of mapping points exhibiting tensile stresses as a function of map size and number of loading cycles for the Sample D16_D.

Figure 6.5.12 as well as Figure 6.5.14 through to Figure 6.5.17 present the respective graph and histogram plots showing the point to point stress variations for the different number of sets of loading cycles for sample D16_D. The graph and histograms highlight the fact that similar results and explanations are applicable to sample D16_D as compared to sample D16_C. This indicates satisfactory consistence in the results. Again the fluctuations observed for the underside are probably due to the EDM cutting.

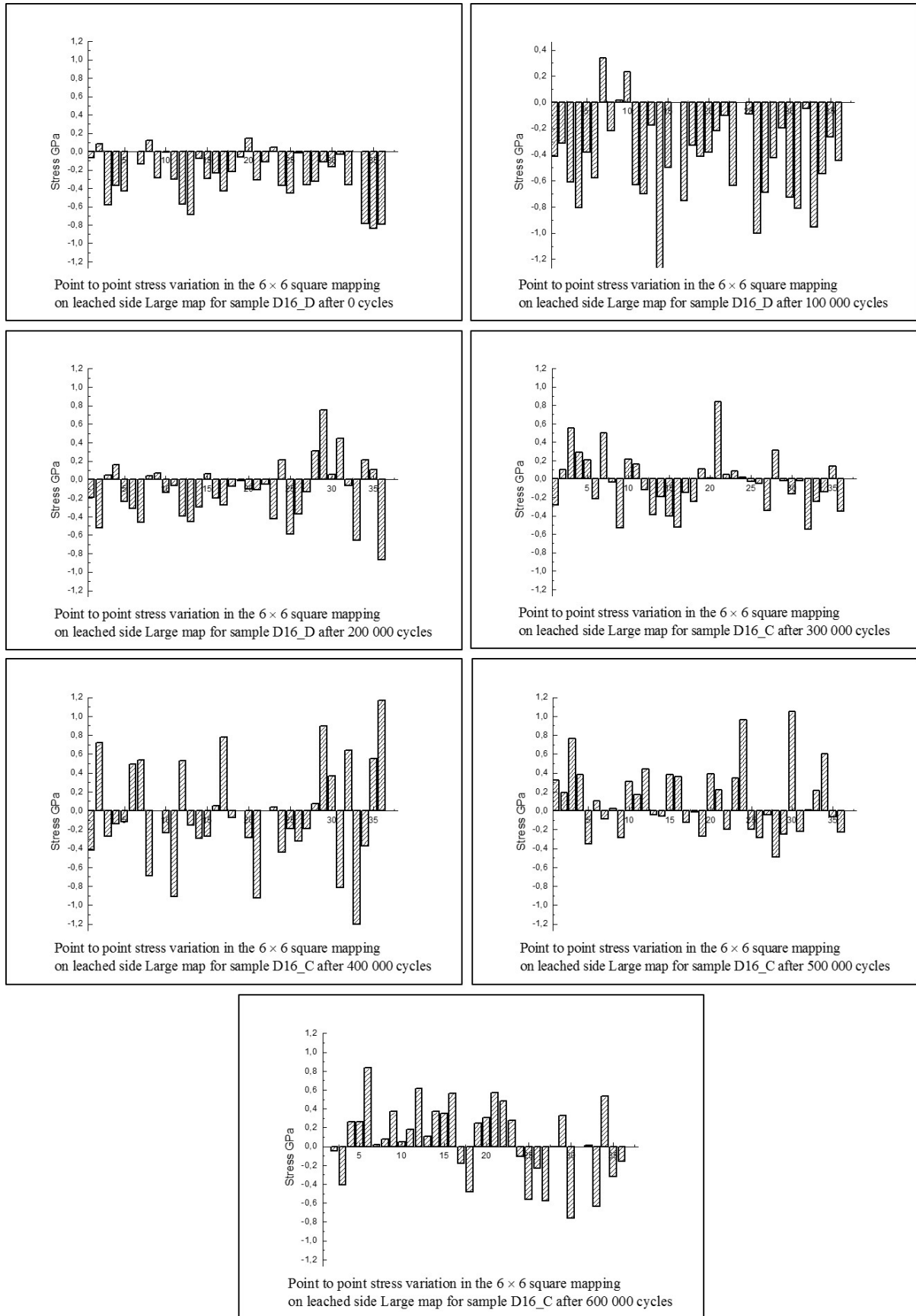


Figure 6.5.14: Point to point stress variation as a function of the number of cycles for Sample D16_D on the leached surface. The histograms represent the stress at each point for the respective number of cycles. This is for the large map.

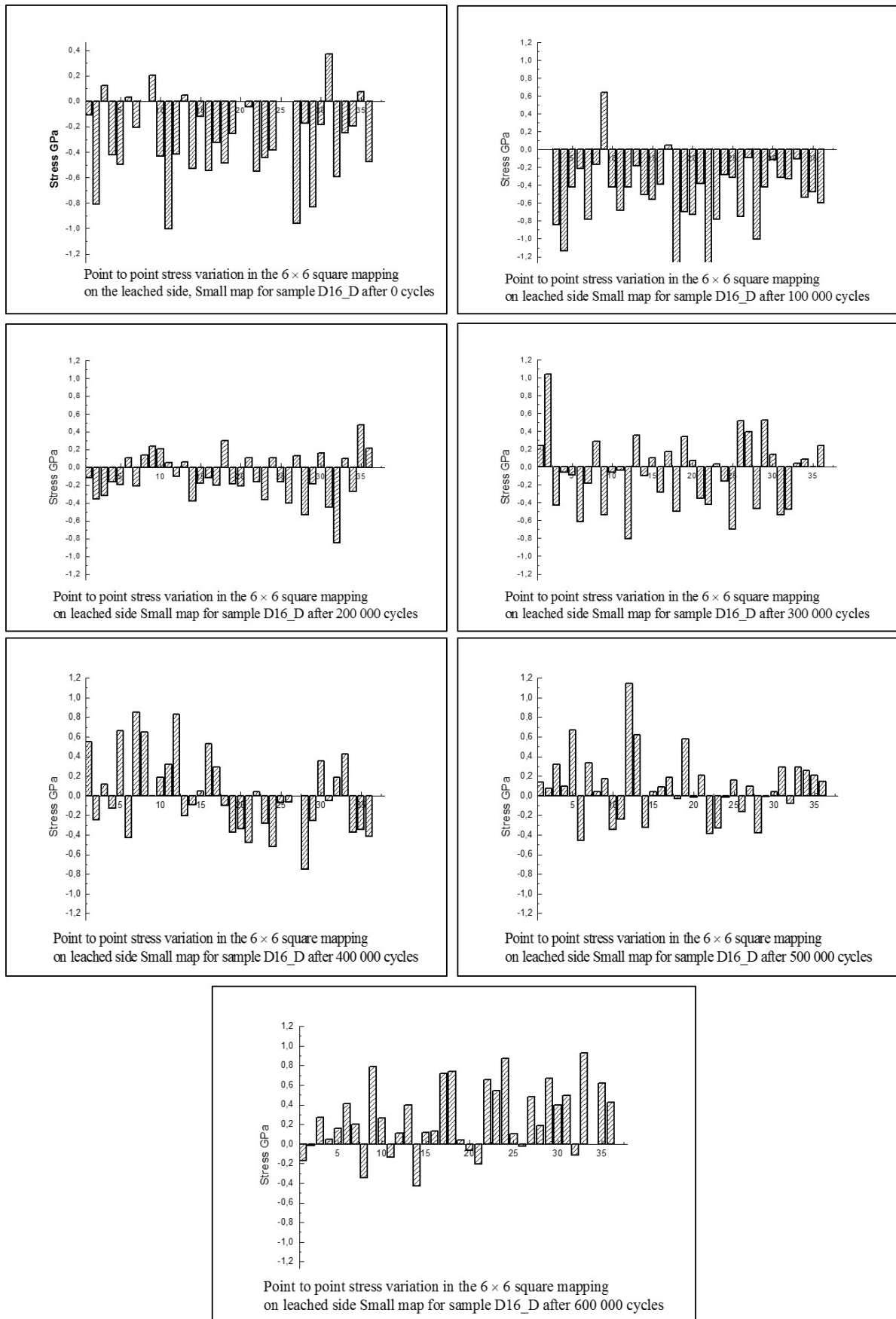


Figure 6.5.15: Point to point stress variation as a function of the number of cycles for Sample D16_D on the leached surface. The histograms represent the stress at each point for the respective number of cycles. This is for the small map.

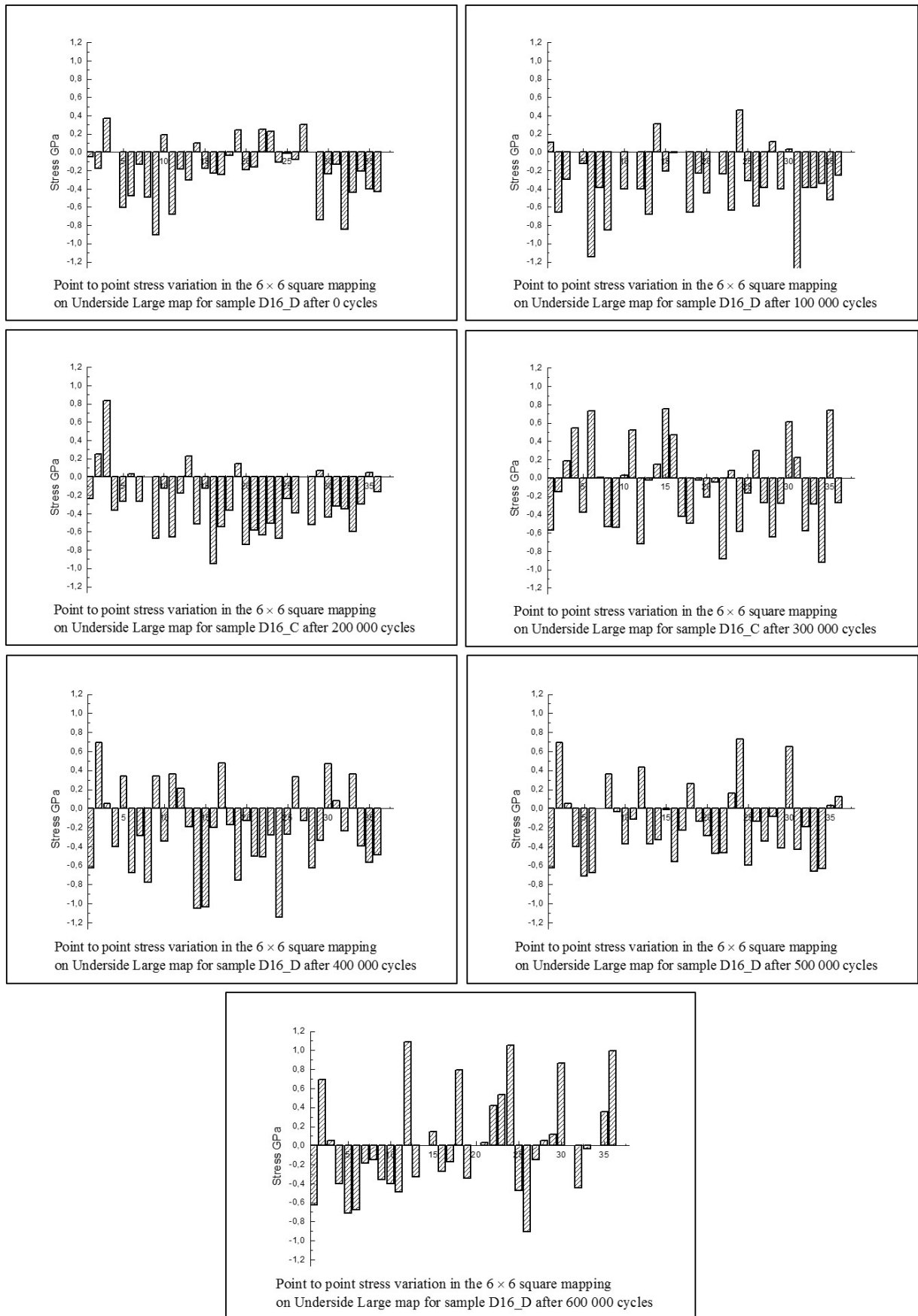


Figure 6.5.16: Point to point stress variation as a function of the number of cycles for Sample D16_D on the underside surface. The histograms represent the stress at each point for the respective number of cycles. This is for the large map.

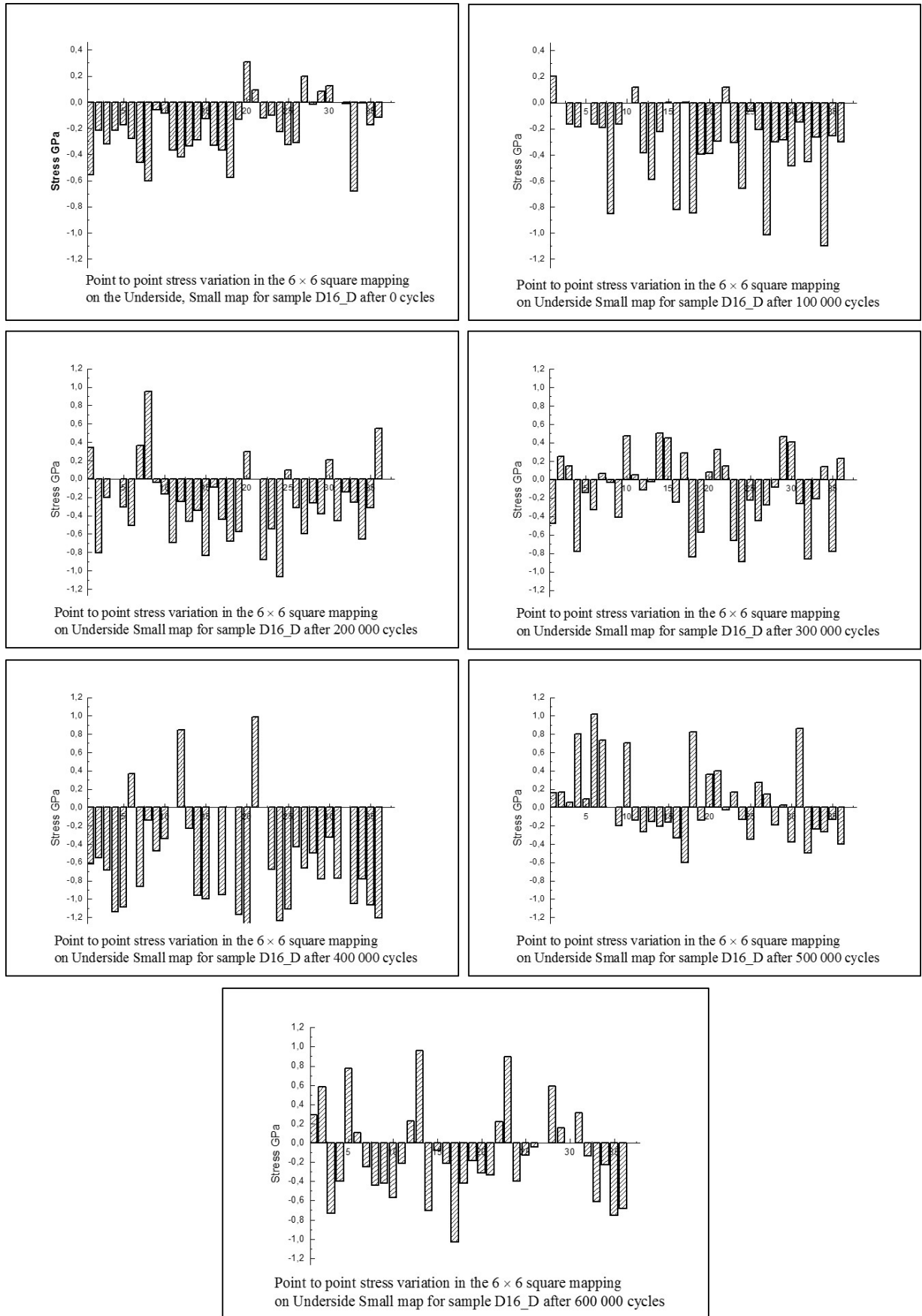
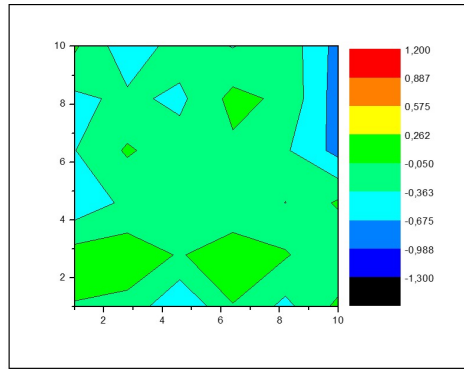
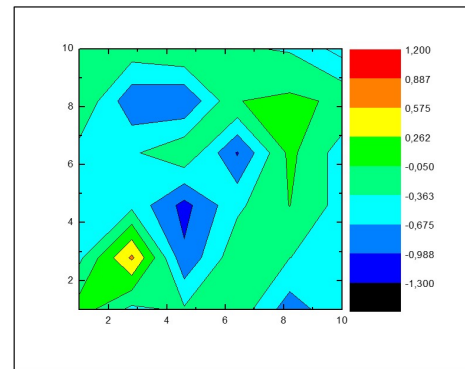


Figure 6.5.17: Point to point stress variation as a function of the number of cycles for Sample D16_D on the underside surface. The histograms represent the stress at each point for the respective number of cycles. This is for the small map.

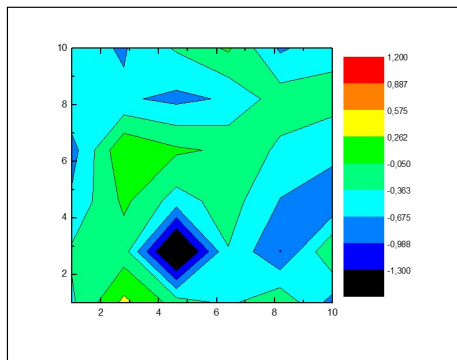
2D colour maps were plotted for the leached side of sample D16_D, showing the distribution of the calculated stresses, are presented in Figures 6.5.18 and 6.5.19. Again only selected plots are shown here. It can be observed that as with histograms, the results observed for sample D16_D are very comparable to those for sample D16_C. Similarly 2D colour maps for the underside were plotted (see Figure 6.5.20 and 6.5.21), with interpretation consistent with earlier samples.



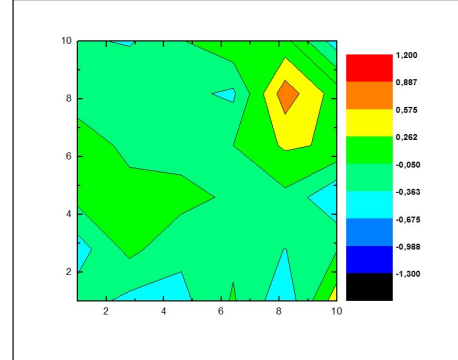
2D Surface map showing the stress after 0 cycles



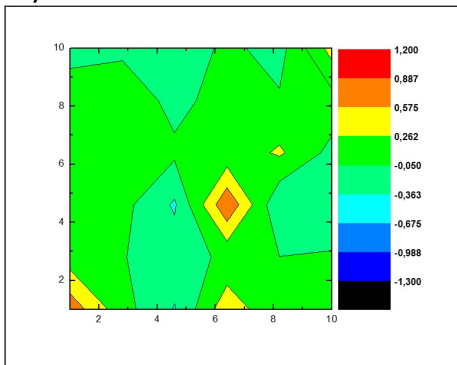
2D Surface map showing the stress after 50 000 cycles



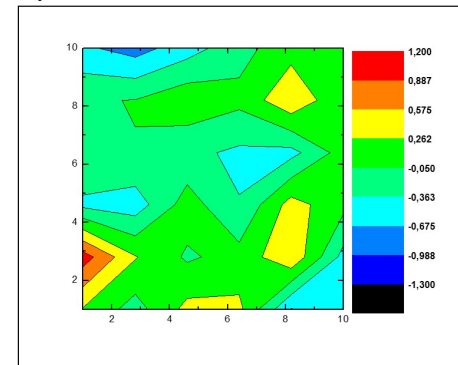
2D Surface map showing the stress after 100 000 cycles



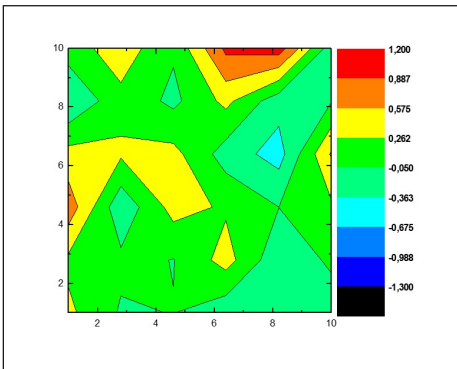
2D Surface map showing the stress after 200 000 cycles



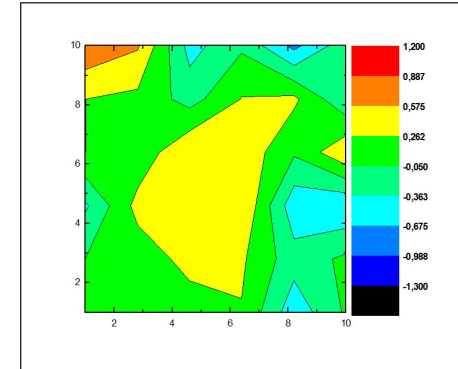
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles

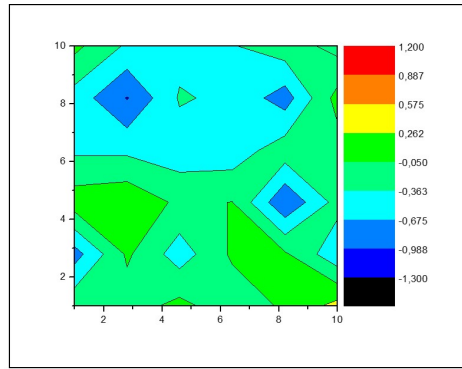


2D Surface map showing the stress after 500 000 cycles

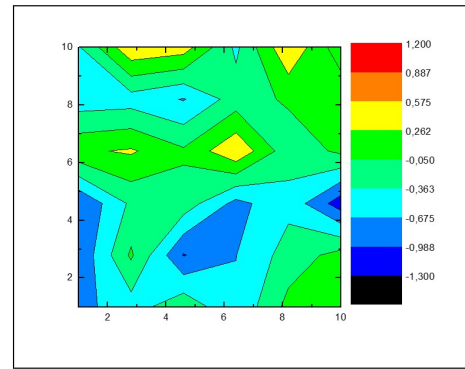


2D Surface map showing the stress after 600 000 cycles

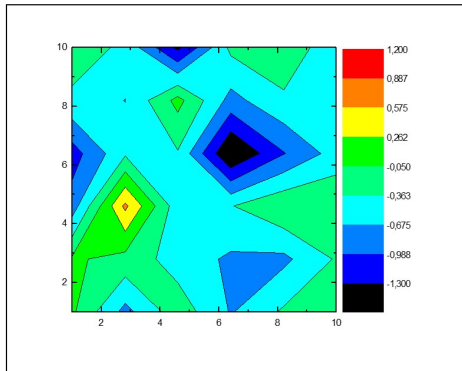
Figure 6.5.18: 2D Surface maps showing the nature and distribution of stress for the large map, as a function of the number of cycles for Sample D16_D. These are results for the leached side.



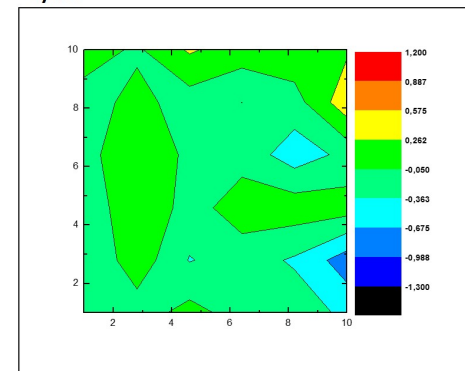
2D Surface map showing the stress after 0 cycles



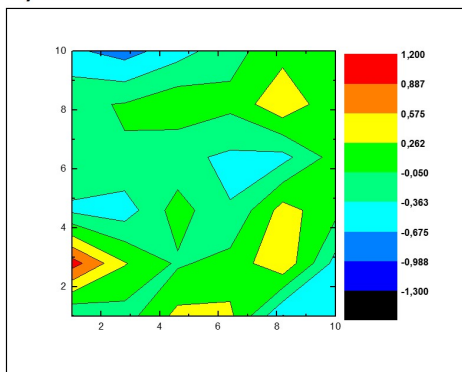
2D Surface map showing the stress after 50 000 cycles



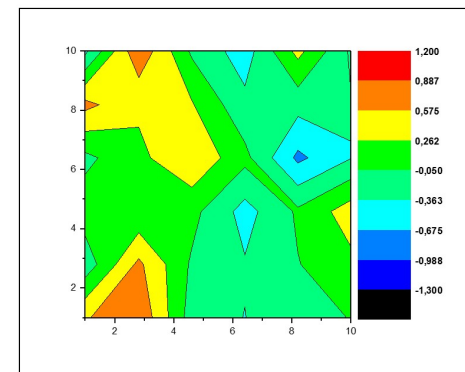
2D Surface map showing the stress after 100 000 cycles



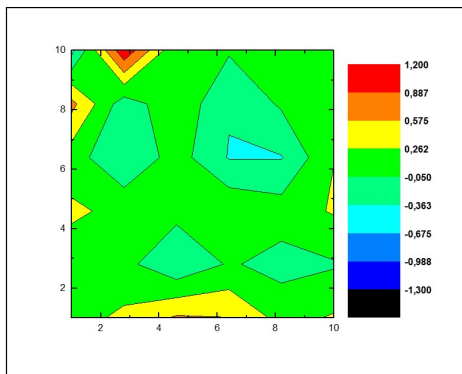
2D Surface map showing the stress after 200 000 cycles



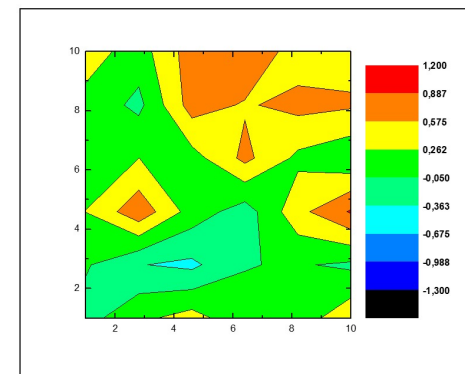
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles



2D Surface map showing the stress after 500 000 cycles



2D Surface map showing the stress after 600 000 cycles

Figure 6.5.19: 2D Surface maps showing the nature and distribution of stress for the Small map, as a function of the number of cycles for Sample D16_D. These are results for the leached side.

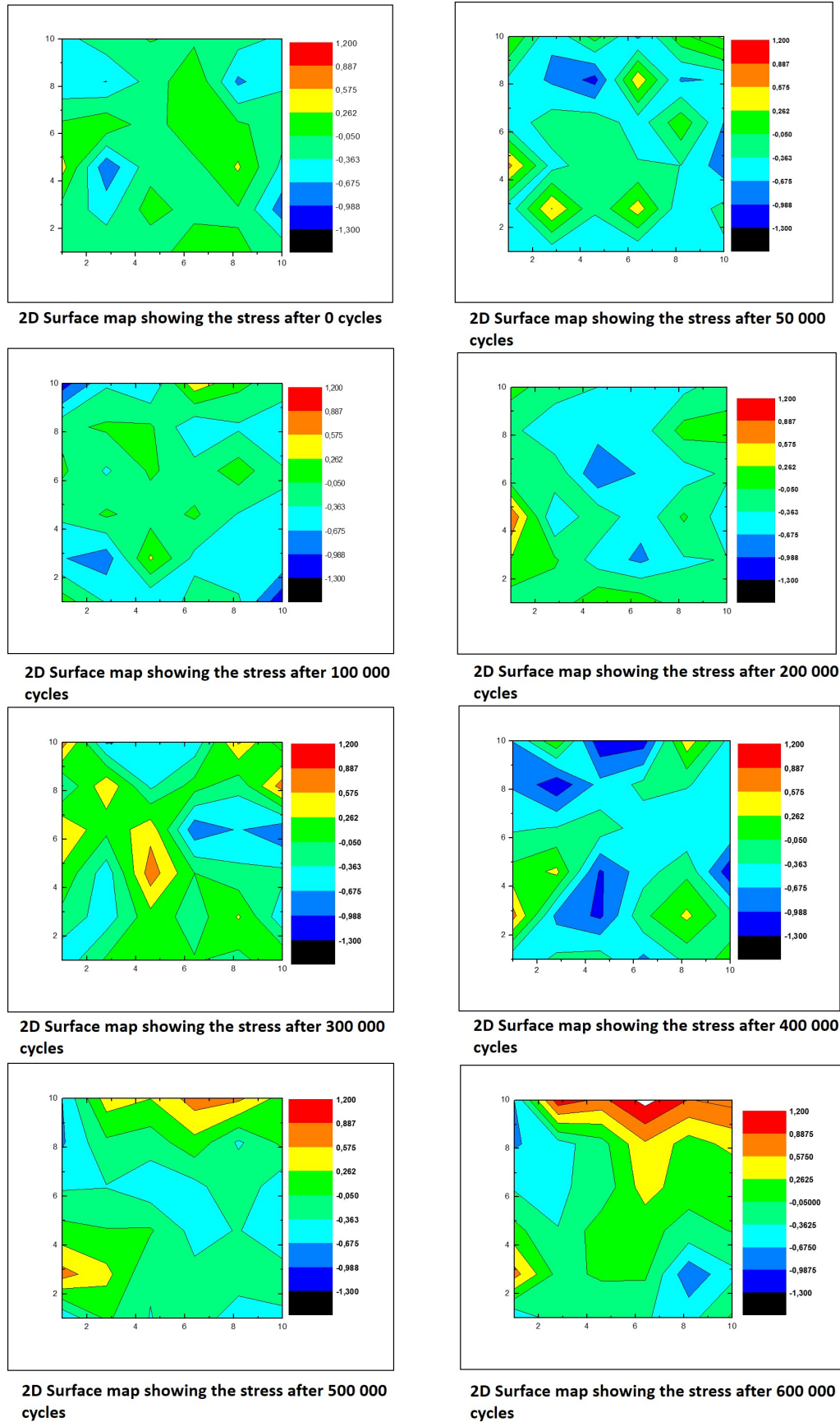
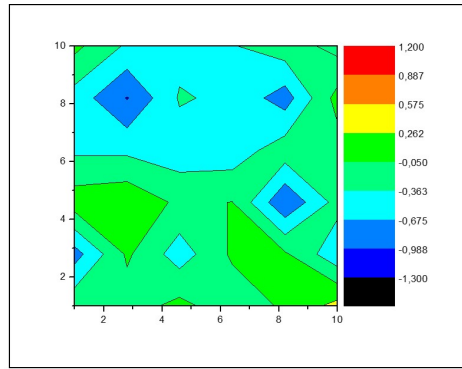
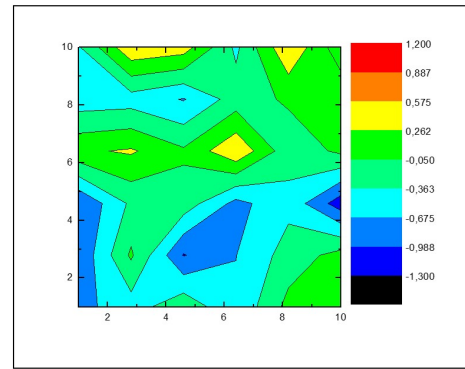


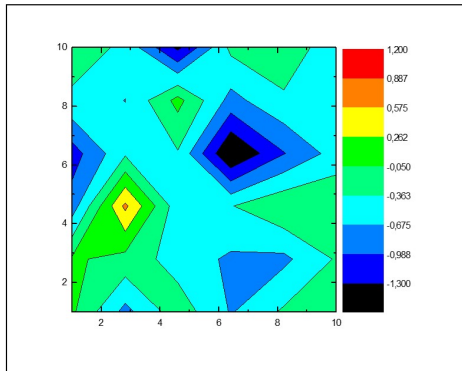
Figure 6.5.20: 2D Surface maps showing the nature and distribution of stress for the large map, as a function of the number of cycles for Sample D16_D. These are results for the underside.



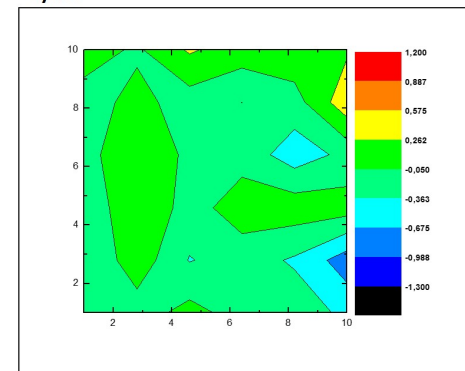
2D Surface map showing the stress after 0 cycles



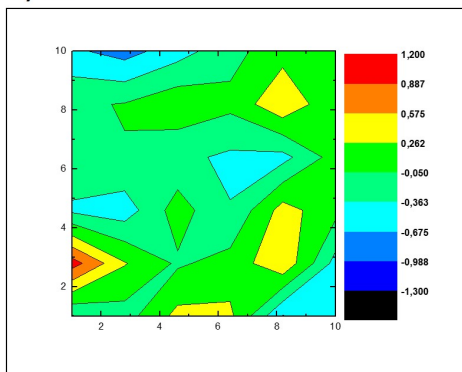
2D Surface map showing the stress after 50 000 cycles



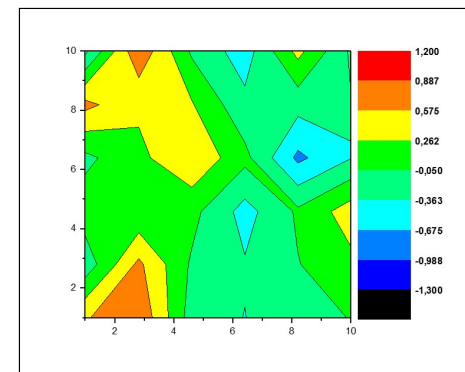
2D Surface map showing the stress after 100 000 cycles



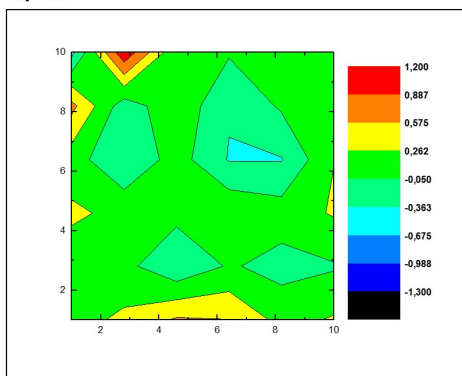
2D Surface map showing the stress after 200 000 cycles



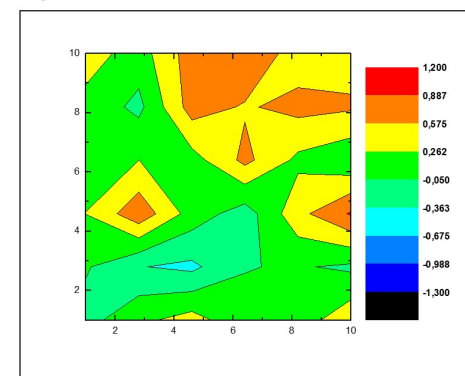
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles



2D Surface map showing the stress after 500 000 cycles



2D Surface map showing the stress after 600 000 cycles

Figure 6.5.21: 2D Surface maps showing the nature and distribution of stress on the underside for the small map, as a function of the number of cycles for Sample D16_D.

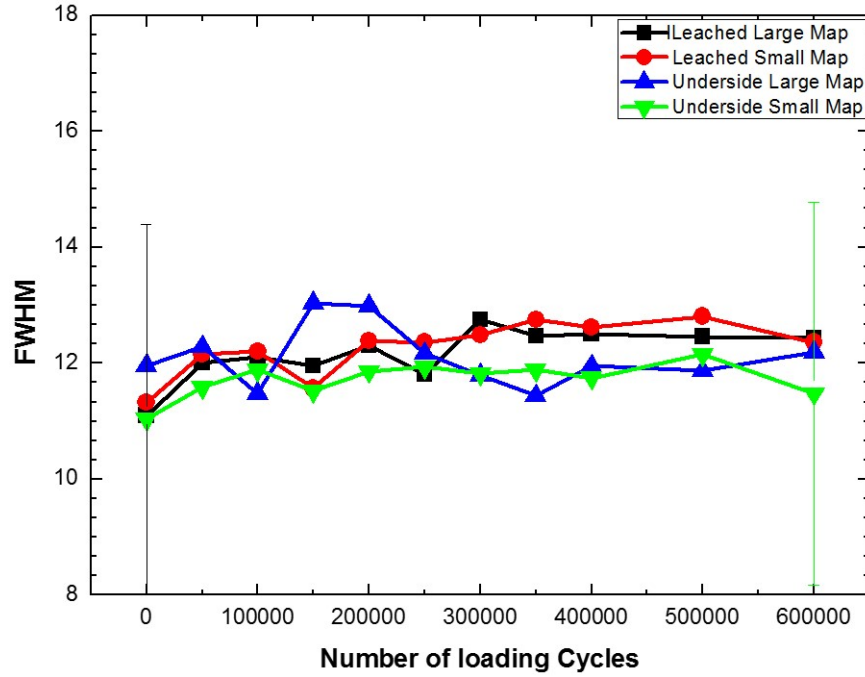


Figure 6.5.22: FWHM of sample D16_D as a function of the number of loading cycles. The data represents the average width value across the surface calculated over 36 mapping points. The error bars indicate the standard deviation in data.

Figure 6.5.22 indicates the plotted full width measured at half maximum (FWHM) against the number of loading cycles. While some fluctuations are evident, they all within error range and the results suggest that there is no significant change in the FWHM as a function of the number of loading cycles. This is an indication to some degree of the quality of the diamond to diamond bonds as they seem to effectively redistribute the load hence there is minimal deformation observed.

6.5.3 Sample D16_F

The sample was subjected to 600000 cycles of loading. Again the results obtained are summarised in a plot of the calculated average stresses as a

function of the number of loading cycles and 2D colour maps highlighting the distribution of these stresses. Visual inspection of the samples did not show any cracks present on either side of the disc sample.

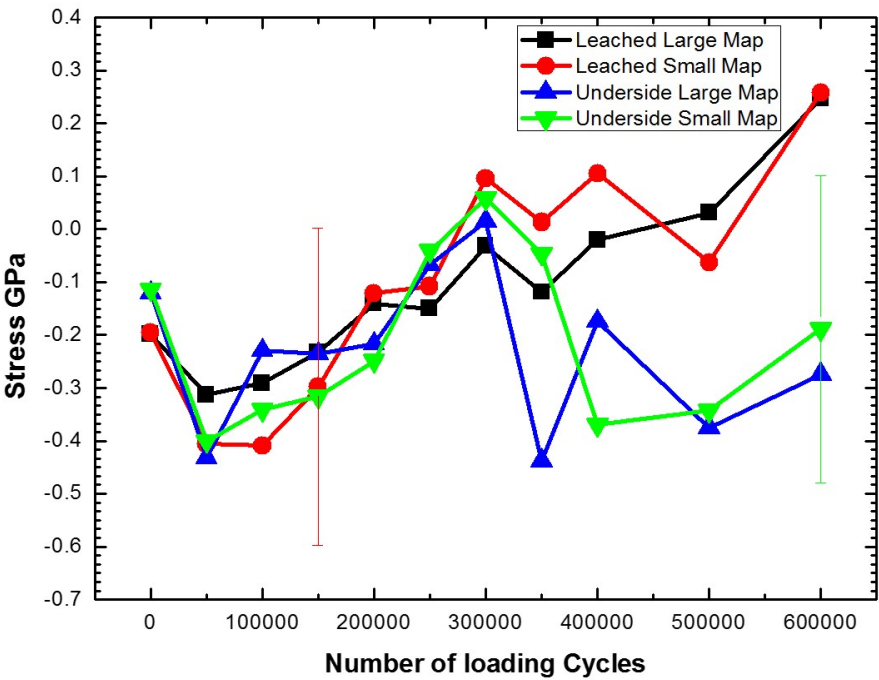


Figure 6.5.23: A comparison of the calculated average stress for the Large and Small maps on both sides of the Sample D16_F, plotted as a function of the number of loading cycles. The error bars indicate the standard deviation in data.

Table 6.6 and Figure 6.5.23 tabulates and compares the calculated average stress for the large and small maps on both sides of the Sample D16_F, as a function of map size and number of loading cycles. The results are comparable to those reported earlier for samples D16_C and D16_D.

Table 6.6: Showing the calculated average stresses and the full width measured at half maximum for the Sample D16_F. Units for peak position and FWHM are cm^{-1} .

	Leached Large Map		Leached Small Map		Underside Large Map		Underside Small Map	
Cycles	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})	Calculated Stress (GPa)	FWHM (cm^{-1})
0	-0.199	11.67	-0.196	11.12	-0.121	11.16	-0.114	11.69
50 000	-0.313	11.83	-0.406	11.37	-0.432	11.85	-0.400	11.60
100 000	-0.291	12.06	-0.409	12.02	-0.230	10.91	-0.340	11.3
150 000	-0.328 $\pm$ 0.30	11.91	-0.299	11.59	-0.236	12.51	-0.316	10.56
200 000	-0.141	12.15	-0.121	12.18	-0.217	11.59	-0.249	11.13
250 000	-0.150	12.13	-0.108	11.86	-0.067	12.26	-0.041	12.50
300 000	-0.032	12.27	0.096	12.25	0.015	11.61	0.059	11.49
350 000	-0.119	12.45	0.013	12.51	-0.438	12.05	-0.045	11.93
400 000	-0.400	12.69	0.105	12.34	-0.175	11.44	-0.370	12.37
500 000	0.031	12.84	-0.063	12.54	-0.375	11.62	-0.343	11.34
600 000	0.276	12.95	0.258	13.02	-0.0274	12.37	-0.189 $\pm$ 0.29	11.64

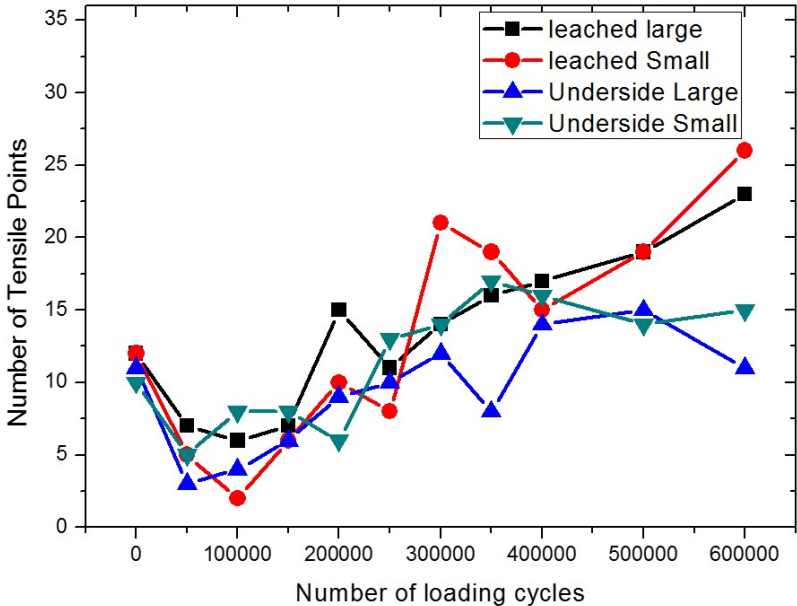


Figure 6.5.24: Shows a plot of the number of mapping points exhibiting tensile stresses as a function of map size and number of loading cycles for Sample D16_F.

Figure 6.5.24 shows the number of tensile points in the mapping grid area with Figure 6.5.25 through to Figure 6.5.28 showing the histograms plotted for the leached side. The plots exhibit similar trends to those observed for previous samples D16_C and D16_D. Similarly histograms for the underside surface plotted in Figure 6.5.27 and Figure 6.5.28 show fluctuating behaviour as observed with previous samples and again this is attributed to the EDM cutting. The consistency of the observed results is very satisfactory.

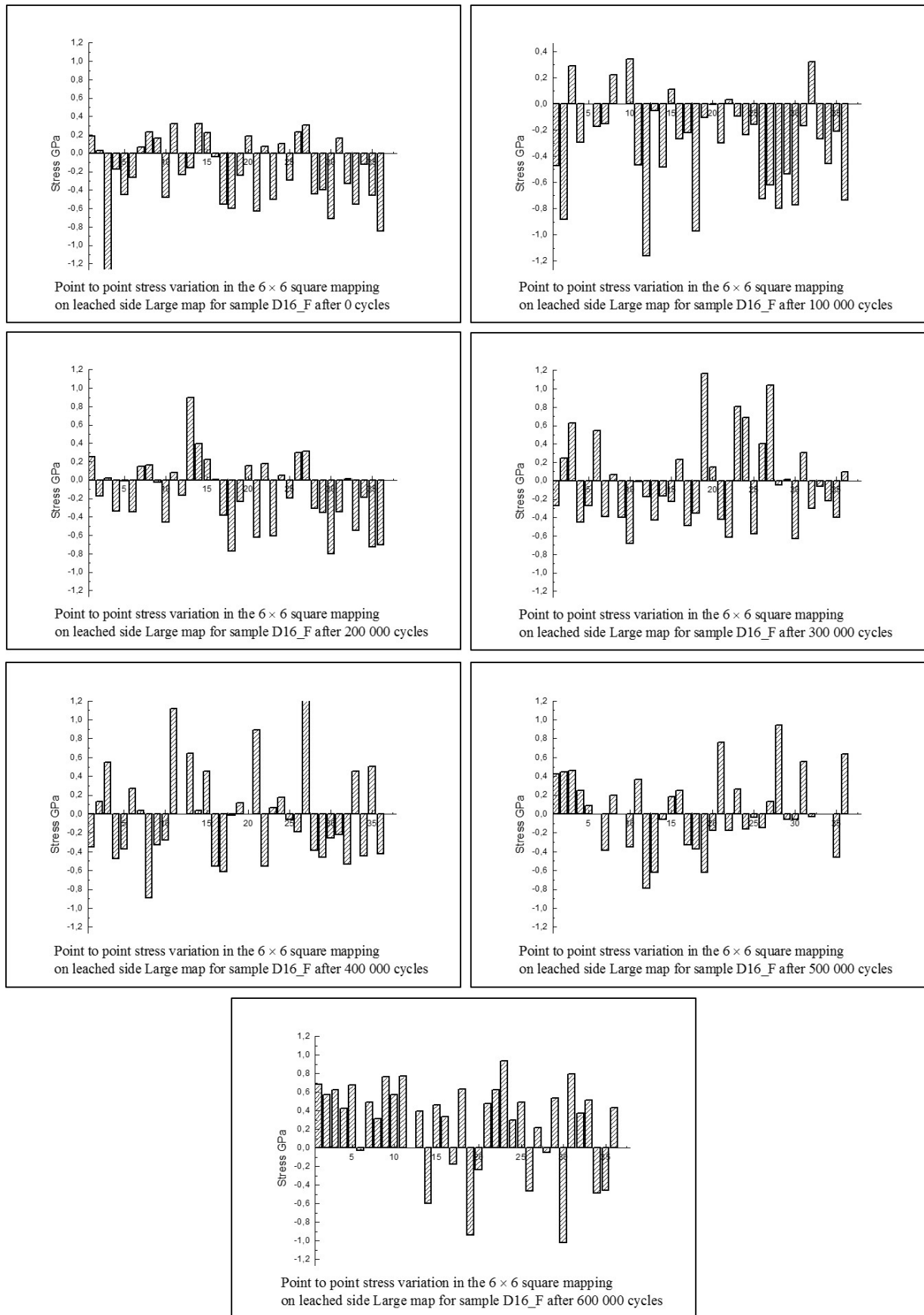


Figure 6.5.25: Point to point stress variation as a function of the number of cycles for Sample D16_F on the leached surface. The histograms represent the stress at each point for the respective number of cycles. This is for the Large map.

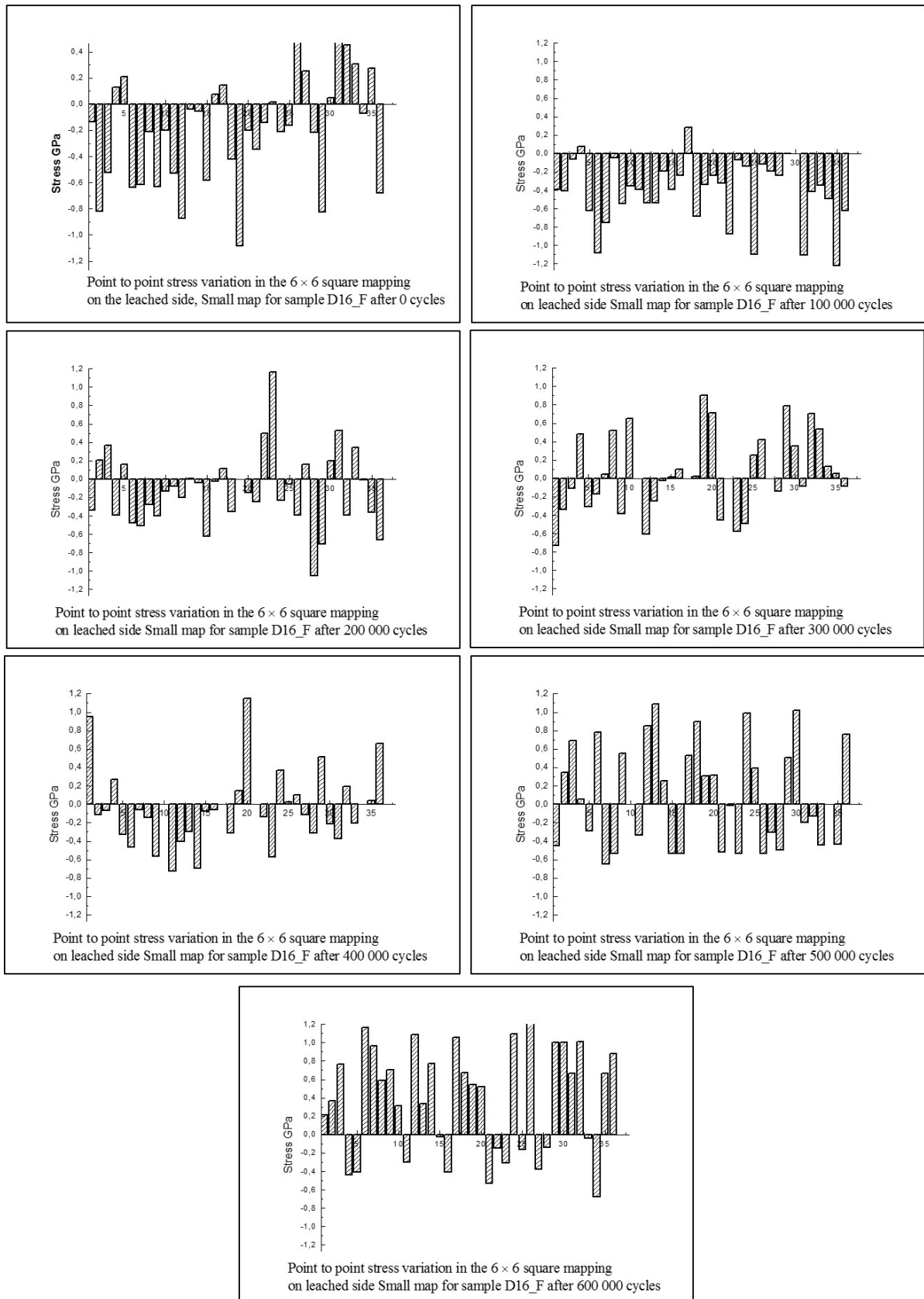


Figure 6.5.26: Point to point stress variation as a function of the number of cycles for Sample D16_F on the leached surface. The histograms represent the stress at each point for the respective number of cycles. This is for the small map.

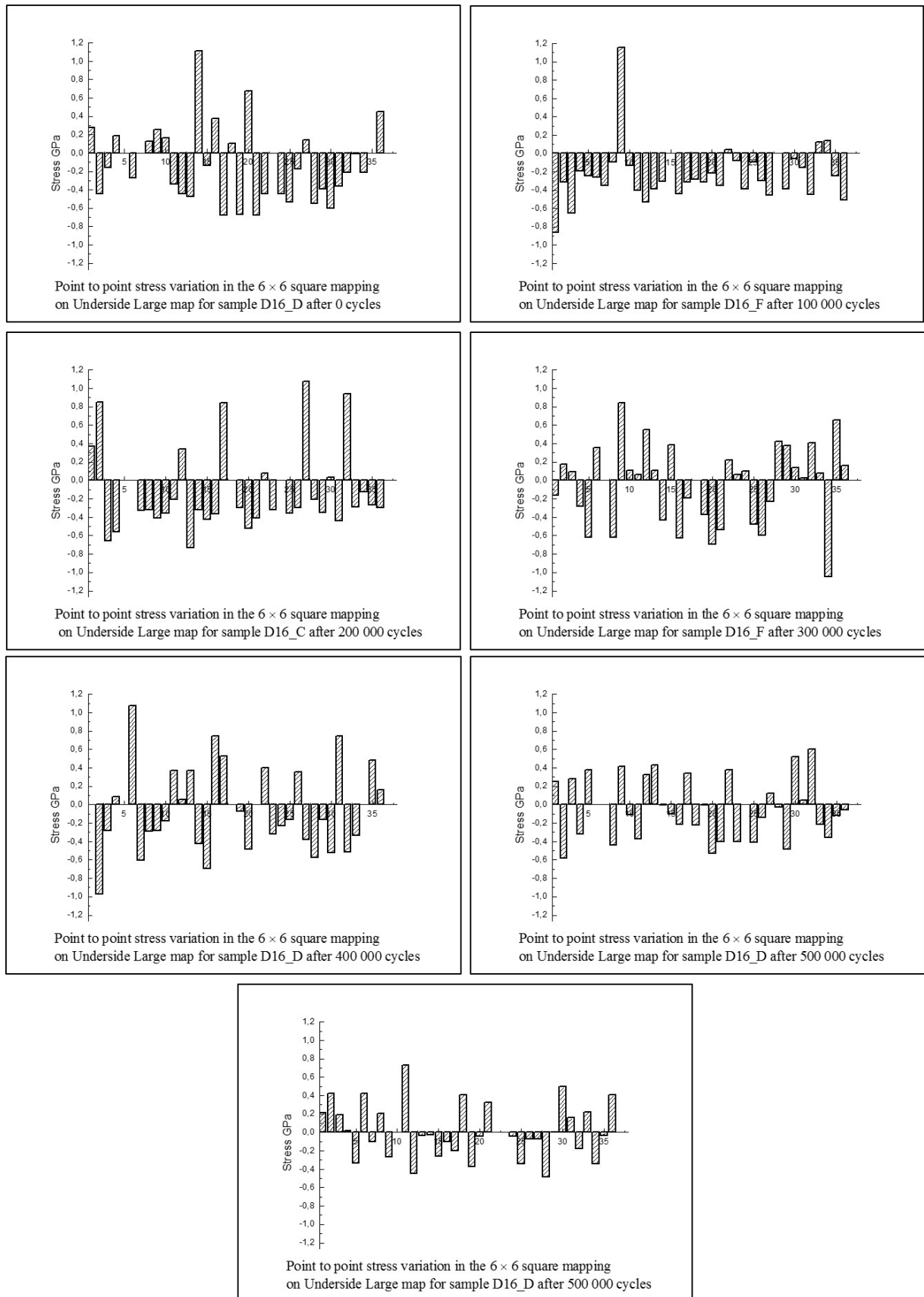


Figure 6.5.27: Point to point stress variation as a function of the number of cycles for Sample D16_F on the underside surface. The histograms represent the stress at each point for the respective number of cycles. This is for the large map.

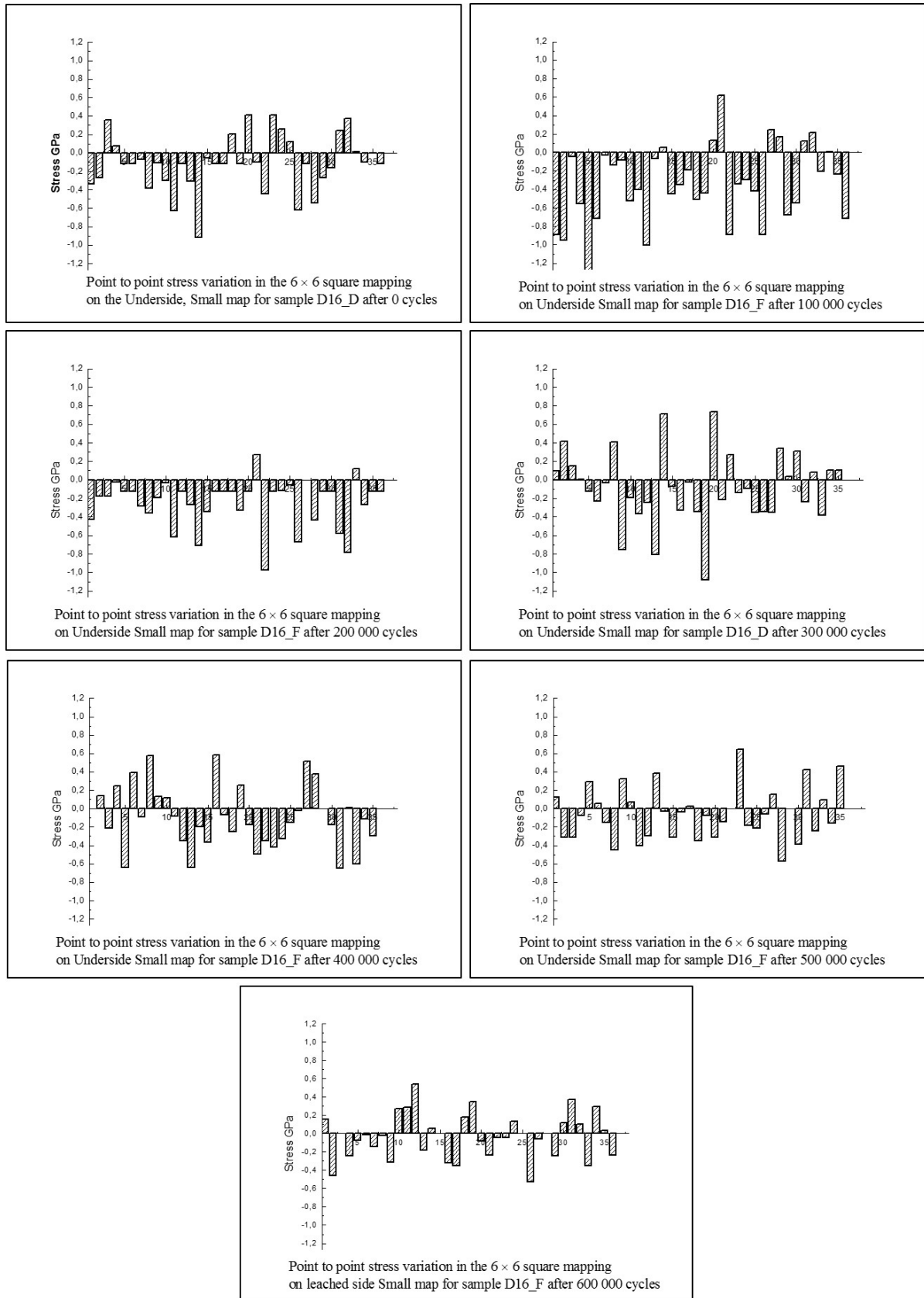


Figure 6.5.28: Point to point stress variation as a function of the number of cycles for Sample D16_F on the underside surface. The histograms represent the stress at each point for the respective number of cycles. This is for the small map.

The 2D colour maps in Figure 6.5.18 and Figure 6.5.19 show the distribution of the calculated stresses for the leached side's large and small maps, respectively. The same explanations as in samples D16_C and D16_D are applicable here since the results are clearly comparable. 2D colour maps were plotted for the underside of the sample as shown in Figure 6.5.20 through to Figure 6.5.21.

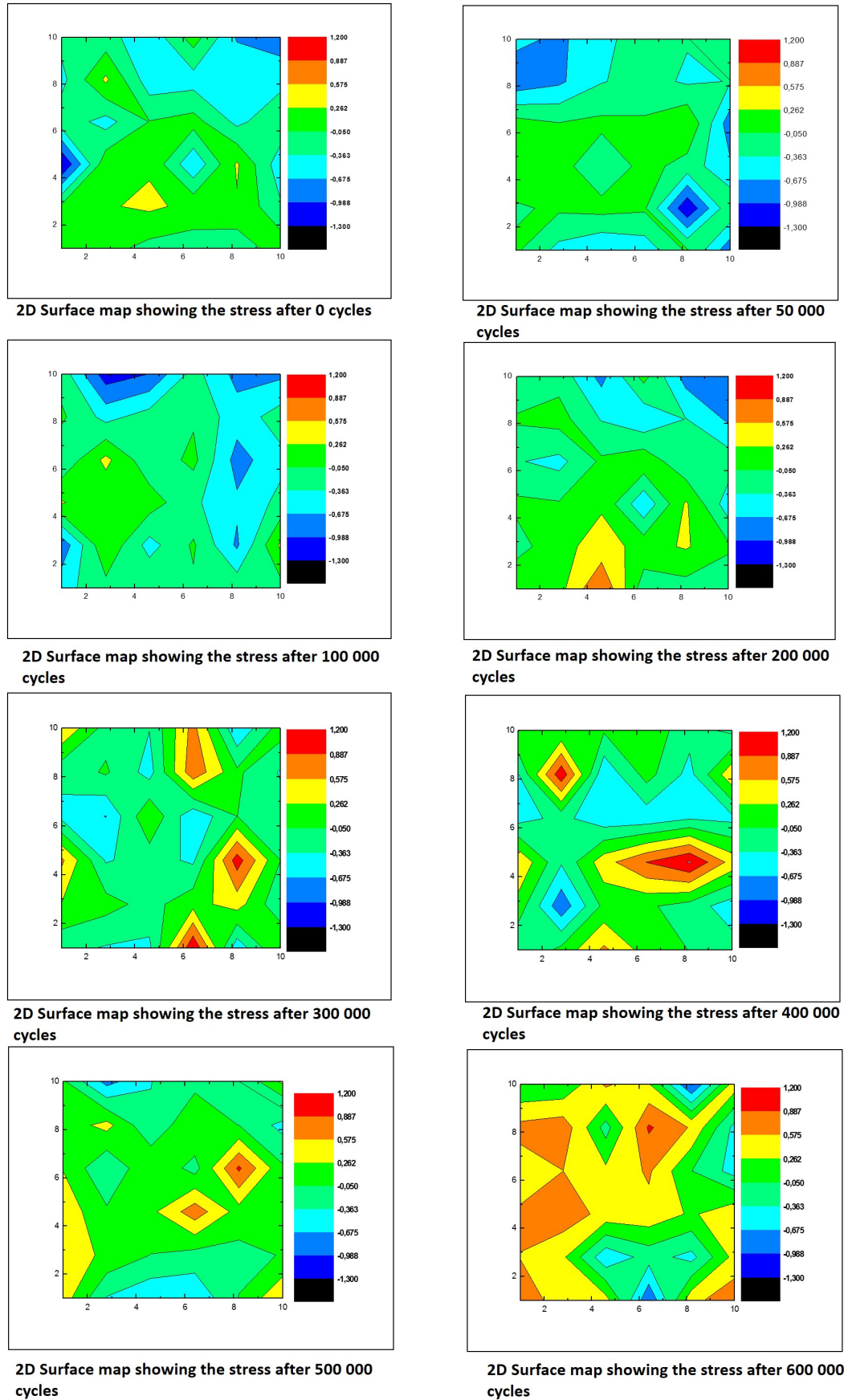
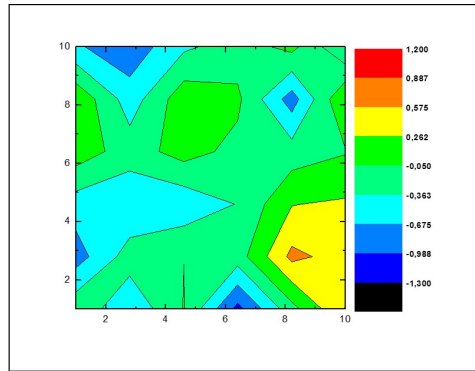
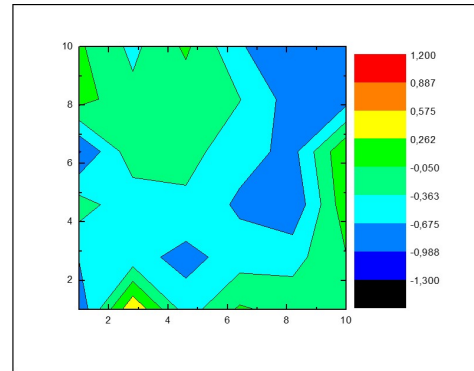


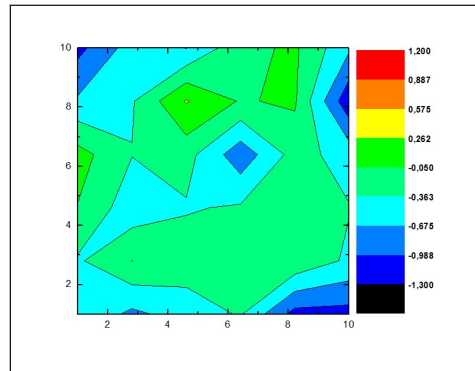
Figure 6.5.29: 2D Surface maps showing the nature and distribution of stress for the Large map, as a function of the number of cycles for Sample D16_F. These are results for the Leached side.



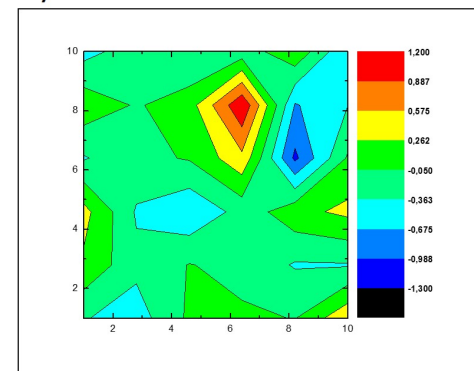
2D Surface map showing the stress after 0 cycles



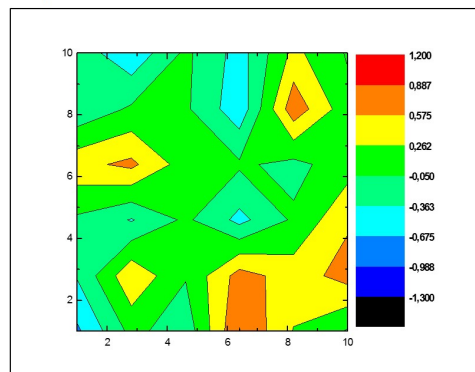
2D Surface map showing the stress after 50 000 cycles



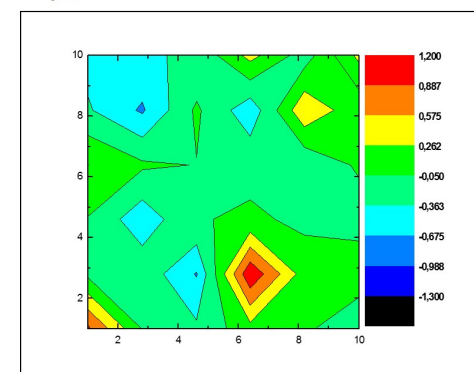
2D Surface map showing the stress after 100 000 cycles



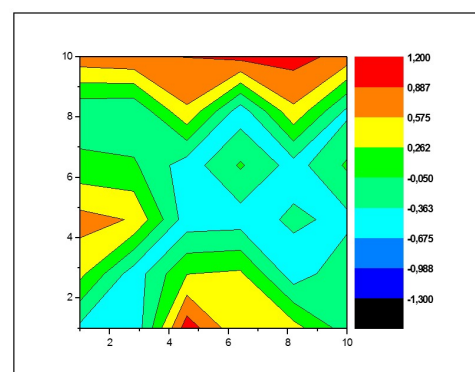
2D Surface map showing the stress after 200 000 cycles



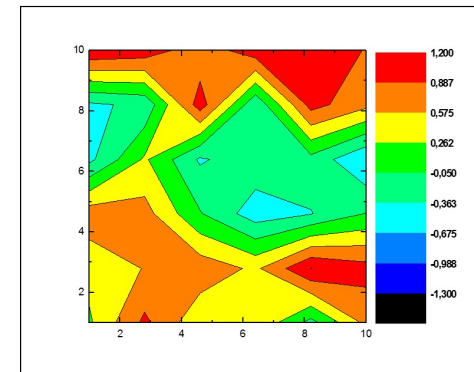
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles

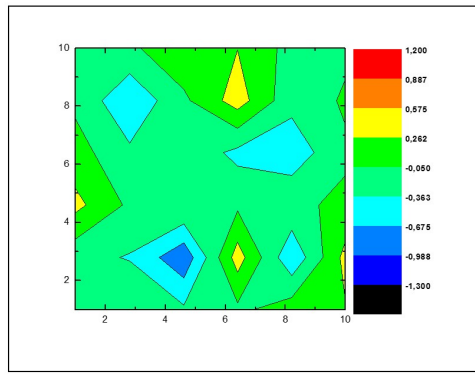


2D Surface map showing the stress after 500 000 cycles

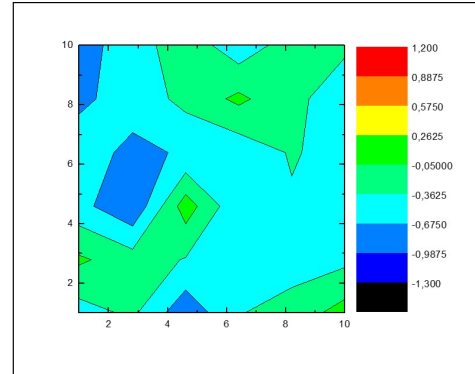


2D Surface map showing the stress after 600 000 cycles

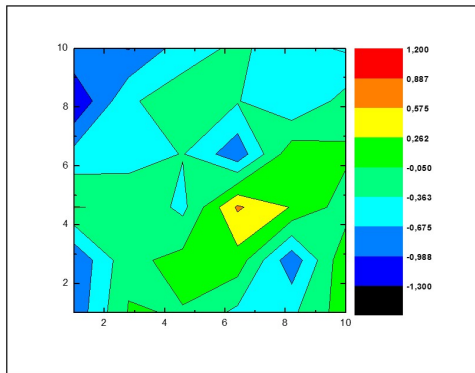
Figure 6.5.30: 2D Surface maps showing the nature and distribution of stress for the Small map, as a function of the number of cycles for Sample D16_F. These are results for the Leached side.



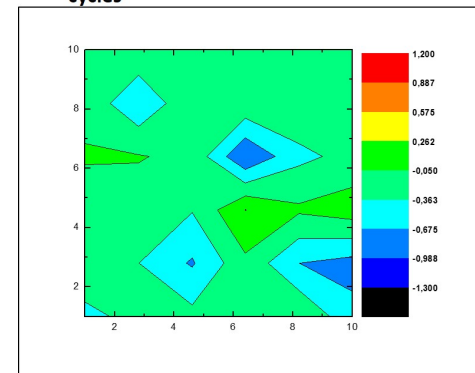
2D Surface map showing the stress after 0 cycles



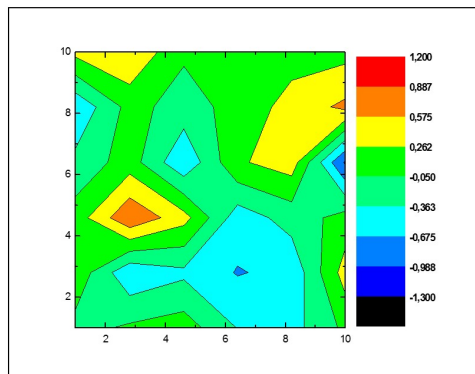
2D Surface map showing the stress after 50 000 cycles



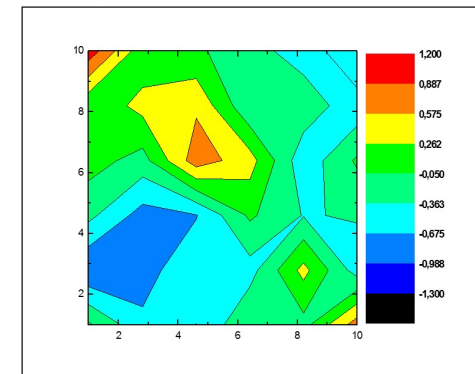
2D Surface map showing the stress after 100 000 cycles



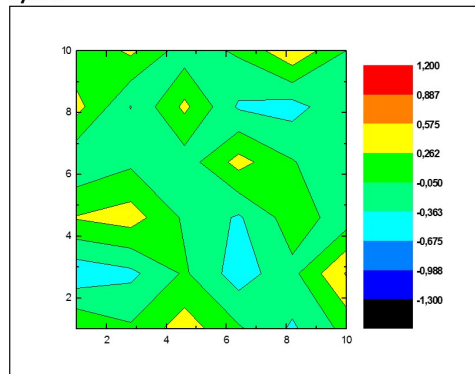
2D Surface map showing the stress after 200 000 cycles



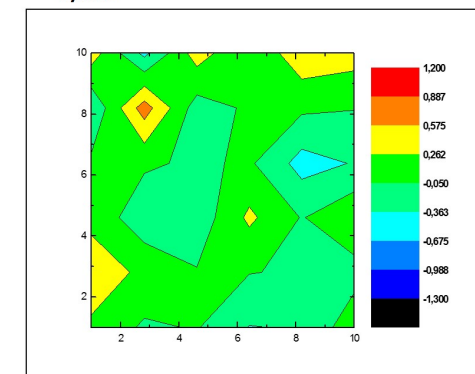
2D Surface map showing the stress after 300 000 cycles



2D Surface map showing the stress after 400 000 cycles



2D Surface map showing the stress after 500 000 cycles



2D Surface map showing the stress after 600 000 cycles

Figure 6.5.31: 2D Surface maps showing the nature and distribution of stress for the Large map, as a function of the number of cycles for Sample D16_F. These are results for the Underside.

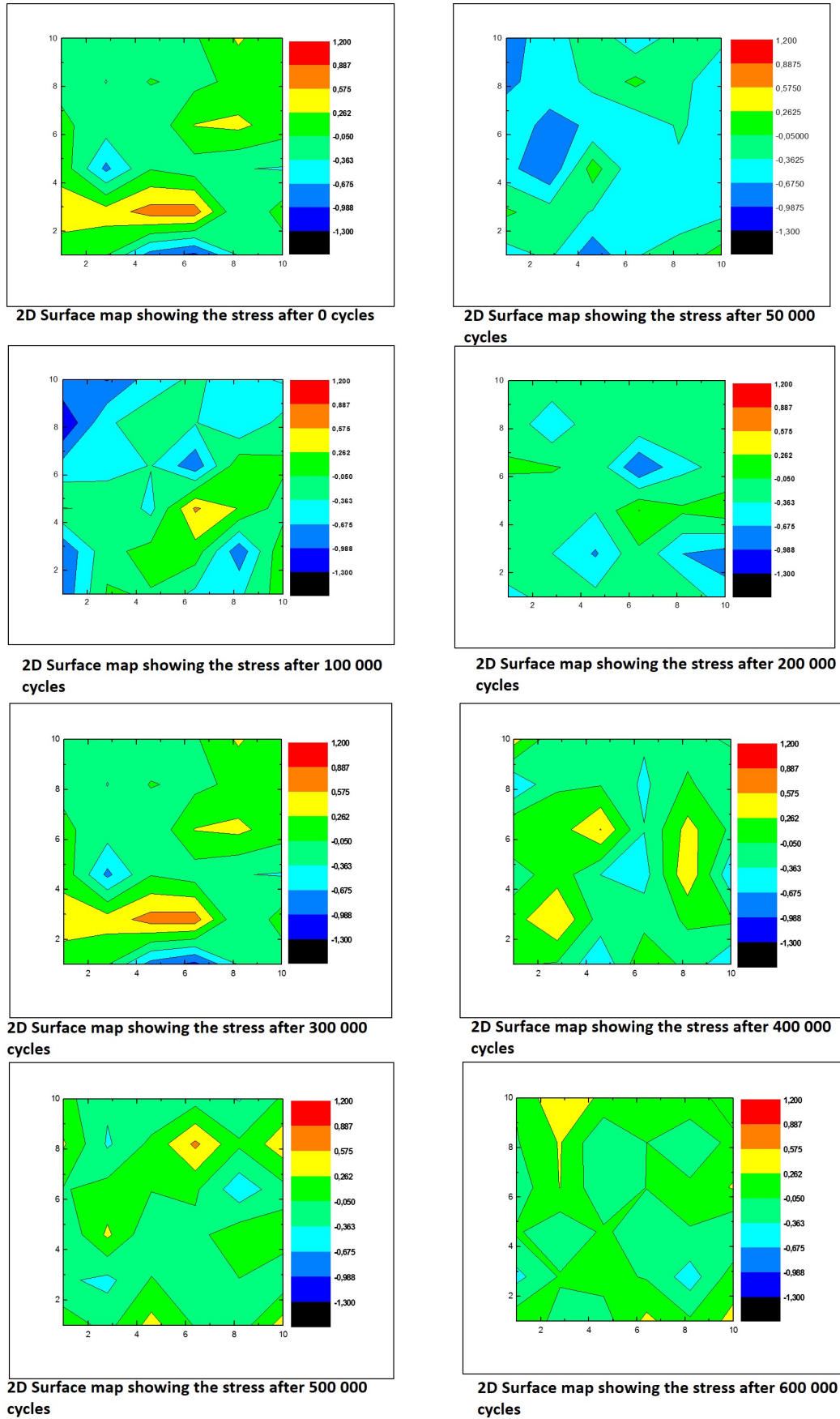


Figure 6.5.32: 2D Surface maps showing the nature and distribution of stress for the Small map, as a function of the number of cycles for Sample D16_F. These are results for the Underside.

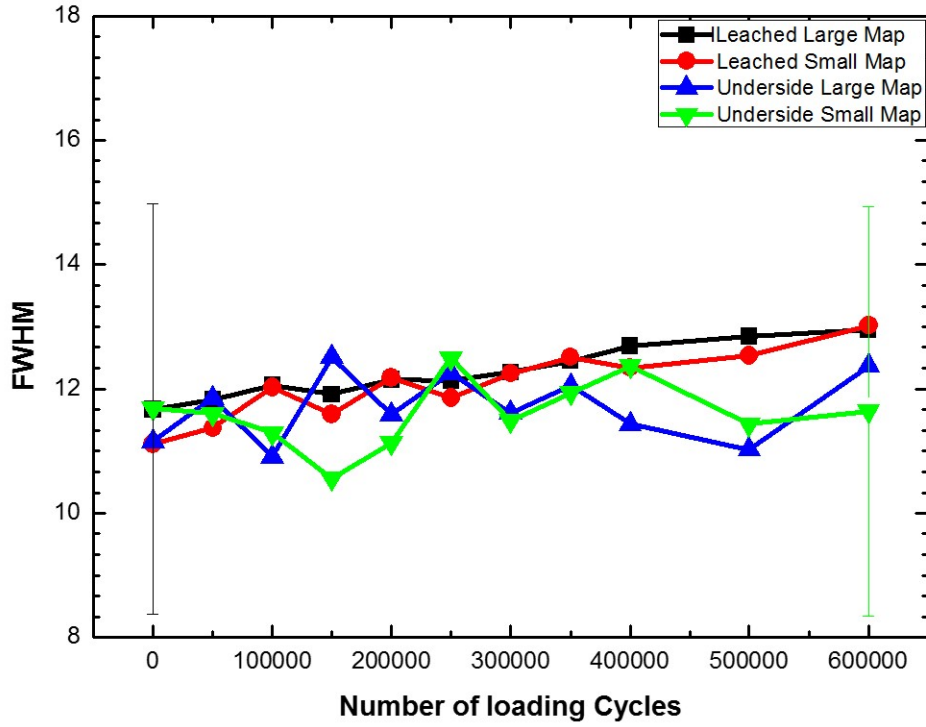


Figure 6.5.33: FWHM of sample D16_F as a function of the number of loading cycles. The data represents the average width value across the surface calculated over 36 mapping points. The error bars indicate the standard deviation in data.

The width of the Raman peak, measured as the full width at half maximum (FWHM) as recorded in Table 6.6. and Figure 6.5.33 notably shows no meaningful change as also observed with samples D16_C and D16_D.

6.6 X-ray Diffraction Stress Results

In this section, the X-ray diffraction stress measurements results for the three samples namely D16_C, D16_D and D16_F, are reported. The XRD-based residual stress measurements were carried out using the X-ray stress analyser (Bruker D8 Discover), at NECSA which consists of an area detector and a 6 axis goniometer. The Leptos software version 7, which is part of the Bruker

AXS suite of software for residual stress analyses, was employed for the stress analysis. The measurements were done on an area around the centre of the sample and on both side of the sample. Using the biaxial stress model, care was taken to precisely determine the stress components σ_{11} and σ_{22} and tabulating them. All the samples were subjected to 600000 cycles of cumulative fatigue loading conducted in intervals of 50000 cycles followed by X-ray diffraction and Micro Raman stress measurements with the aim of observing the transformation and change in the residual stress state on both surfaces of the PCD disc samples. For reporting purposes average stress values are normally used and these can be calculated by finding the average of the two stress components σ_{11} and σ_{22} . The relevant error is similarly calculated. The results in this section are largely represented in tabular and graphical format.

6.6.1 Sample D16_C

The sample was subjected to 600000 fatigue loading cycles and then stress measurements were conducted on both sides of the sample. Table 6.7 details the biaxial stress components, as well as the calculated average stress values for the sample D16_C, on the leached side.

Table 6.7: Table showing the measured stress values and the error for Sample D16_C on the leached side.

Number of Cycles	Stress (GPa)					
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$	$\sigma_{Average}$	Error (Average)
0	-0.111	0.064	-0.055	0.065	-0.112	0.035
50 000	-0.151	0.036	-0.115	0.043	-0.044	0.031
100 000	-0.131	0.040	-0.161	0.051	-0.028	0.035
150 000	-0.092	0.027	-0.079	0.035	-0.070	0.035
200 000	-0.105	0.023	-0.164	0.029	-0.166	0.031
250 000	-0.092	0.028	-0.119	0.024	-0.127	0.031
300 000	-0.105	0.027	-0.091	0.027	-0.114	0.027
350 000	-0.124	0.024	-0.134	0.028	-0.131	0.029
400 000	-0.138	0.025	-0.111	0.025	-0.100	0.027
500 000	-0.119	0.025	-0.112	0.027	-0.112	0.027
600 000	-0.145	0.022	-0.143	0.028	-0.121	0.029

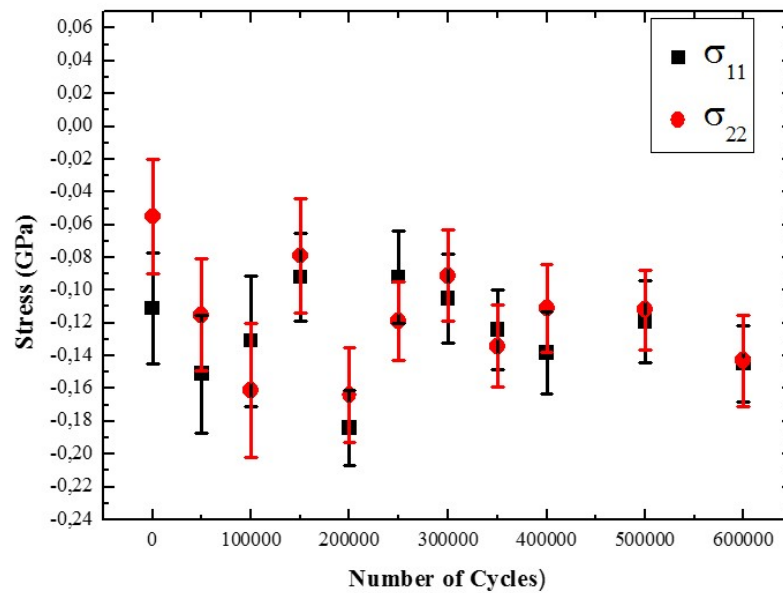


Figure 6.6.1: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_C on the Leached side.

The information in Table 6.7 suggests that the stress state on the leached side

remains confined to the compressive stress regime even after 600000 fatigue loading cycles. The data is also represented in a scatter plot showing the trend of the two stress components before averaging, see Figure 6.6.1. The scatter plot also shows the same trend.

The underside of the sample is where the one ball through which the sample was being loaded centrally, was in contact with the sample. Table 6.8 and Figure 6.6.2 reports the stress variation on the underside of Sample D16_C.

Table 6.8: Table Showing the measured stress values and the error for Sample D16_C on the underside.

Number of Cycles	Stress (GPa)			
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$
0	0.007	0.045	-0.099	0.045
50 000	-0.140	0.054	-0.173	0.043
100 000	-0.045	0.041	-0.124	0.035
150 000	-0.183	0.031	-0.112	0.029
200 000	-0.130	0.025	-0.115	0.024
250 000	-0.122	0.028	-0.114	0.027
300 000	-0.101	0.029	-0.125	0.028
350 000	-0.150	0.026	-0.186	0.025
400 000	-0.123	0.028	-0.153	0.027
500 000	-0.152	0.024	-0.144	0.021
600 000	-0.106	0.029	-0.127	0.028

The results can also be averaged and represented graphically. Figure 6.6.3 shows the variation of the calculated average stress plotted against the number of loading cycles for both the leached side and underside of Sample D16_C.

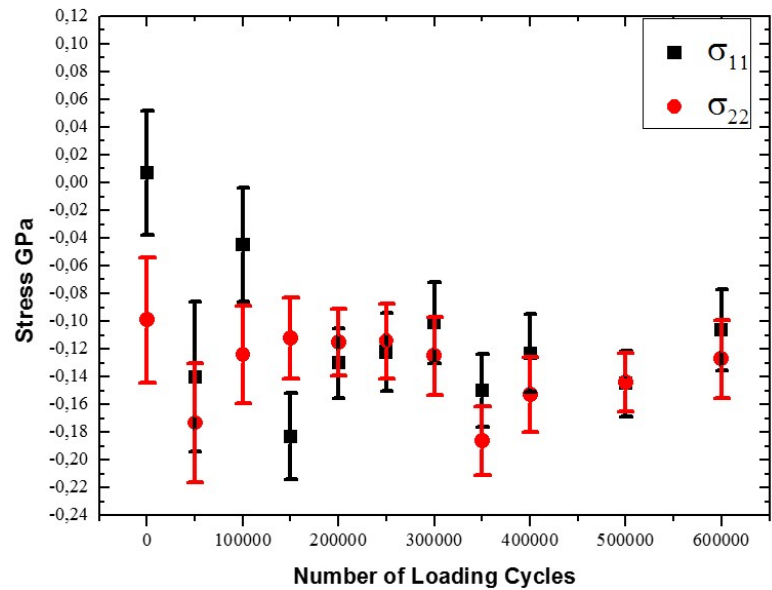


Figure 6.6.2: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_C on the underside.

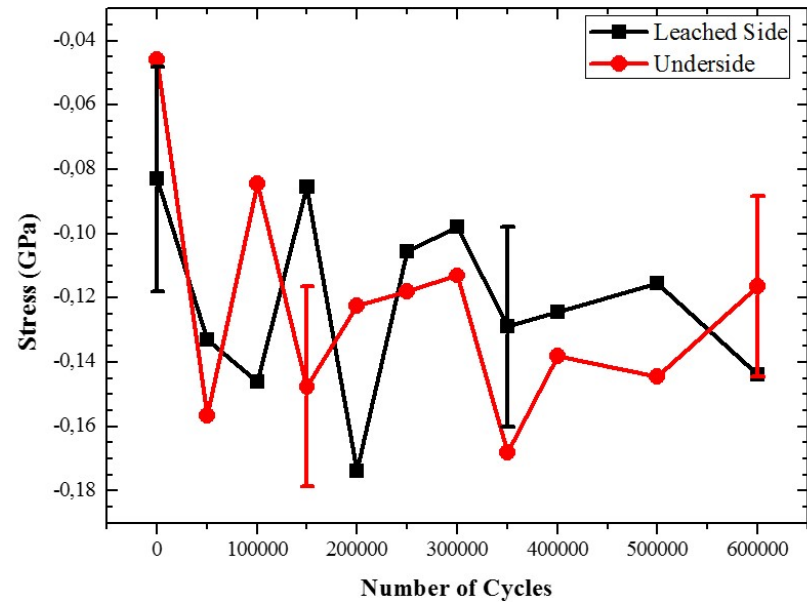


Figure 6.6.3: Stress plot showing the stress variation as a function of number of loading cycles for the average stress for Sample D16_C on both the leached and underside.

6.6.2 Sample D16_D

Sample D16_D was also subjected to alternating sets of fatigue loading and X-ray diffraction and micro Raman stress measurements. Again the number of the loading cycles cumulatively reached 600000 cycles. Table 6.9 shows the stress values of the stress components and the calculated average values on both surfaces of the samples, namely the leached side and the underside.

Table 6.9: Table showing the measured stress values and the error for Sample D16_D on the leached side.

Number of Cycles	Stress (GPa)					
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$	$\sigma_{Average}$	Error (Average)
0	-0.078	0.03	-0.115	0.043	-0.097	0.037
50 000	-0.127	0.04	-0.113	0.04	-0.120	0.040
100 000	-0.103	0.04	0.006	0.05	-0.049	0.045
150 000	-0.102	0.037	-0.142	0.034	-0.122	0.036
200 000	-0.099	0.027	-0.125	0.025	-0.112	0.026
250 000	-0.136	0.026	-0.099	0.03	-0.118	0.028
300 000	-0.127	0.03	-0.115	0.029	-0.121	0.030
350 000	-0.116	0.03	-0.075	0.026	-0.096	0.028
400 000	-0.089	0.029	-0.099	0.028	-0.094	0.029
500 000	-0.073	0.028	-0.041	0.028	-0.057	0.028
600 000	-0.118	0.023	-0.091	0.027	-0.105	0.025

Again the stress values obtained fluctuated within the compressive stress range only. Figure 6.6.4 shows the two stress components for the sample on the leached side.

The two components show a compressive residual stress on the leached side of the sample, with the components quite similar and comparable to each other. Table 6.10 shows the results for the underside of the sample.

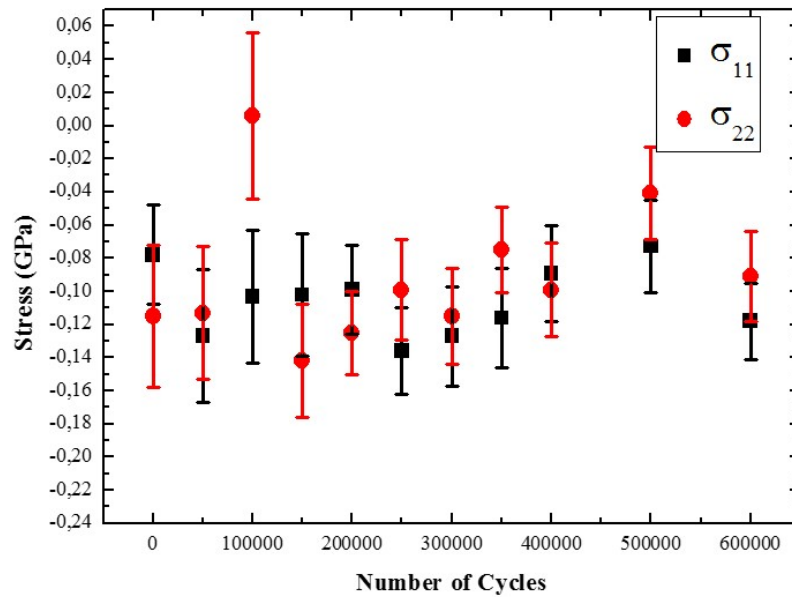


Figure 6.6.4: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_D on the leached side.

Table 6.10: Table showing the measured stress values and the error for Sample D16_D on the underside.

Number of Cycles	Stress (GPa)					
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$	$\sigma_{Average}$	Error (Average)
0	-0.073	0.033	-0.038	0.04	-0.056	0.037
50 000	-0.078	0.04	-0.041	0.032	-0.060	0.036
100 000	-0.136	0.04	-0.186	0.037	-0.161	0.039
150 000	-0.101	0.035	-0.127	0.028	-0.114	0.032
200 000	-0.149	0.025	-0.082	0.028	-0.116	0.027
250 000	-0.148	0.03	-0.156	0.025	-0.152	0.028
300 000	-0.138	0.029	-0.101	0.028	-0.120	0.029
350 000	-0.126	0.026	-0.143	0.027	-0.135	0.027
400 000	-0.105	0.028	-0.147	0.029	-0.126	0.029
500 000	-0.097	0.027	-0.195	0.027	-0.146	0.027
600 000	-0.081	0.025	-0.121	0.028	-0.101	0.027

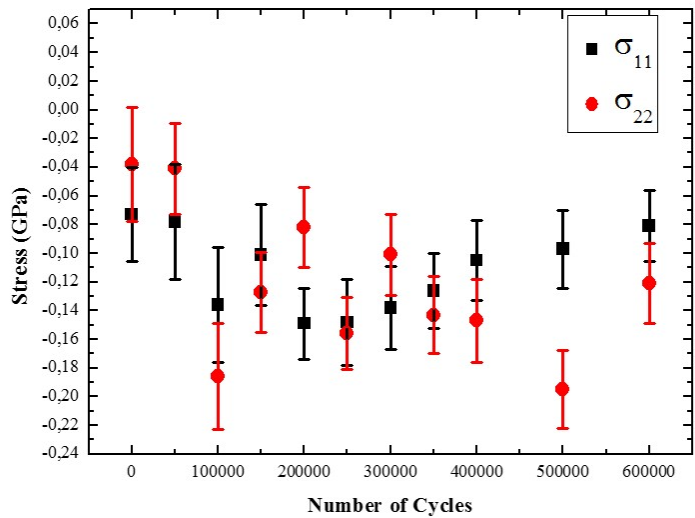


Figure 6.6.5: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_D on the underside.

The calculated average stress values for the stress components σ_{11} and σ_{22} are shown in Tables 6.9 and 6.10 and plotted in the graph in Figure 6.6.6.

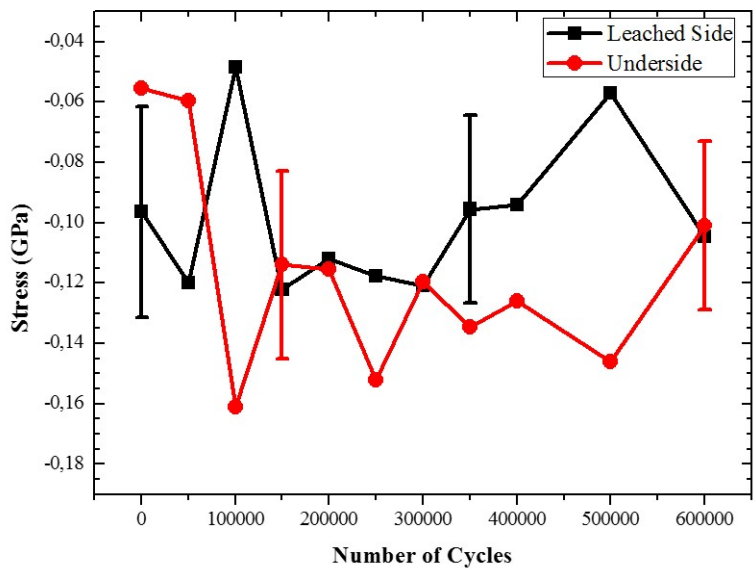


Figure 6.6.6: Stress plot showing the stress variation as a function of number of loading cycles for average stress for Sample D16_D on both the leached and underside.

6.6.3 Sample D16_F

The sample was fatigued up to 600000 cycles as the other two previously discussed samples. The results showing the related stress components and the calculated average stress values for this sample are presented in tabular and graphical format. Table 6.11 shows the stress results as measured on the leached side of the Sample D16_F.

Table 6.11: Table showing the measured stress values on the leached side of the Sample D16_F.

Number of Cycles	Stress (GPa)					
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$	$\sigma_{Average}$	Error (Average)
0	-0.102	0.03	-0.062	0.04	-0.082	0.035
50 000	-0.07	0.032	-0.018	0.03	-0.044	0.031
100 000	-0.021	0.04	-0.017	0.03	-0.019	0.035
150 000	-0.059	0.03	-0.100	0.04	-0.08	0.035
200 000	-0.016	0.031	-0.156	0.03	-0.158	0.031
250 000	-0.128	0.032	-0.134	0.03	-0.131	0.031
300 000	-0.119	0.025	-0.109	0.029	-0.114	0.027
350 000	-0.152	0.029	-0.104	0.028	-0.128	0.029
400 000	-0.086	0.026	-0.116	0.027	-0.101	0.027
500 000	-0.118	0.028	-0.098	0.025	-0.108	0.027
600 000	-0.121	0.03	-0.114	0.028	-0.118	0.029

From Table 6.11, it is can be observed that the results show a fluctuation of the stress values within the compressive stress regime. Figure 6.6.7 is a scatter plot of the results further highlighting the same trend.

Table 6.12 and Figure 6.6.8 show the results and scatter plot for the stress measurements conducted on the underside of the sample. Similar to the leached side the stress values are within the compressive region.

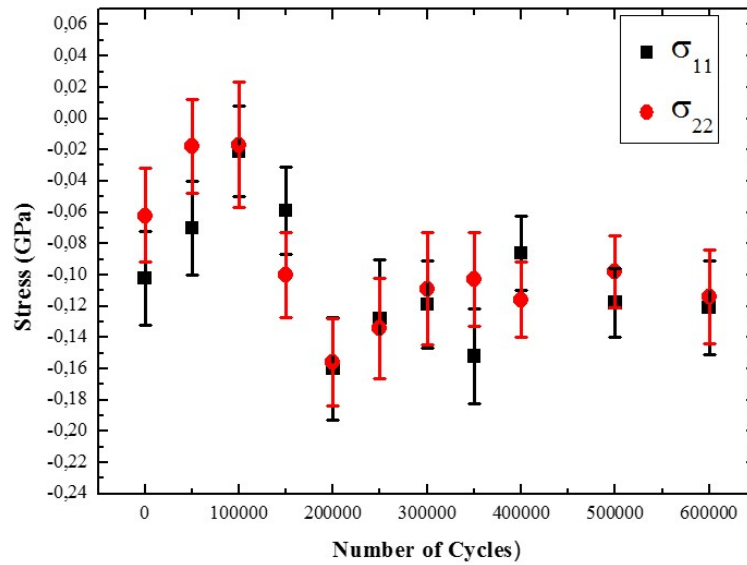


Figure 6.6.7: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_F on the leached side.

Table 6.12: Table showing the measured stress values on the underside of the Sample D16_F.

Number of Cycles	Stress (GPa)					
	σ_{11}	Error $\pm$	σ_{22}	Error $\pm$	$\sigma_{Average}$	Error (Average)
0	-0.124	0.03	-0.101	0.03	-0.113	0.035
50 000	-0.081	0.03	-0.077	0.03	-0.079	0.031
100 000	-0.023	0.03	-0.037	0.04	-0.030	0.035
150 000	-0.023	0.03	-0.123	0.03	-0.133	0.035
200 000	-0.142	0.03	-0.101	0.03	-0.111	0.031
250 000	-0.121	0.04	-0.120	0.03	-0.124	0.031
300 000	-0.128	0.03	-0.097	0.04	-0.094	0.027
350 000	-0.091	0.03	-0.110	0.03	-0.117	0.029
400 000	-0.009	0.02	-0.176	0.02	-0.093	0.027
500 000	-0.087	0.02	-0.101	0.02	-0.094	0.027
600 000	-0.092	0.03	-0.112	0.03	-0.102	0.029

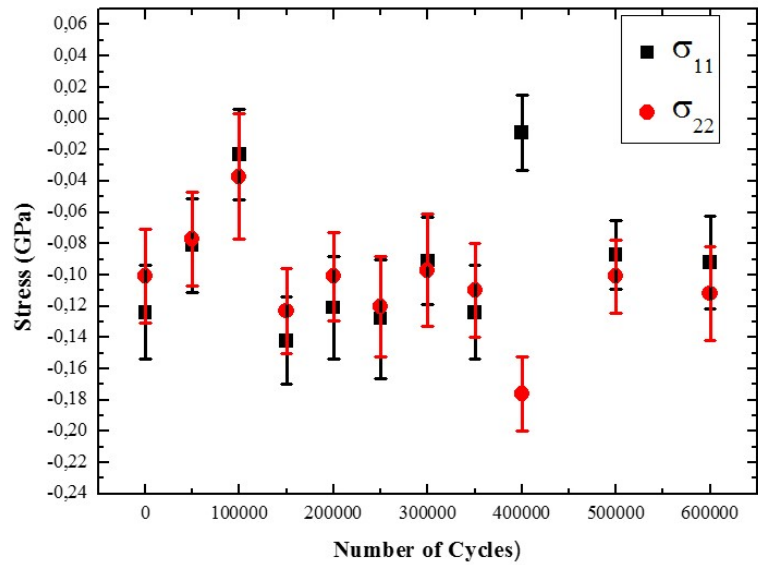


Figure 6.6.8: Scatter plot showing the stress variation as a function of number of loading cycles for the two stress components for Sample D16_F on the underside.

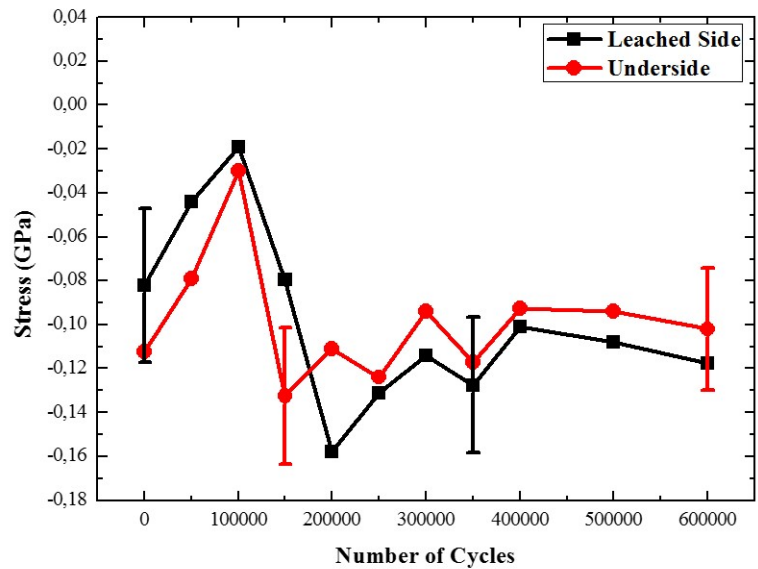


Figure 6.6.9: Stress plot showing the stress variation as a function of number of loading cycles for the average stress for Sample D16_F on both the leached and underside.

Figure 6.6.9 is a plot of the calculated average stress values as a function of

the number of loading cycles for both the leached and underside, depicting a similar trend, with the stresses exhibiting a compressive residual stress state even at the highest number of fatigue loading cycles.

6.7 Summary of the Results

This section discusses the similarities and differences between the two sets of results obtained using the two non-destructive techniques for residual stress measurements on leached samples.

- The measurement of residual stresses using the X-ray diffraction and the micro Raman mapping techniques was successfully conducted. Through the application of a biaxial stress model, the X-ray diffraction method could resolve the measured stress into the stress components σ_{11} and σ_{22} unlike the Raman technique. From Table 6.7 through to Table 6.12 it was observed that on both the leached and underside of the sample, the stress components σ_{11} and σ_{22} are often almost equal or within error range of each other, enabling their averaging without compromising the accuracy of the results. Even though the Raman technique could not resolve the stress into its respective components, the technique showed trends indicative of fatigue type processes on the leached side of the samples which is the cutting face on the tool bits. The results obtained from the underside showed a lot of variation which is probably due to increased roughness introduced by the EDM cutting process that was performed on this surface during the process of detaching the PCD layers from their respective substrates.
- Both techniques used for the stress measurements indicated an average compressive residual stress state for all the samples at the onset of

measurements. However as a function of the number of loading cycles the Raman based results showed a gradual shift towards an average tensile residual stress state in all the samples used from around 250000 cycles onwards. In contrast the X-ray diffraction measured and calculated average residual stresses were observed to be well confined to the compressive region, even at the highest number of loading cycles. Taking into consideration the fact that stresses cannot be measured directly [103] the seemingly conflicting results which appear to be dependent on the technique can be explained by noting that these two techniques derive the stress differently. With X-ray diffraction, the strain in a crystal lattice is measured and the associated residual stress is determined from the elastic constants assuming a linear elastic distortion of the appropriate crystal lattice planes [56]. The Raman method, on the other hand, makes use of the fact that mechanical stresses cause shifts in the Raman vibrational mode(s) in a crystal, and the magnitude of a particular shift is proportionally related to the present strain from which the stress can then be calculated [104]. Fundamentally the two methods are possibly reporting on different type of stresses. With a sampling spot size of $\sim 2 \mu\text{m}$ lateral size, the micro Raman stress mapping technique is measuring stresses which are located within the grains. These stresses are within the type II and type III region of stress classification, (see subsection 4.6.1). By definition type II stresses are micro residual stresses that vary on the scale of an individual grain, whilst type III stresses are micro residual stresses that exist within a grain, essentially as a result of the presence of dislocations and other crystalline defects. This is quite different from the X-ray diffraction system which is equipped with a beam size of $\sim 0.8 \text{ mm}$ at the collimator coupled with the sample being located approximately $\sim 6 \text{ cm}$ from the sample. This results in the method

utilizing X-rays impinging over an area on the sample covering multiple grains and grain boundaries which contribute to the measurement. It is thus safe to assume this technique is measuring Type I stresses which by definition are stresses macro residual stress that develop in the body of a component on a scale larger than the grain size of the material. Individual grain localized stress would be completely different compared to the an average stress over a number of grains. Harker et al, [13], noticed after having employed the X-ray diffraction stress measurement method that while they recorded average residual stresses of approximately -0.3 GPa, the individual grains would exhibit residual localized stresses variations on the order of ~ 0.5 to ~ 0.8 GPa.

- The difference in the results can also be explained by considering the fact that whilst the two systems are both near surface techniques, their respective sampling depths are not the same. In this work the sampling depth for the Raman technique is influenced by the transparency of the sample material, which varied from $1\ \mu\text{m}$ to $20\ \mu\text{m}$. In comparison X-rays are known to penetrate significantly in diamond material [56] and for this work the sampling depth was approximated to be $\sim 240\ \mu\text{m}$. The leaching process that the samples were subjected to is typically confined to the first $100\ \mu\text{m}$ from the cutting surface of the PCD layer. This implies the X-ray diffraction method is sampling into some of the unleached parts of the sample which are still exhibiting compressive stresses even at the highest number of loading cycles. It is suggested in literature that compressive residual stresses after the sintering process are concentrated at the substrate/PCD layer interface becoming less compressive progressively further away from the interface towards the cutting surface [37]. It is thus possible that some of these compressive residual stresses were still locked in within the sample and the X-ray

diffraction method sampled right through this region due to the deep penetration capability.

- From the tabulated results the Raman based residual stress magnitudes were within the range -0.2 GPa to 0.28 GPa at the highest number of loading cycles. The X-ray diffraction based stress results were within the range -0.01 GPa to -0.2 GPa.
- Comparing the Raman stress results for the unleached samples in Chapter 5 and the leached samples, it is evident that the unleached samples exhibited much higher magnitudes of the measured residual stresses suggesting the the observed difference is solely due to the presence of the metallic phase (see figures 5.13.2, 5.14.2 and 5.15.2). This indirectly further points to the notion that it is actually the metallic phase which elastically deforms during the fatigue loading and in turn influences the residual stresses observed within the diamond matrix. It is however the same metallic phase credited with the premature failure of the PCD tool bits due to the different thermal expansion coefficients between the diamond and the metallic binder. It has also been shown in literature that at elevated temperature above 600 °C the metallic binder accelerates graphitisation of the diamond [80]. Thus whilst the leached samples exhibited less compressive stresses initially, their observed extended lifetimes in applications is probably due to lower content of the binder phase in the tool bits. The lower compressive stresses exhibited in the leached samples on the leached side persist for longer hence there is a slower onset of the tensile stress regime resulting in a longer lifetime.
- The width of the Raman peak measured as the full width at half maximum (FWHM) gives an indication of the degree of disorder in a crystal and is useful as a ranking indicator [105]. In general there were no ob-

servable trends in the width data that correlated with the shift from a compressive residual stress state to a tensile regime for the leached samples. Whilst the unleached samples showed slightly different results compared to the leached samples, the difference is sufficient to draw significant findings.

- As mentioned in section 6.2, the samples were loaded with exactly the same orientation into the jig, making sure the support balls were located in more or less the same contact points for every set of fatigue measurements. This was done to check for possible localized areas of damage due to the support balls being in contact with the leached side surface of the samples. No evidence of any regions of stress related damage were observed for all the samples. We believe this speaks to the quality of the PCD samples as they seem to efficiently and evenly distribute the stress within the diamond matrix during the fatigue loading of the samples.

6.8 Comparison with Published Work

Even though not much work has been done in the area of detached PCD Raman stress measurements, credible Raman based stress data for comparison does exist in literature. Catledge et al [86] found compressive stresses ranging from 0.4 GPa to 1.2 GPa after carrying out Raman stress measurements on a section of polished PCD. The stresses measured in our work compare very well with this range. In other work Lin et al [9] obtained stress results averaging 0.6 GPa using strain gauge rosettes on the surface of PCD cutter. The work was centered on establishing the relationship between WC-Co to PCD thickness ratio. Again the values obtained in our work compare very well with their obtained values.

Since the X-ray diffraction based stress measurement method is a standard

test there is a lot of credible data for comparison. In one such work the magnitude of the residual stresses in thick samples of polycrystalline diamond were measured on samples produced by both plasma torch and microwave plasma low pressure growth techniques. Harker et al [13] reported the results showing residual stress levels of ± 0.3 GPa. Ferreira et al, [106], used both the X-ray diffraction and micro-Raman spectroscopy techniques to conduct stress studies on HFCVD diamond films with different levels of boron doping. The type and magnitude of the residual stress they observed from X-ray and micro-Raman measurements agreed well only for undoped films, disagreeing when the doping level increased. The discrepancy is attributed to the domain size characteristic of each technique. The authors explain it as follows “In the X-ray technique the X-ray beam is scattered by the crystalline part of the diamond grain, and the effect of lattice distortion is averaged over a large sample area through the whole depth of the film. In contrast, micro-Raman spectroscopy is a local technique that probes only the spot-size area with a penetration of $5.0\text{ }\mu\text{m}$ from the surface. In the region where the grain size is smaller than the Raman spot size, the relative contribution of the grain boundaries to the stress measurement is higher, which is tensile for films thickness lower $8.0\text{ }\mu\text{m}$ (steady state). This is in excellent agreement with the present work.

In other work, Welzel and his colleagues, [101] studying thin films and regions near the surface of bulk materials reported in one of their copper specimens stresses in the range 0.1 GPa to 0.2 GPa which compares well with stress results measured in our work. Also Balasingh and Singh, [107] using the X-ray diffraction stress measurement method, reported stresses around -0.033 GPa in silicon carbide samples.

McNamra et al. [48], used Raman spectroscopy to determine thermal residual stress in four polycrystalline diamond grades after sintering and manufactur-

ing. They reported observing an introduction of additional tensile stresses on unleached samples after the PCD samples were exposed to high temperatures using the oil quenching technique at 600 °C . Interestingly they also observed that the binderless coarse grain samples used in the study exhibited least sensitivity to thermal treatment, with the residual stresses remaining largely unchanged. According to McNamara et al the removal of the cobalt second phase from the surface of the microstructure had the effect of limiting this increase of tensile stresses on the specimen surface. Prior to heat treatment, they report observing average residual stresses in excess of 1.5 GPa for all the samples along the surface of the specimen.

Chapter 7

Conclusions

This thesis presents a study of fatigue type processes firstly in non-leached PCD and then leached PCD at room temperature conditions. Diamond disc samples of dimensions 19 mm in diameter and 2 mm in thickness, EDM cut from their respective substrates, were subjected to alternating sets of mechanical fatigue loading experiments and residual stress analysis using the Raman spectroscopy for the non-leached PCD samples. Two complimentary non destructive techniques were however employed for the measurements on the leached samples, namely Raman spectroscopy and the X-ray diffraction stress analysis technique. A biaxial stress model was assumed in the work for both techniques.

The first set of fatigue tests and the subsequent Raman measurements on non-leached PCD disc samples revealed a trend in which an initial average compressive residual stress would be observed on the surface of the samples prior to any fatigue measurements and then as the number of loading cycles increased cumulatively, this stress state would gradually shift from being compressive to being tensile in nature. All measurements were done on the cutting surface (the surface in contact with the three support balls). Histograms showing the measured stresses for individual points provided an alternative view

of the data by showing that with increasing numbers of cycles more points exhibited tensile stresses. The data were also illustrated by 2-D surface maps as an alternative mode of presentation confirming the observed trends. Zancy [108], in his work investigating the fracture of PCD under monotonic and no-impact cyclic loading, reported a reduction in the fracture stress due to repeated loading. Similarly in this current work as the number of loading cycles increase the number of tensile point increased which can lead to the reduction in fracture stress as observed by Zancy. This novel application of Raman spectroscopy was published in [93].

Literature reports given earlier that leached PCD shows improved wear resistance in application compared to unleached PCD, it was thus relevant to extend the scope of the current investigation to incorporate these types of samples. To investigate this second part of the work, X-ray diffraction and the Raman stress analysis method were used. The samples were slightly different in terms of dimensions but nevertheless comparable to the non-leached PCD samples. Again the samples had been EDM cut from their substrates and unlike with the non-leached samples, with the leached samples care was taken to load the samples with the same orientation every time for the fatigue, Raman as well X-ray diffraction stress measurements. The Raman stress results exhibited similar trends to those shown by the non-leached samples where an initial average compressive residual stress would be observed on the leached side (the side in contact with the three support balls), and after being subjected to a cumulative number of fatigue loading cycles, would deteriorate as the number of loading cycles increased. On the contrary the X-ray diffraction based stress results measured on the same surface, showed that the residual stresses remained compressive even at the highest number of loading cycles. Several factors had to be looked at to explain the apparent disagreement in the results.

- **Sampling depth:** Whilst the two techniques could be considered to be near surface techniques, there exists fundamental differences between the two methods, that contributed towards the difference in the results. In this work the sampling depth of the Raman technique was influenced by the transparency of the sample material which varied between $1\mu m$ to $20\mu m$. The X-ray diffraction technique on the other hand, had a penetration depth of approximately $240\mu m$ as determined by the equipment used. Thus whilst the Raman method was sampling the surface region the X-ray diffraction technique clearly was probing much deeper into the material hence different stresses observed.
- **Spot Size:** The sampling spot size for the Raman method was $\sim 2\mu m$, whilst the X-ray beam size was 0.8 mm at the collimator and the fact that the sample was located $\sim 6\text{ cm}$ from the collimator indicates clearly that instead of a small spot the X-ray beam impinged on an area. This raised the question of the type of residual stresses that were measured by the two techniques. By definition Type II stresses are micro residual stresses that vary on the scale of an individual grain and Type III stresses are micro residual stresses that exist within a grain, essentially as a result of the presence of dislocations and other crystalline defects. It is thus plausible that the Raman method was reporting on these two types of stresses. On the other hand Type I stresses are macro residual stress that develop in the body of a component on a scale larger than the grain size of the material. It is our firm belief that because of its larger beam size these are the stresses that X-ray diffraction method was probing.

It was thus possible to account for the observed results very satisfactorily by considering the probing beam size and sampling depth for the two techniques. As the XRD method finds wide application as a standard tool for stress as-

assessment in manufacturing and maintenance, this has important implications for the correct understanding of this technique in industry. The present work suggests that Raman spectroscopy has an important role to play as a complementary stress evaluation technique, here illustrated specifically in the context of the determination of residual stress state in PCD discs.

The obtained results make it apparent that the number of mapping points exhibiting tensile stress is an important parameter which may be more useful as an indicator of imminent tool failure than average stress state. With further studies it might be possible to develop a model which examines the relationship of these mapping points or the crack density and the critical stress intensity factor. This relationship may be a better indicator of the possibility of failure in the studied material.

While the actual fatigue crack growth in PCD was not observed, the Raman results conclusively showed that contrary to the school of thought that diamond can only be fatigued at elevated temperature, it is possible to influence PCD via fatigue type processes at standard room and temperature conditions. However, the picture as far as the improved lifetimes of PCD materials is concerned is not complete without the consideration of the high temperature environment in which the tool-bits function. Further studies which include high temperature measurements would contribute immensely to the knowledge gap that still exists.

7.1 Future work

- It is known in industry that thermal fatigue plays an important role in the lifetime of the PCD materials. In order to closely mimic the conditions under which the PCD tool-bits operate, in-situ fatigue measurements need to be performed at high temperature to investigate the

effect of elevated temperature on the residual stress state. At the same time, possible phase changes in the constituent phases of PCD can be monitored.

- The obtained results make it apparent that the number of mapping points exhibiting tensile stress is an important parameter which may be more useful as an indicator of imminent tool failure than average stress state. With further studies it might be possible to develop a model which examines the relationship of these mapping points or the crack density and the critical stress intensity factor. This relationship may be a better indicator of the possibility of failure in the studied material.
- According to the Hall-Petch effect theory there is a relationship between the grain size distribution and the strength of the material of the specimen. There is thus the need to investigate how the grain size distribution in the PCD samples influences their respective fatigue behaviour at standard room temperature conditions and at elevated temperatures.
- The residual stresses in the bulk of the PCD samples contribute to the surface measured residual stresses. Using the neutron diffraction technique the stress gradient showing how the stresses vary as a function of depth can be established.
- Minor phases do exist within the PCD material and their contribution towards the observed fatigue behaviour will need to be evaluated.

Bibliography

- [1] Tolansky S., The Microstructure of diamond surfaces, NAG Press Ltd, 1955.
- [2] Berman R., Physical properties of diamond, Clarendon Press, 1965.
- [3] Rangarajan G., Materials Science, Tata McGraw-Hill Education, reprint edn., 2004.
- [4] Spear K.E., Dismukes J.P., Synthetic diamond: emerging CVD science and technology, Vol. 25, John Wiley & Sons, 1994.
- [5] Hannay J., Proceedings of the Royal Society of London, (1854-1905), **30**, No. 200 - 205, 450–461.
- [6] Hall H.T., Review of Scientific Instruments, 1960, **31**, No. 2, 131.
- [7] Petrovic M., Ivankovic A., Murphy N., Journal of the European Ceramic Society, 2012, **32**, No. 12, 3021–3027.
- [8] Lin T.P., Cooper G.A., Hood M., Materials Science and Engineering, 1993, **163**, No. 1, 23–31.
- [9] Lin T.P., Hood M., Cooper G.A., Smith R.H., Journal of the American Ceramic Society, 1994, **77**, No. 6, 1562–1568.
- [10] Bell J., Stuivinga M., Thornton A., Wilks J., Journal of Physics D: Applied Physics, 1977, **10**, No. 10, 1379–1387.

- [11] Paggett J., Drake E., Krawitz A., Winholtz R., Griffin N., International Journal of Refractory Metals and Hard Materials, 2002, **20**, No. 3, 187–194.
- [12] Dunn K., Lee M., Journal of Materials Science, 1979, **14**, No. 4, 882–890.
- [13] Harker A.B., Howitt D.G., Chen S., Flintoff J.F., James M.R., In: Proc. SPIE 2286, Window and Dome Technologies and Materials IV.
- [14] Rats D., Bimbault L., Vandenbulcke L., Herbin R., Badawi K.F., Journal of Applied Physics, 1995, **78**, No. 8, 4994–5001.
- [15] Jia H., Jia X., Xu Y., Wan L., Jie K., Ma H., Science China Physics, Mechanics and Astronomy, 2011, **54**, No. 1, 98–101.
- [16] Brown L., Cumulative deformation of synthetic type 1b and IIb diamond, Ph.D. thesis, University of Hull, UK, 2003.
- [17] Ferrari A., Robertson J., Physical Review B, 2001, **64**, No. 7, (075414) 1–13.
- [18] Field J.E., The Properties of natural and synthetic diamond, Academic Press, 1992.
- [19] Li H., Bradt R.C., Diamond and Related Materials, 1992, **1**, No. 12, 1161–1167.
- [20] Brookes C., O'Neill J., Redfern B., Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 1971, **322**, No. 1548, 73–88.
- [21] Klein C.A., Cardinale G.F., Diamond and Related Materials, 1993, **2**, No. 5, 918–923.
- [22] DeVries R., Materials Research Bulletin, 1975, **10**, No. 11, 1193–1199.

- [23] Callister W., Materials Science and Engineering: An Introduction, Wiley, 1999.
- [24] Gordon Davies I., Properties and Growth of Diamond, Emis Data Review, Vol. 9, INSPEC, the Institution of Electrical Engineers, 1994.
- [25] Bundy F., Physica A: Statistical Mechanics and its Applications, 1989, **156**, No. 1, 169–178.
- [26] Bruton E., Diamonds, Chilton Book Company, 1981.
- [27] Davies G., Diamond, Adam Higler Ltd, 1984.
- [28] Berman R., Simon S.F., Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie, 1955, **59**, No. 5, 333–338.
- [29] Ager J.W., Veirs D.K., Rosenblatt G.M., Physical Review B, 1991, **43**, No. 8, 6491–6499.
- [30] Burns R., Chumakov A., Connell S., Dube D., Godfried H., Hansen J., Härtwig J., Hoszowska J., Masiello F., Mkhonza L., et al., Journal of Physics: Condensed Matter, 2009, **21**, No. 36, 364224.
- [31] Bergman L., Nemanich R., Journal of Applied Physics, 1995, **78**, No. 11, 6709–6719.
- [32] Field J.E., The properties of natural and synthetic diamond, Academic Press, 1979.
- [33] Damm O., Friction and wear of the selected metal- ceramic and polycrystalline diamond slidding couples, Ph.D. thesis, Faculty of Engineering , University of the Witwatersrand, 1995.
- [34] Sneddon M., Hall D., Journal of Petroleum Technology, 1988, **40**, No. 12, 1593–1601.

- [35] Krawitz A., Winholtz R.A., Drake E., Griffin N., International Journal of Refractory Metals and Hard Materials, 1999, **17**, No. 1, 117–122.
- [36] Roy D.A., 2nd International Industrial Diamond Conference Proceedings, 2007.
- [37] Martin Z.F., Raman studies into the behaviour of different types of deformation in polycrystalline diamond, Masters dissertation, University of Oxford, UK, 1999.
- [38] Ritchie R.O., International Journal of Fracture, 1998, **100**, No. 1, 55–83.
- [39] Colomban P., Journal of Advanced Engineering Materials, 2002, **4**, No. 8, 535–542.
- [40] Schaefer F., Lang E.P., Bick M., Knorr A.F., Marx M., Motz C., Procedia Structural Integrity, 2017, **5**, No. Supplement C, 547–554, 2nd International Conference on Structural Integrity, ICSI 2017, 4-7 September 2017, Funchal, Madeira, Portugal.
- [41] Pan J., Fatigue testing and analysis: theory and practice, Elsevier Butterworth -Heinemann, 2005.
- [42] Kundu T., Fundamentals of fracture mechanics, CRC Press Taylor & Francis Group, 2008.
- [43] Hearn E.J., Mechanics of materials 1: an introduction to the mechanics of elastic and plastic deformation of solids and structural components, Butterworth-Heinemann, Oxford, 1997.
- [44] Rolfe S.T., Barsom J.M., Fracture and fatigue control in structures: applications of fracture mechanics, ASTM International, 1987.
- [45] Lawn B., Fracture of brittle solids, Cambridge University Press, 1993.

- [46] Morrell R., Danzer R., Supancic a.W.H., Puchegger S., Peterlik H., International Journal of Refractory Metals and Hard Materials, 2010, **28**, No. 4, 508–515.
- [47] Miess D., Rai G., Journal of Materials Science and Engineering, 1996, **209**, No. 1-2, 270–276.
- [48] McNamara D., Carolan D., Alveen P., Murphy N., Ivanković A., Ceramics International, 2014, **40**, No. 8, 11543–11549.
- [49] Webster G., Ezeilo A., International Journal of Fatigue, 2001, **23**, S375–S383.
- [50] Morante J., Samitier J., Benrakkad M., Microelectronics Journal, 1997, **28**, No. 4, 433–448.
- [51] Xu C., Huang C., Ai X., The International Journal of Advanced Manufacturing Technology, 2006, **32**, No. 11, 1083–1089.
- [52] Catledge S.A., Vohra Y.K., Ladi R., Rai G., Daimond and Related Materials, 1996, **5**, No. 10, 1159–1165.
- [53] Cornelius J., The Influence of Machining Parameters on the wear behaviour of Polycrystalline Diamond when it is Used to Mill Soft Matrix Hard Particle Components, Masters dissertation, University of the Witwatersrand School of Engineering, 2002.
- [54] Horst C., Characterization and Failure Analysis of Plastics, ASM International, 1992.
- [55] Aplitsiotis N., Measurement Of Residual Stresses and Distortion in Rapidly Quenched Components, Masters dissertation, Texas Tech University, 2000.

- [56] Fitzpatrick M., Fry A., Holdway P., Kandil F., Shackleton J., Suominen L., Determination of residual stresses by X-ray diffraction, Vol. 52, National Physical Laboratory, 2 edn., 2005.
- [57] Withers P., Bhadeshia H., Materials Science and Technology, 2001, **17**, No. 4, 355–365.
- [58] Noyan I., Cohen J., Residual Stress: Measurement by Diffraction and Interpretation, Materials Research and Engineering, Springer New York, 2013.
- [59] Withers P., Bhadeshia H., Materials Science and Technology, 2001, **17**, No. 4, 355–365.
- [60] Lu J., Handbook of Measurement of Residual Stresses, Fairmont Press, 1996.
- [61] Withers P., Reports on Progress in Physics, 2007, **70**, No. 12, 2211–2264.
- [62] Šarga P., Menda F., American Journal of Mechanical Engineering, 2013, **1**, No. 7, 335–338.
- [63] Rossini N., Dassisti M., Benyounis K., Olabi A.G., Materials & Design, 2012, **35**, 572–588.
- [64] Schajer. G., Experimental Mechanics, 2010, **50**, No. 2, 245–253.
- [65] Huang X., Liu Z., Xie H., Acta Mechanica Solida Sinica, 2013, **26**, No. 6, 570–583.
- [66] Ruud C., NDT International, 1982, **15**, No. 1, 15–23.
- [67] Koistinen D., Marburger R., Transactions of the American Society of Metals, 1959, **51**, 537–555.

- [68] Pineault J., Materials Park, OH: American Society for Metals International, 2002, 484–497.
- [69] Anderoglu O., Residual stress measurement using X-ray diffraction, Masters dissertation, Texas A&M University, 2004.
- [70] Raj B., Jayakumar T., Mahadevan S., Rai S.K., Journal for Nondestructive Evaluation, 2009, **28**, No. 3, 157–162.
- [71] Cullity B.D., Weymouth J.W., Elements of X-Ray Diffraction, Addison-Wesley Publishing Company Inc, 1978.
- [72] Ma C.H., Huang J.H., Chen H., Thin Solid Films, 2002, **418**, No. 2, 73–78.
- [73] Yeager M., Ruud C., Chen P., Journal of Nondestructive Evaluation, 1991, **10**, No. 3, 79–87.
- [74] Lewis I.R., Edwards H., Handbook of Raman spectroscopy: from the research laboratory to the process line, CRC Press, 2001.
- [75] Colthup N., Introduction to Infrared and Raman Spectroscopy, Academic Press, 2012.
- [76] Smith E., Dent G., Modern Raman spectroscopy: a practical approach, Jogn Wiley & Sons, Ltd, 2005.
- [77] Long D., The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules, John Wiley & Sons, Ltd, 2002.
- [78] Chalmers J., Griffiths P., Handbook of vibrational spectroscopy, Handbook of Vibrational Spectroscopy, Vol. 1, J. Wiley, 2002.
- [79] Szymanski H.A., Raman spectroscopy: Theory and practice, Springer Science & Business Media, 1967.

- [80] Erasmus R., Comins J., Mofokeng V., Martin Z., Daimond and Related Materials, 2011, **20**, No. 7, 907–911.
- [81] Nemanich R., Solin S., Martin R.M., Physics Review B, 1981, **23**, No. 12, 6348–6355.
- [82] Campbell I., Fauchet P.M., Solid State Communications, 1986, **58**, No. 10, 739–741.
- [83] Mohrbacher H., Van Acker K., Blanpain B., Van Houtte P., Celis J.P., Journal of Materials Research, 1996, **11**, No. 07, 1776–1782.
- [84] Mitra S., Brafman O., Daniels W., Crawford R., Physical Review, 1969, **186**, No. 3, 942–944.
- [85] Grimsditch M., Anastassakis E., Cardona M., Physical Review B, 1978, **18**, No. 2, 901–904.
- [86] Catledge S.A., Vohra Y.K., Journal of Applied Physics, 1995, **78**, No. 12, 7053–7058.
- [87] Boppart H., Van Straaten J., Silvera I.F., Physical Review B, 1985, **32**, No. 2, 1423–1425.
- [88] Whalley E., Lavergne A., Wong P., Review of Scientific Instruments, 1976, **47**, No. 7, 845–848.
- [89] Griffin N.D., Hughes P.R., Polycrystalline diamond partially foreign patent documents depleted of catalyzing material, 2004.
- [90] Börger A., Supancic P., Danzer R., Journal of the European Ceramic Society, 2004, **24**, No. 10, 2917–2928.
- [91] Beesley. M., Lasers and Their Applications, Taylor & Francis, 1978.

- [92] Shiri P.R., Raman Scattering in Carbon Nanotubes, Masters dissertation, University of the Witwatersrand School of Physics, 2007.
- [93] Vhareta M., Erasmus R., Comins J., Diamond and Related Materials, 2014, **45**, 34–42.
- [94] Lammer A., Materials Science and Technology, 1988, **4**, No. 11, 949–955.
- [95] Katzman H., Libby W.F., Science, 1971, **172**, No. 3988, 1132–1134.
- [96] Belnap D., ASM International, Member/Customer Service Center Materials Park OH 44073-0002 United States, 2010, 2424–2434.
- [97] Feng C., Gen X., Xu G.P., Transactions of Nonferrous Metals Society of China, 2010, **20**, No. 2, 227–232.
- [98] Walmsley J., Materials Science and Engineering: A, 1988, **105**, 549–553.
- [99] Yahiaoui M., Paris J.Y., Delbé K., Denape J., Gerbaud L., Colin C., Ther O., Dourfaye A., International Journal of Refractory Metals and Hard Materials, 2016, **56**, 87–95.
- [100] Beaton T., Oilfield Technology, 2014, 20–24.
- [101] Welzel U., Ligot J., Lamparter P., Vermeulen A., Mittemeijer E., Journal of Applied Crystallography, 2005, **38**, No. 1, 1–29.
- [102] Waseda Y., Matsubara E., Shinoda K., X-ray Diffraction Crystallography, Springer Science & Business Media, 2011.
- [103] Mani A., Aubert P., Mercier F., Khodja H., Berthier C., Houdy P., Surface and Coatings Technology, 2005, **194**, No. 2, 190–195.
- [104] Dietrich B., Bukalo V., Fischer A., Dombrowski K.F., Bugiel E., Kuck B., Richter H.H., Applied Physics Letters, 2003, **82**, No. 8, 1176–1178.

- [105] Ager J.W., Drory M.D., Phys. Rev. B, 1993, **48**, 2601–2607.
- [106] Ferreira N., Abramof E., Corat E., Trava-Airoldi V., Carbon, 2003, **41**, No. 6, 1301–1308.
- [107] Balasingh C., Singh A., Metals Materids And Processes, 2000, **12**, No. 2, 269–280.
- [108] Zacny K., Society of Petroleum Engineers, 2012, **27**, 145–157.

Appendix A

Conferences and Publications

1. M. Vhareta, R.M. Erasmus and J.D. Comins. Investigation of fatigue type processes in polycrystalline diamond tools using Raman spectroscopy. Diamond and Related materials Vol. 45, pp. 34-42, November 2014 .
2. M. Vhareta, R.M. Erasmus and J.D. Comins. Micro-Raman and X-ray Diffraction stress analysis of residual stresses in fatigue loaded leached Polycrystalline Diamond discs. The 9th International Conference of the African Materials Research Society (AMRS2017). Gaborone, Botswana. (Oral Presentation)
3. M. Vhareta, R.M. Erasmus and J.D. Comins. Residual stress measurements in leached polycrystalline diamond using X-ray diffraction and Raman spectroscopy techniques. The 9th International Conference on Mechanical Stress Evaluation by Neutron and Synchrotron Radiation 2017, Skukuza, South Africa. (Oral Presentation).
4. M. Vhareta, R.M. Erasmus and J.D. Comins. Residual stress measurements in leached polycrystalline diamond using X-ray diffraction and Raman spectroscopy techniques. The 9th African Laser Centre Student

Workshop 2016, Stellenbosch, South Africa. (Oral Presentation).

5. M. Vhareta, R.M. Erasmus and J.D. Comins. Investigation of fatigue type processes in polycrystalline diamond tools using Raman spectroscopy. South African Institute of Physics, 56th Annual Conference, Port Elizabeth, South Africa 2015. (Oral Presentation).
6. M. Vhareta, R.M. Erasmus and J.D. Comins. Investigation of fatigue type processes in polycrystalline diamond tools using Raman spectroscopy. The 10th International Conference on the Science of Hard Materials (ICSHM10) 2014, Cancun, Mexico. (Oral Presentation).
7. M. Vhareta, R.M. Erasmus and J.D. Comins. Investigation of fatigue type processes in polycrystalline diamond tools using Raman spectroscopy. The African Laser Center Workshop 2014. Stellenbosch, South Africa. (Oral Presentation).
8. M. Vhareta, R.M. Erasmus and J.D. Comins. Use of Raman Spectroscopy to study fatigue type processes in polycrystalline diamond (PCD). World Conference on Non-Destructive testing (WCNDT). April 2012. Durban, South Africa. (Oral Presentation).
9. M. Vhareta, R.M. Erasmus and J.D. Comins. Use of Raman Spectroscopy to study fatigue type processes in polycrystalline diamond (PCD). The 6th International Conference of the African Materials Research Society. December 2011. Victoria Falls, Zimbabwe. (Oral Presentation).
10. M. Vhareta, R.M. Erasmus and J.D. Comins. Use of Raman Spectroscopy to study fatigue type processes in polycrystalline diamond (PCD). African Laser Center Workshop. October 2011. Stellenbosch, South Africa. (Oral Presentation).

11. M. Vhareta, R.M. Erasmus and J.D. Comins. Use of Raman Spectroscopy to study fatigue type processes in polycrystalline diamond (PCD) South African Institute of Physics (SAIP), 56th Annual Conference. July 2011. Pretoria, South Africa. (Poster Presentation).
12. M. Vhareta, R.M. Erasmus and J.D. Comins. Use of Raman Spectroscopy to study fatigue type processes in polycrystalline diamond (PCD). African Laser Centre Workshop. September 2010. Stellenbosch, South Africa. (Poster Presentation).

Papers in Preparation

1. M. Vhareta, R.M. Erasmus and J.D. Comins. Micro-Raman and X-ray Diffraction stress analysis of residual stresses in fatigue loaded leached Polycrystalline Diamond discs.
2. M. Vhareta, R.M . Erasmus and J.D. Comins. Raman studies of Residual Stresses in leached Polycrystalline Diamond .



Investigation of fatigue-type processes in polycrystalline diamond tools using Raman spectroscopy

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ABSTRACT

Polycrystalline diamond (PCD) cylindrical tool-bits used in oil well drilling are susceptible to fracture due to the hostile environment of randomly occurring impact loads to which they are subjected. The fact that the tool-bits fail after repeated use suggests the possibility of fatigue type processes in PCD. The study of stress fields on the surface of the PCD thus becomes crucial in the quest to have extended lives for these tool-bits. Since the diamond Raman peak reveals both the nature and magnitude of the stress present in the material, this technique can be employed as a non-destructive measurement tool to investigate these stress fields. Raman stress measurements at room temperature were carried out using a 36 point mapping array in area close to the size of the PCD samples. The mapping points provided histograms of the magnitude and nature of these small individually stressed regions showing a general compressive stress for the lower numbers of fatigue cycles which deteriorates to a high proportion of tensile regions. The data are also illustrated by 2-D surface maps as an alternative mode of presentation again confirming the change from surface stresses being dominantly compressive to dominantly tensile with exposure to the higher numbers of fatigue cycles. Whereas a general compressive stress is desirable in the PCD layer as it inhibits the propagation of cracks, on the contrary tensile stresses facilitate the formation of cracks ultimately leading to catastrophic failure of the tool-bits.

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1. Introduction

Diamond is a remarkable material with unique properties resulting in numerous applications [1]. One of its industrial applications is in oil well drilling and the tool-bits employed generally have a polycrystalline diamond (PCD) layer sintered onto a tungsten carbide substrate. These PCD tool-bits are subjected to very harsh working environments where they are exposed to cyclic fluctuating impact loads. Such hostile environments induce cyclic stresses that often result in the formation and propagation of cracks which can inevitably lead to the premature failure of the tool-bits.

Fatigue behaviour of materials has been studied and investigated for a range of materials over a number of decades. Relaxation of residual stress under cyclic load in metals has been studied by e.g. Zhuang and Halford [2]. The paper by Pook [3] gives a multi-decade overview of three-dimensional effects at cracks and sharp notches, while Suryanarayana [4] reviews the mechanical properties of nanocrystalline

and glassy materials, including how fatigue processes feature in these materials.

Fatigue behaviour in polycrystalline diamond has been previously reported [5]. Bell et al. [6] remarked that repeated indentations of a single crystal diamond surface by a spherical diamond indenter may result in the progressive build up of damage. Results obtained by Lin et al. [7] having conducted laboratory rock-cutting tests with single PCD cutting tools showed the progressive degradation of the tool-bits after cutting tens of linear metres of rock. In other research work Dunn and Lee [8] in investigating the fracture and fatigue of sintered diamond compacts concluded that the fracture stress of a diamond compact is reduced under cyclic loading. Paggett et al. [9] conducted studies on residual stress and stress gradients in polycrystalline diamond compacts and observed that the sintering process parameters can influence surface residual stress. Catledge et al. [10] did interesting work on micro-Raman stress investigations and concluded that residual stresses in polycrystalline diamond cutting tools can be accurately measured using this technique. These investigations indicate the importance of the stress state of the surface of PCD tool-bits in determining their lifetime.

In general, fatigue failure is considered to be the tendency of a material or structure to fracture by means of progressive brittle cracking under repeated stress of any intensity considerably below the normal strength of the material or structure [9]. It has been established that a

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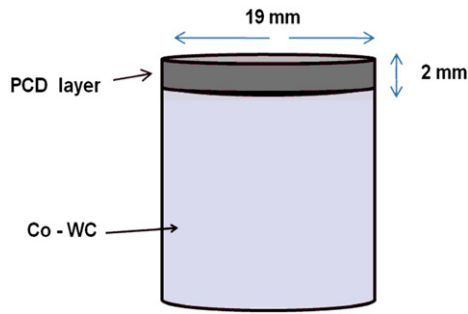


Fig. 1. A diagram of a typical cylindrical tool-bit showing the dimensions of the PCD layer.

compressive stress state on the surface of the PCD tool-bits inhibits crack initiation and propagation and this can possibly extend their life [11]. Conversely tensile residual stresses on the surface of the PCD tool-bits encourage the crack formation. Thus an understanding of the mechanism of fatigue crack growth and propagation in PCD materials is critically important for their improved lifetime.

2. The influence of stress on the Raman peak

Diamond has a triply-degenerate Raman peak at 1332.5 Rcm^{-1} [1]. The position of the Raman peak conveys information on the nature and structure of the material under study. Since the Raman effect is a result of the interaction between photons and Raman-active vibrational mode(s) in a crystal, any stresses present cause changes in an observed Raman band. If an applied stress results in the compression of the unit cell then the force constant of the vibration and consequently the frequency is altered. The same argument also holds when the exerted stress results in the unit cell dilating. Grimsditch et al. [13] showed that when a compressive stress is applied to diamond, the position of the Raman peak shifts linearly with stress to higher frequency. Conversely, a shift of the Raman peak position to lower frequency is associated with the presence of tensile stress in the diamond. Studies of this type have been carried out on PCD samples by Erasmus et al. [12].

The dependence of the Raman shift $\Delta\nu$ on the applied stress σ is given by the equation

$$\Delta\nu = \nu - \nu_0 = -\alpha\sigma, \quad (1)$$

where α is the piezo-Raman coefficient, ν_0 is the Raman peak frequency of the unstressed natural diamond and ν is the observed Raman peak frequency [13]. The reference for the Raman peak position of an unstressed diamond was a high quality type IIa natural diamond.

For the piezo-Raman coefficient α , the value reported by Bergman and Nemanich [14] was used, namely $1.9 \text{ cm}^{-1}/\text{GPa}$.

3. Experimental details

3.1. Specimen preparation

The source of the PCD samples used in the present fatigue experiments was the same production batch of tool-bits each consisting of a PCD layer of diameter 19 mm and thickness 2 mm sintered onto a Co-WC substrate. A diagram of a typical tool-bit is shown in Fig. 1. The PCD layers were detached from their respective substrates using Electron Discharge Machining (EDM) and slightly polished.

3.2. Transverse rupture strength measurements

Prior to conducting the fatigue studies, it was necessary to determine the average maximum strength of the sample PCD material. For this purpose Transverse Rupture Strength (TRS) measurements were made using the ball on three balls arrangement shown in Fig. 2 installed in a 5500R Instron test machine. Each of three typical PCD disc samples was respectively placed and supported as shown in Fig. 2, then loaded centrally until fracture occurred. The respective rupture strengths were recorded, leading to an average maximum strength of $3470 \pm 150 \text{ N}$. The balls in the setup were made of stainless steel.

3.3. Fatigue studies

The fatigue studies were conducted under constant amplitude cyclic loading with load control at a frequency of 10 Hz. Each PCD disc specimen was held by the ball on three ball arrangement shown in Fig. 2, mounted within an Instron SYN 179 servo-hydraulic test machine and subjected to a predetermined number of fatigue cycles under standard room temperature and pressure conditions.

The choice of loading conditions for the fatigue experiments was selected by subjecting several test samples to different loads slightly lower than their measured average maximum strength. The aim was to identify the conditions under which a substantial number of loading cycles would not result in fracture of the PCD samples and thus ensure that the planned Raman studies could be performed. In practice the fatigue experiments were conducted with a load of 3100 N which is 89% of the measured average maximum strength of the sample material. Börger et al. [15,16] have performed finite element modelling for the three balls on ball arrangement and the expected stress field according to their calculations is given in Fig. 3. The percentage of the maximum tensile stress component in the disc (0–100%) is plotted, illustrating

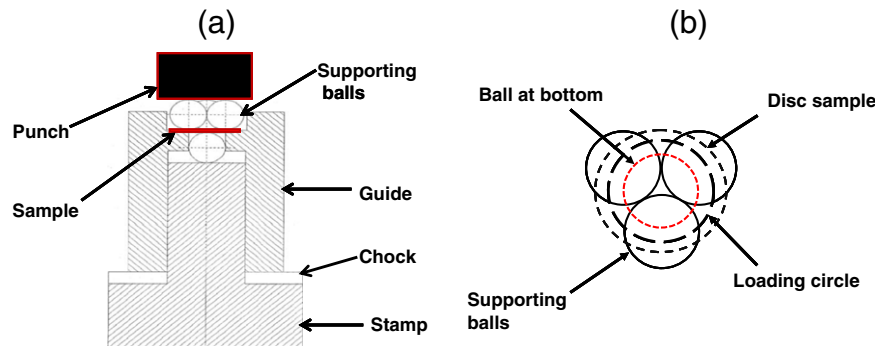


Fig. 2. (a) Shows the ball on three ball arrangement and the configuration of the sample and the balls. For the actual cyclic loading, the chock is removed, allowing the guide to slide downwards. This results in the sample being held only by the spherical balls and ensures a small vertical cavity such that the sample can flex vertically. The flexing distance in the experiments was 0.1 mm. (b) Shows a plan view of the positioning of the four balls and the diameter of the loading circle relative to the sample [15].

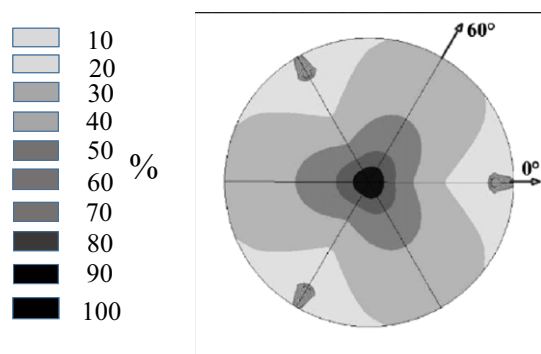


Fig. 3. The expected stress field for the ball on three ball test [15], where the percentage of the maximum tensile stress component is plotted. The view is of the tensile stress surface of the disc showing the positive (tensile) first principal stresses.

that the maximum tensile stress can be expected at the centre of the disc. The maximum stress calculated using this model, the dimensions of our test rig and the material properties of PCD is found to be 7.68 GPa.

3.4. Raman stress measurements

All Raman stress measurements were made using a Jobin-Yvon T64000 Raman instrument operated in the single spectrograph mode. The 514.5 nm line of an Ar⁺ ion laser was used as the excitation source with power of 2.4 mW at the sample. Previous work [12] has indicated that there would be no noticeable heating of the sample under these power conditions. A grating of 1800 grooves/mm was used to disperse the backscattered light onto a CCD detector. The spectral resolution was $\sim 0.9 \text{ cm}^{-1}$. The Raman spectrograph fitted with a modified Olympus BX40 microscope and using a 2 mm confocal pinhole was operated in the 2-D micro-Raman mapping mode with a computer controlled motorised X–Y stage.

The 2-D mapping was done over a square array of 6×6 points by sequential translation of the X–Y stage under the $20\times$ objective lens of the microscope. The array point size is determined by the focal properties of the objective lens and is $\sim 2 \mu\text{m}$, this being similar to the grain size of the PCD. For these maps the upper surface of the samples that was in contact with the three supporting balls, was used. The average values (peak position and stress) reported subsequently is the average of the 36 points in the array. The reported error is one standard error (calculated as $(\text{one standard deviation} / \sqrt{N})$, where N is the number of measurements).

Arrays of three varying sizes were tested in order to determine whether there was good agreement in the average surface stress for representative unstressed and stressed samples. These arrays ranged from a small map around the centre of the sample to a medium map and a large map that essentially covered the PCD disc specimens as shown in Fig. 4. The map areas were $\sim 36 \text{ mm}^2$ for the small map, $\sim 100 \text{ mm}^2$ for the medium map and $\sim 225 \text{ mm}^2$ for the large map. The mapping point separation for the different map sizes was $\sim 1000 \mu\text{m}$

Table 1

The peak position and full width at half maximum of the respective diamond Raman peaks of fatigued samples B and G as a function of map size.

	Cycles	Map size	Peak position (cm^{-1})	FWHM (cm^{-1})
Sample B	250000	Small	1334.83 ± 0.08	13.27 ± 0.14
		Medium	1334.89 ± 0.08	12.88 ± 0.99
		Large	1334.83 ± 0.07	13.05 ± 0.16
Sample G	600000	Small	1333.27 ± 0.07	14.99 ± 0.19
		Medium	1333.46 ± 0.09	14.88 ± 0.25
		Large	1334.59 ± 0.08	15.50 ± 0.31

for the small map, $\sim 1500 \mu\text{m}$ for the medium map and $\sim 2500 \mu\text{m}$ for the large map.

It was found that the different sized maps showed very little variation in the average Raman peak position and full width at half maximum (FWHM) for specimens subject to no fatigue. In the cases of fatigued samples, a difference was only noticeable for large numbers of cycles. Typical results are shown in Table 1 for fatigued samples B and G, respectively and in Fig. 5 for an unfatigued sample A and a fatigued sample G respectively.

The mapping arrays in Fig. 4 can be compared to the expected stress field distribution in Fig. 3 in order to see how the array points are distributed across the stress field contours. In the case of smaller numbers of cycles, such as for sample B, the different map sizes give very similar results, implying that the sample has not yet experienced any significant effect due to the fatigue cycling. At a larger number of cycles, such as for sample G, an effect is noticeable. The small and medium map sizes cover mainly the areas experiencing the larger fractions of maximum tensile stress (Fig. 3). The larger map size includes more points in the areas experiencing smaller tensile stresses during the loading process. One would thus expect the larger map to have a more compressive overall average stress (higher Raman peak position relative to unstressed diamond), while the medium and smaller maps should yield a less compressive overall average stress (Raman peak position less than for large map). This trend is illustrated in our data in Table 1.

In order to determine the overall response of the samples to the fatiguing process at larger number of cycles, the large maps were used for the studies of the suite of fatigued samples subjected to different numbers of cycles reported in the present work.

3.5. SEM studies

A JEOL JSM7500F field emission scanning electron microscope operated at 15 keV in a vacuum of $5.1 \times 10^{-4} \text{ Pa}$ was then used to determine the presence of localised areas of damage on the surface of the samples.

4. Experimental results

4.1. Raman studies on PCD samples undergoing different numbers of fatigue cycles

As discussed in the preceding section, the samples used in the present work were from the same batch processed under the same

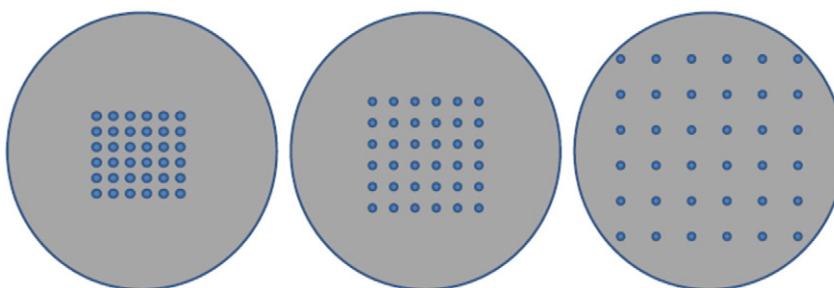


Fig. 4. The three different map sizes examined for this work; the distributions of the mapping points are illustrated for the small, medium and large maps.

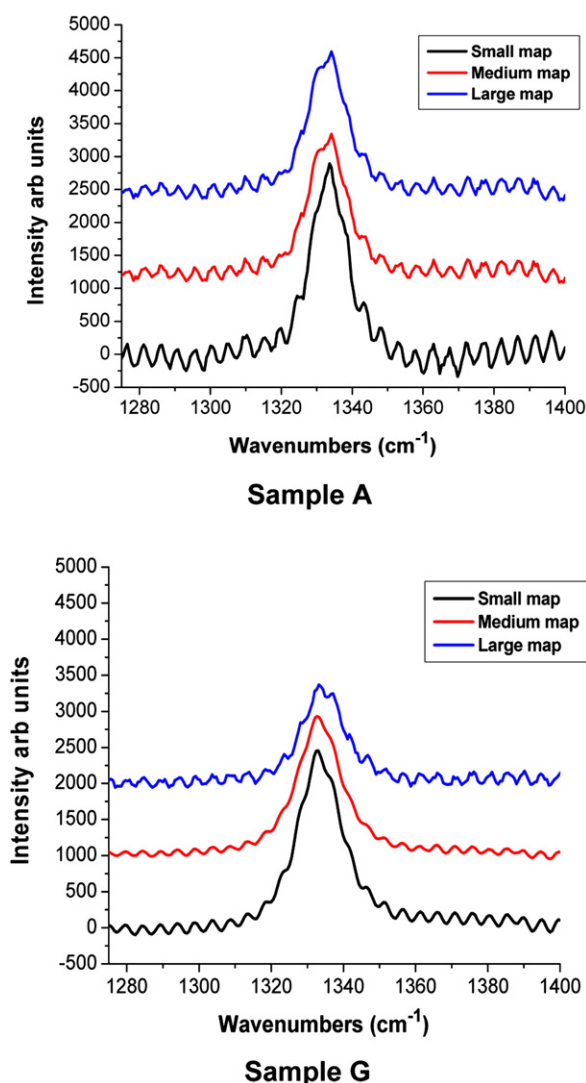


Fig. 5. Average Raman spectra for three different map sizes for an unstressed PCD sample (sample A) and a stressed PCD sample (sample G) subjected to 600 000 cycles. The spectra have been vertically displaced and stacked for comparison purposes. The apparent periodicity in the background for some of the spectra results from an instrumental effect and does not affect the peak position or peak width being measured.

conditions. Accordingly, it was initially expected that the samples fatigued with the same load, but with a relatively lower number of loading cycles would exhibit less disorder and deformation than those

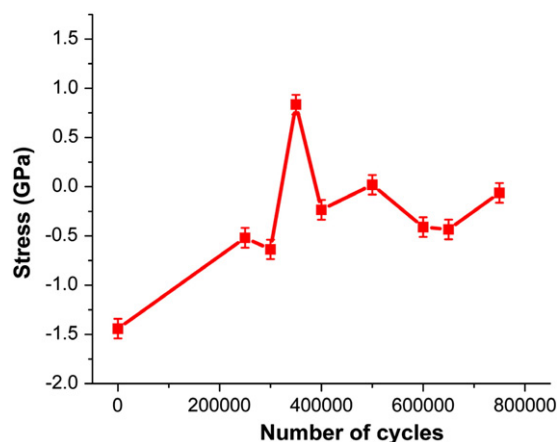


Fig. 6. Variation of average surface stress as function of number of fatigue cycles for the nine samples used (A–I).

Table 2

The average Raman peak position, average FWHM and calculated average surface stress as a function of the number of fatigue cycles for sample B.

Cycles	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Stress (GPa)
250 000	1333.58 ± 0.07	14.01 ± 0.27	-0.53 ± 0.02
300 000	1333.74 ± 0.02	12.29 ± 0.08	-0.60 ± 0.03
350 000	1333.55 ± 0.03	12.51 ± 0.11	-0.50 ± 0.02
400 000	1333.63 ± 0.02	12.64 ± 0.09	-0.36 ± 0.01
450 000	1333.35 ± 0.02	12.89 ± 0.10	-0.42 ± 0.01
500 000	1332.93 ± 0.02	12.64 ± 0.09	-0.17 ± 0.01
550 000	1332.45 ± 0.02	12.89 ± 0.10	0.08 ± 0.01
575 000	1332.34 ± 0.05	13.76 ± 0.22	0.14 ± 0.01

subject to a higher number of cycles. Accordingly the diamond Raman signatures, namely the peak frequency and the FWHM would be expected to undergo a consistent trend as a function of the number of loading cycles. The calculated average surface stress as a function of the number of fatigue cycles resulting from the Raman data for nine nominally similar PCD samples (A–I) is shown in Fig. 6.

The results shown in Fig. 6 show an irregular trend in which the average surface stress as a function of the number of fatigue cycles changes progressively from a compressive stress regime to that approaching a state of average tensile stress for the greatest number of cycles. This would suggest that on average, samples subjected to many fatigue cycles are more likely to be subject to cracking. The irregular form of the graph in Fig. 6 also indicates that the nominally similar samples display significantly different behaviour under the fatigue conditions; in particular sample D displays significant average tensile stress with a relatively limited number of cycles. This result is consistent with the practical experience with tool-bits in which apparently similar PCD cutters fracture unexpectedly with only limited use.

Having established the above results in which nine PCD samples were influenced by a range of fatigue cycles, with indications of changes to the nature of the average surface stress, a second approach was adopted in which individual samples were subjected to alternating applications of fatigue cycles and subsequent Raman studies. The brittle nature of the sample material resulted in several of the samples fracturing before attaining the desired number of cycles. Of the nine samples whose results are shown in Fig. 6, only five survived the series of alternating fatigue experiments and Raman measurements with the number of cycles increasing each time. These were samples A, B, E, F and G. The results for samples B and G will be presented in detail as being

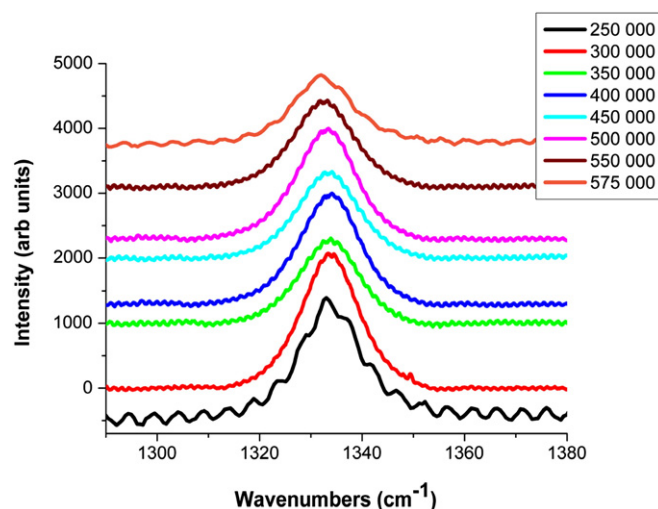


Fig. 7. The measured averaged Raman spectra as a function of the number of cycles for sample B. The spectra have been displaced and stacked for comparison. The apparent periodicity in intensity of some of the spectra is a result of an instrumental effect and does not affect the peak position or peak width being studied.

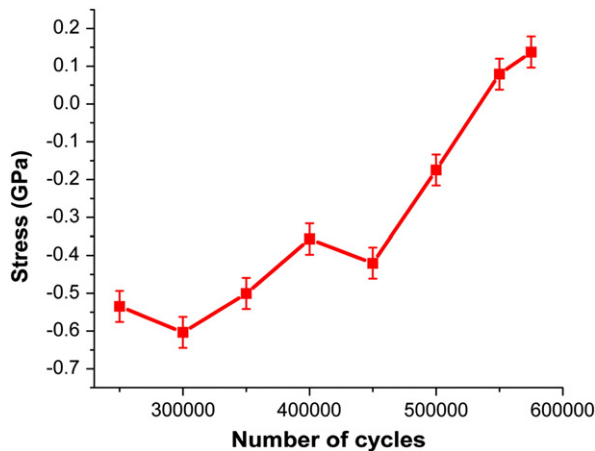


Fig. 8. Average surface stress variation as a function of number of cycles for sample B.

representative of situations in which the initial number of fatigue cycles was the smallest and largest, respectively.

4.2. Sample B

The initial number of fatigue cycles applied to sample B was 250,000. Table 2 shows the subsequent number of cycles to which the sample was subjected, the respective average Raman peak positions, their average FWHM and the calculated average surface stress. Fig. 7 shows the averaged Raman spectra obtained for the different numbers of cycles. The spectra indicate a progressive shift of the frequency to lower wavenumbers and subsequently a change in the nature of the calculated average surface stress.

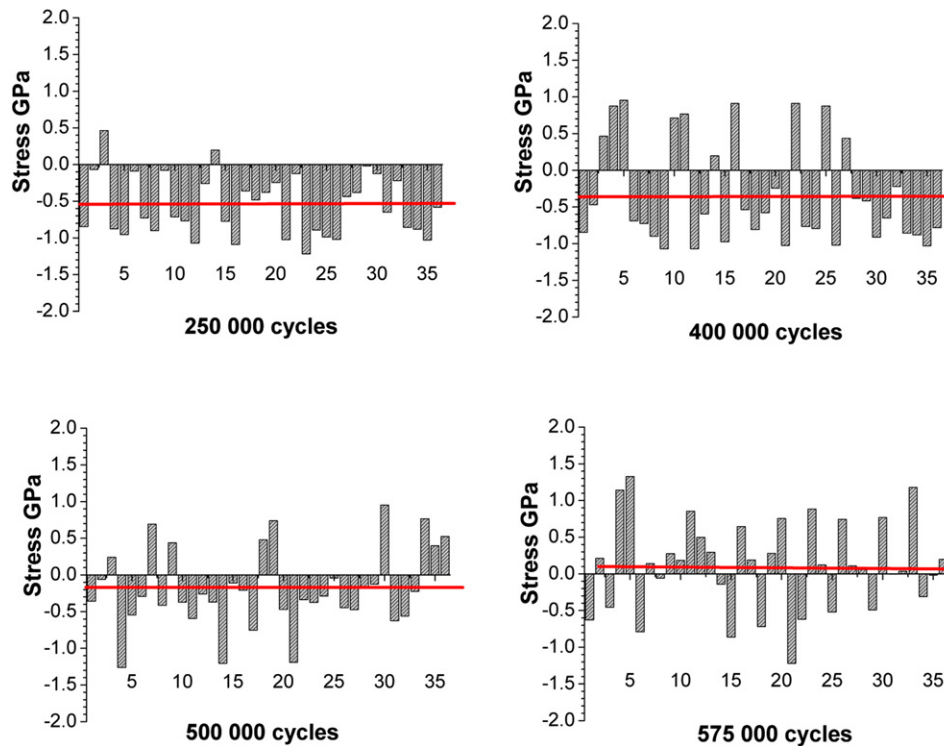


Fig. 9. The respective diagrams for sample B show the individually measured stress (either compressive or tensile) for the 36 mapping points constituting the 6×6 square map at various stages in the fatigue process shown in each case by the number of fatigue cycles (the order of the mapping points for each of the diagrams is random since the samples were not replaced in a consistent orientation in the Instron test machine after each series of fatigue cycles). The red line parallel to the abscissa indicates the average stress.

Fig. 8 illustrates the change in the nature of the calculated average surface stress for Sample B from being compressive to being tensile in nature as the number of fatigue cycles increases. The calculated stress changes from -0.53 GPa to 0.14 GPa.

The series of diagrams for sample B constituting Fig. 9 show the individually measured stresses (either compressive or tensile) for the 36 points constituting the respective 6×6 square maps at various stages in the fatiguing process. The order of the mapping points for each of the diagrams is random since the sample was not replaced in the same orientation in the Instron test machine after each series of fatigue cycles. The red line parallel to the abscissa in each of the diagrams indicates the average surface stress of the sample at the termination of the particular stage of the stressing process.

Using the individual mapping points and the results of the micro-Raman spectra for sample B once more, surface maps were generated to show the nature of the stresses and their distribution in the mapped area at the terminal stage of each fatigue series. These results that provide a different perspective of the stress distributions are shown in Fig. 10. The 2D surface maps clearly show the changes that are taking place within the sample as the number of fatigue cycles increases. In particular it is seen that the regions of predominantly compressively stressed regions present after the lower ranges of fatigue cycles give way to regions of tensile stress.

The surface maps of Fig. 10 are consistent with the histograms of Fig. 9. As the number of fatigue cycles increases, there exists an increasing number of mapping points and more extended regions associated with stresses tensile in nature.

4.3. Sample G

The initial number of fatigue cycles applied to sample G was 600,000. Table 3 shows the subsequent number of cycles to which the sample was subjected, the respective average Raman peak positions, their

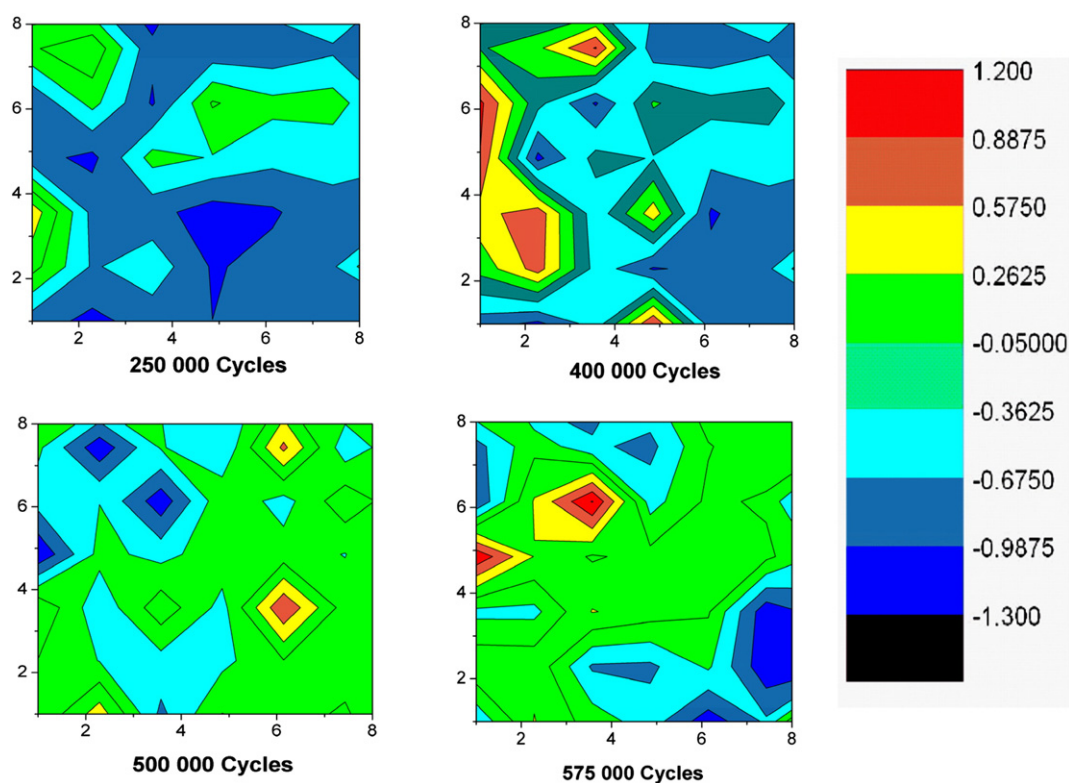


Fig. 10. Two dimensional surface maps showing the nature and distribution of surface stress as a function of the number of cycles for sample B. Compressive stresses are shown by the colours black to deep green; and tensile stresses are indicated by the colour range yellow to red.

average FWHM and the calculated average surface stress. Fig. 11 shows the Raman spectra obtained for the fatigue cycles. These again indicate a progressive shift of the frequency to lower wavenumbers and subsequently a change in the nature of the calculated average surface stress from being compressive in nature to being tensile (Fig. 12). The FWHM values show clear broadening at the highest number of cycles indicating an increasing degree of plastic deformation in the diamond crystals.

Fig. 13 for sample G was generated in the same manner as Fig. 9 for sample B. Using the individual mapping points and the results of the micro-Raman spectra for sample G once more, surface maps were generated to show the nature of the stresses and their distribution in the mapped area at the terminal stage of each fatigue series (Fig. 14). The 2D surface maps clearly show the changes that are taking place within the sample as the number of fatigue cycles increases. In particular it is seen that predominantly compressively stressed regions present after the lower ranges of fatigue cycles give way to substantial regions of tensile stress. These surface maps associated with the largest number of fatigue cycles used in the present work emphasise the changes that are taking place within the sample as the number of fatigue cycles increases. There is also good consistency between Figs. 13 and 14.

For comparison purposes, Figs. 15 and 16 illustrate the respective effects of the multiple fatigue cycles for the samples B, E, F and G. The

average stress variations for the samples are shown in Fig. 15, while in Fig. 16 the number of mapping points exhibiting tensile stress is indicated. Although there are obvious variations in detail in the results for the various samples there are also common trends. In particular the average surface stress is compressive during the earlier phase in which the number of fatigue cycles remains relatively limited while in the later phase of a large number of cycles the average surface stress becomes tensile in nature for all the samples. A comparison of the data for the mapping

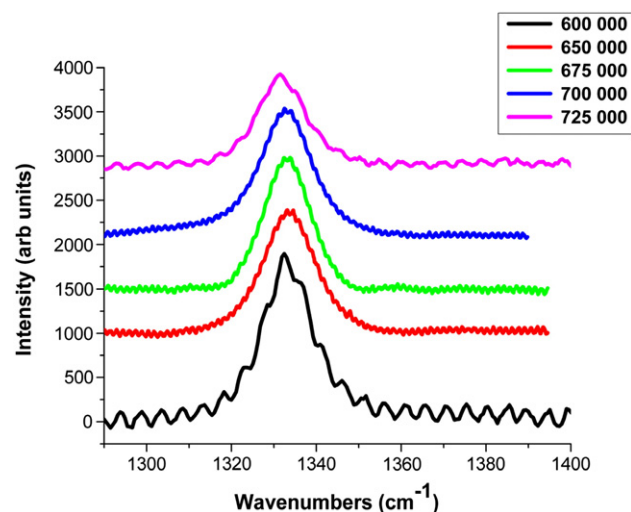


Fig. 11. The measured Raman spectra as a function of number of cycles for sample G. The spectra have been displaced and stacked for comparison. The apparent periodicity in intensity of some of the spectra is a result of an instrumental effect and does not affect the peak position or peak width being studied.

Table 3

The average Raman peak position, average FWHM and calculated average surface stress as a function of the number of fatigue cycles for sample G.

Cycles	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Stress (GPa)
600000	1333.28 ± 0.08	13.41 ± 0.27	-0.38 ± 0.02
650000	1333.57 ± 0.03	12.30 ± 0.10	-0.61 ± 0.03
675000	1333.08 ± 0.03	13.48 ± 0.11	-0.20 ± 0.01
700000	1333.69 ± 0.02	13.49 ± 0.08	-0.05 ± 0.01
725000	1331.76 ± 0.07	17.14 ± 0.25	0.36 ± 0.02

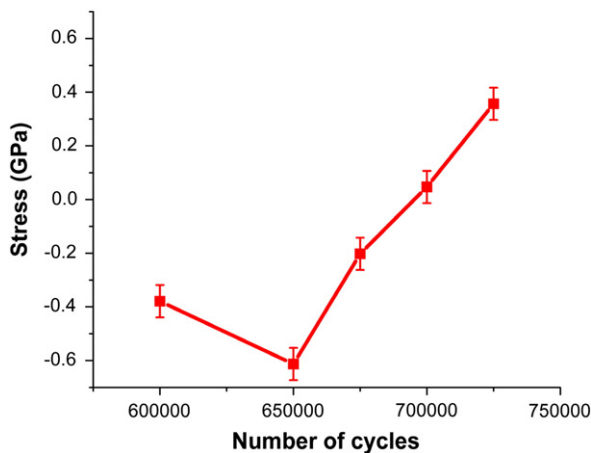


Fig. 12. Average surface stress variation as a function of number of cycles for sample G.

points shows that for the earlier phase of limited fatigue cycles there are relatively few points in which the local stress is tensile and that the number increases substantially when the samples have been subjected to a large number of cycles. These measurements confirm the differing nature of the mapping points and hence indicate that the fatigue cycles produce localised damage.

4.4. Scanning electron microscopy

Scanning electron microscopy (SEM) was conducted to try and find evidence of localised damage due to fatigue. No clear such evidence was found. Energy dispersion spectra (EDS) were carried out on samples B, E, F and G to determine their respective weight and atomic compositions. Representative results are shown in Table 4 for samples B and G.

Variations in the compositions of the samples are present including different diamond concentrations.

5. Discussion

To the best of our knowledge the present work is the first report of the successful application of Raman spectroscopy to the characterisation of fatigue processes in PCD diamond. In particular the results show the presence of an average compressive stress in all samples prior to the fatigue cycling which is initially reduced and ultimately leads to an average tensile stress when a sufficiently large number of fatigue cycles are applied.

In the PCD used in this paper, the diamond particles are bonded together by diamond–diamond growth taking place during the sintering process. The diamond particles thus form an intergrown matrix with pools and small channels of cobalt dispersed through this matrix. The diamond particles form the bulk of the PCD with the result that the PCD has hardness and wear resistance properties close to that of diamond. The Raman spectroscopy technique does not detect the stress state of the sintering aid and binder material, namely the cobalt present in pores between the diamond grains. It is very likely that the cobalt is deformed plastically (i.e. beyond its yield limit) during the fatigue cycling at room temperature, thereby influencing the resultant stress state of the interlocking diamond matrix. Further investigations of this aspect are being made with X-ray and neutron diffraction techniques. The conditions for crack formation are enhanced by the presence of tensile stresses, thus it is possible that progressive breaking of the inter-grain bridges associated with diamond to diamond bonding occurs during the fatigue cycles. Further work is required in this regard. The total resultant stress state of the PCD disc is therefore dependent on the distribution of component stress states between the diamond matrix and the cobalt binder phase. We speculate that at lower numbers of fatigue cycles the cobalt component is affected first, with the diamond matrix showing a measurable response at a larger number of

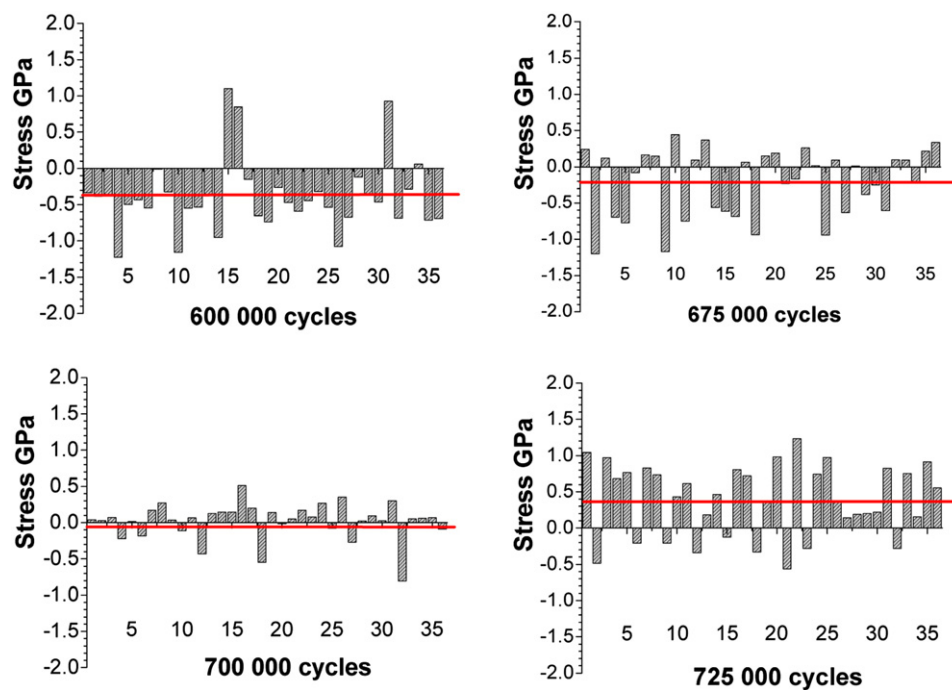


Fig. 13. The respective diagrams for sample G show the individually measured stress (either compressive or tensile) for the 36 mapping points constituting the 6×6 square map at various stages in the fatigue process shown in each case by the number of fatigue cycles (the order of the mapping points for each of the diagrams is random since the samples were not replaced in a consistent orientation in the Instron test machine after each series of fatigue cycles). The red line parallel to the abscissa indicates the average stress.

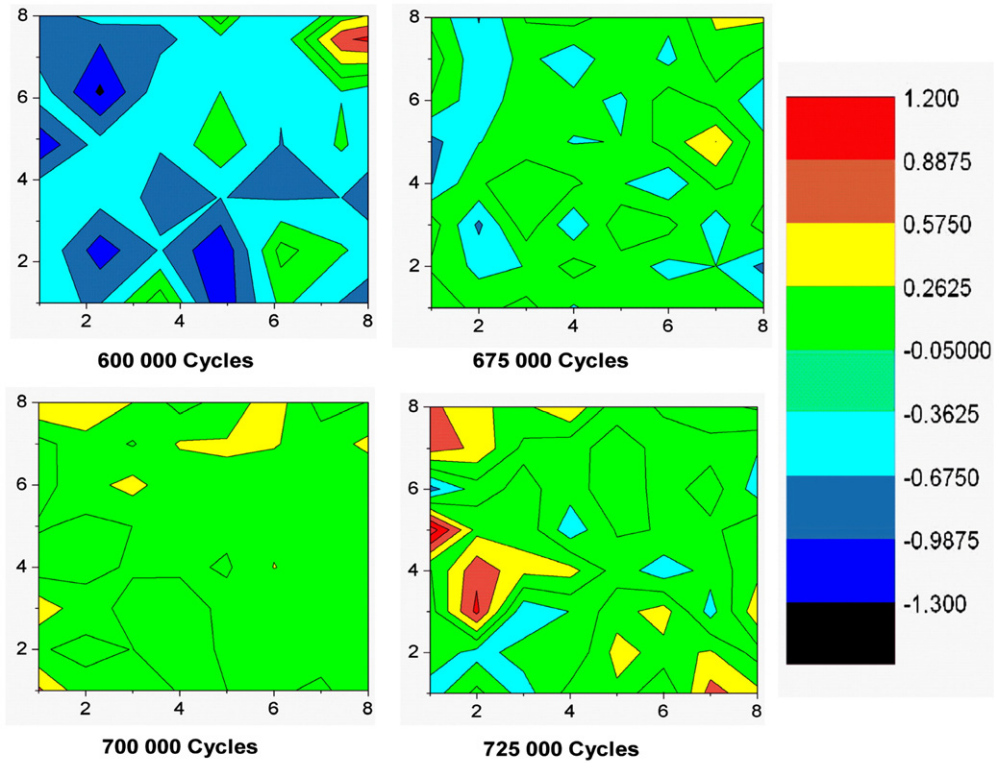


Fig. 14. Surface maps showing the nature and distribution of surface stress as a function of the number of cycles for sample G. Compressive stresses are shown by the colours black to deep green; and tensile stresses are indicated by the colour range yellow to red.

cycles. This would be consistent with our data, but requires verification with powder diffraction techniques as mentioned.

There is no clear correspondence between the stress contours reported in Fig. 3 and the measured stress distributions in Figs. 10 and 14. There are two possible contributions in this regard. The order of the mapping points for each of the diagrams is random since the samples were not replaced in a consistent orientation in the Instron test machine after each series of fatigue cycles as mentioned earlier in the paper. This results in the angular information related to the 3-lobed pattern in Fig. 3 not being imaged. The other possibility is that the array used for the large map has relatively few points near the central area of the disc, thus the detrimental effect of the relatively large

tensile stresses experienced by the central part of the disc is not efficiently sampled.

The samples used in the present work display variations in their properties even though they were manufactured in the same batch. The average surface stresses of the individual samples show a considerable variation from one sample to the next. Some samples with a lower number of fatigue cycles exhibited an average tensile stress and a number of tensile mapping points greater than those with a higher number of cycles. These variations are considered to arise from a combination of sources. The compositional variations shown by the EDS results indicate differing conditions during their batch synthesis. An example would be temperature gradients at the time of sintering. Furthermore the

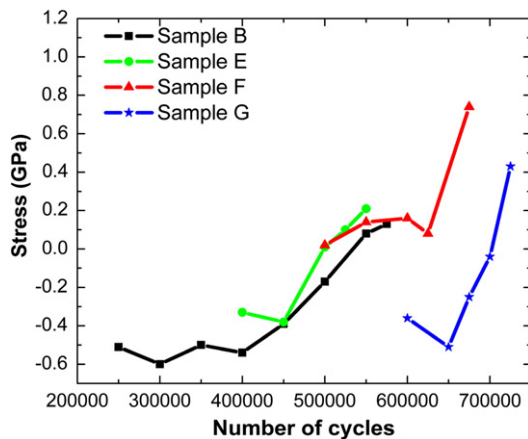


Fig. 15. Average surface stress variations as a function of the number of cycles for samples B, E, F and G.

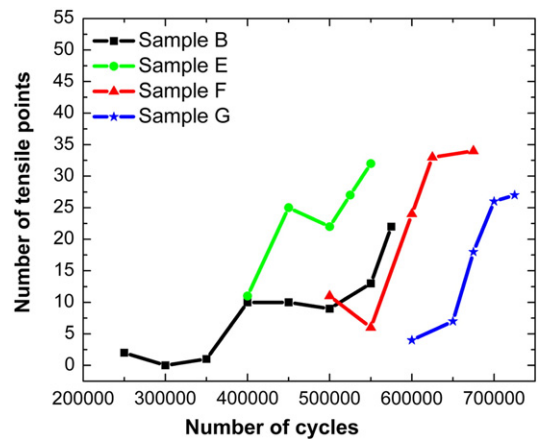


Fig. 16. The number of mapping points exhibiting tensile stress as a function of the number of fatigue cycles for samples B, E, F and G.

Table 4

Representative EDS measurement of the weight and atomic compositions of representative samples B and G.

Element	Weight %	Atomic %
<i>Sample B</i>		
C	82.71	91.82
Co	7.79	6.49
O	6.50	1.47
W	3.00	0.22
Total	100.00	
<i>Sample G</i>		
C	89.04	92.65
Co	8.97	7.01
O	1.46	0.31
W	0.54	0.04
Total	100.00	

hardness of the diamond grains is highly dependent on grain size and orientation [17]. It is known from the use of PCD tool-bits that failure under practical conditions occurs erratically and the present results suggest that sample variability is the probable origin.

SEM images obtained for the near surface regions did not show any evidence of damage. It is possible that damage or micro-cracks are present but invisible at the level of magnification that could be attained. For both sample B and sample G the FWHM of the average Raman peak showed significant increases for the highest number of fatigue cycles. The increases are significant enough to anticipate localised damaged areas.

Prime novelty statement

Experiments using Raman spectroscopy have determined the effects of multiple fatigue cycles on polycrystalline diamond (PCD) discs. With an increasing number of fatigue cycles, the average compressive surface stress reduces in magnitude with some samples ultimately exhibiting an average surface tensile stress. Such conditions promote crack initiation and provide an explanation of catastrophic failure of tool-bits in drilling operations.

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References

- [1] J.E. Field, *The Properties of Natural and Synthetic Diamond*, second ed. Academic Press, London, 1992.
- [2] W.Z. Zhuang, G.R. Halford, Investigation of residual stress relaxation under cyclic load, *Int. J. Fatigue* 23 (2001) S31–S37.
- [3] L.P. Pook, A 50-year retrospective review of three-dimensional effects at cracks and sharp notches, *Fatigue Fract. Eng. Mater. Struct.* 36 (2013) 699–723.
- [4] C. Suryanarayana, Mechanical behavior of emerging materials, *Mater. Today* 15 (2012) 486–498.
- [5] T.P. Lin, M. Hood, G.A. Cooper, Residual stresses in polycrystalline diamond compacts, *J. Am. Ceram. Soc.* 77 (1994) 1562–1568.
- [6] J.G. Bell, M.E.C. Stuivinga, A.G. Thornton, J. Wilks, Cracking and fatigue of diamond, *J. Phys. D. Appl. Phys.* 10 (1977) 1379–1387.
- [7] T.P. Lin, G.A. Cooper, M. Hood, Fatigue test on polycrystalline diamond compacts, *J. Mater. Sci. Eng. A* 163 (1993) 23–31.
- [8] K.J. Dunn, M. Lee, Fracture and fatigue of sintered diamond compact, *J. Mater. Sci.* 14 (1979) 882–890.
- [9] J.W. Paggett, E.F. Drake, A.D. Krawitz, R.A. Winholtz, N.D. Griffin, Residual stress and stress gradients in polycrystalline diamond compacts, *Int. J. Refract. Met. Hard Mater.* 20 (2002) 187–194.
- [10] S.A. Catledge, Y.K. Vohra, R. Ladi, G. Rai, Micro-Raman stress investigations and X-ray diffraction analysis of polycrystalline diamond (PCD) tools, *Diamond Relat. Mater.* 5 (1996) 1159–1165.
- [11] R.O. Ritchie, Mechanisms of fatigue-crack propagation in ductile and brittle solids, *Int. J. Fract.* 100 (1999) 55–83.
- [12] R.M. Erasmus, J.D. Comins, V. Mofokeng, Z. Martin, Application of Raman spectroscopy to determine stress in polycrystalline diamond tools as a function of tool geometry and temperature, *Diamond Relat. Mater.* 20 (2011) 907–911.
- [13] M.H. Grimsditch, E. Anastassakis, M. Cardona, Effect of uniaxial stress on the zone-center optical phonon of diamond, *Phys. Rev. B* 18 (1978) 901–904.
- [14] L. Bergman, R.J. Nemanich, Raman and photoluminescence analysis of stress state and impurity distribution in diamond thin films, *J. Appl. Phys.* 78 (1995) 6709–6719.
- [15] A. Börger, P. Supancic, R. Danzer, The ball on three balls test for strength testing of brittle discs: stress distribution in the disc, *J. Eur. Ceram. Soc.* 22 (2002) 1425–1436.
- [16] A. Börger, P. Supancic, R. Danzer, The ball on three balls test for strength testing of brittle discs: part II: analysis of possible errors in the strength determination, *J. Eur. Ceram. Soc.* 24 (2004) 2917–2928.
- [17] A. Lammer, Mechanical properties of polycrystalline diamonds, *Mater. Sci. Technol.* 4 (1988) 949–955.