

Chapter 3: Experimental

In this chapter the experimental techniques, apparatus, procedures and pertinent calculations will be described. Where necessary, results from some of the calibration procedures, conducted on the equipment used, will be presented.

3.1: Chemicals

All the chemicals used for processing are tabulated in table 3.1.1.

TABLE 3.1.1: Chemicals used for processing

Chemical	Particle Size (μm)	Supplier, Purity
Al	50-70	Saarchem, 99.9%
$\alpha\text{-Al}_2\text{O}_3$	2-5	Sumitomo, 99.99%
AlB_{12}	2-5	Poly Metals SA, 98%
B	2-5	Johnson Matthey, 99.5%
Mg	70-100	Saarchem, 99.9%
h-BN	1-2	H. C. Stark
MgB_2	8-10	Superconductive Ind., 99.5%
TiB_2	2-5	H. C. Stark
TiC	2-5	H. C. Stark
TiCN	2-5	H. C. Stark
TiN	2-5	H. C. Stark
WC	2-5	H. C. Stark
PVP K30	-	Fluka
Stearic Acid	-	Hopkin and Williams, 96%
Paraffin	-	Associated Chemical Suppliers
Hexane	-	Saarchem, 99.99%
Methanol	-	Saarchem, 99.5%
Ethanol	-	Saarchem, Abs. 99.9%
1-propanol	-	Saarchem, 99.7%

2-propanol	-	Saarchem, 99.7%
2-butanol	-	Saarchem, 99.5%
t-butyl alcohol	-	Saarchem, 99.5%
Water	-	Distilled and deionised
Argon	-	Afrox, UHP

3.2: Equipment

3.2.1: Furnaces

3.2.1.1: The Tube Furnace

A custom built tube furnace to run to a maximum temperature of 1600°C was used. An α -Al₂O₃ tube, which was inserted into the furnace, was used for loading samples into. The furnace was initially evacuated to levels of 200 mtorr for 30 minutes and then backfilled with argon gas to room pressure. After which a constant argon flow rate of 10 ml/min was maintained for the duration of the sintering cycle. The furnace temperature was monitored with a standard Pt-Rh thermocouple and no independent temperature verification was done on this furnace.

In a typical sintering cycle, the furnace was heated from ambient temperatures to 600°C at 20°C/min and held at this temperature for 5 minutes. The furnace was then heated at 10°C/min to 1400°C and held at that temperature for 60 minutes. The furnace was then cooled at 20°C/min to ambient conditions. At temperatures below 900°C the furnace cooled down at a slower heating rate than the programmed heating rate.

3.2.1.2: The Hot Isostatic Press

A custom built hot isostatic press (HIP) from Flow Autoclave Systems Inc., rated at 1500°C and 2 kbar was used to produce sintered compacts at temperatures of 1400°C and 20 MPa. Compacts were encapsulated in niobium pots evacuated and electron beam welded closed³⁹. These encapsulates were placed into the HIP furnace chamber and the chamber was evacuated and back filled with argon. The furnace was pressured to 20 MPa and heated to 1400°C at a heating rate of 10°C/min. At 1400°C the

temperature was held for 1 hour and then cooled at 20°C/min. At ambient temperatures the encapsulates were removed from the furnace and then the compacts were removed from the encapsulates.

3.2.1.3: The Uniaxial Hot Press

An uniaxial hot press, purchased from Thermal Technology Industries, was used for the bulk of the synthesis work conducted in this thesis. The furnace is heated by carbon elements. The maximum obtainable furnace temperature is 2100°C and the furnace is water cooled. A maximum pushing force of 100 000 N can be applied to compacts during the furnace cycle. The force is applied through graphite punches uniaxially from the bottom graphite punch. A rotary vacuum pump is attached to the press and is capable of vacuum levels of 10 mtorr. A picture of this furnace is presented in figure 3.2.1.



Figure 3.2.1: The uniaxial hot press

Before sintering all graphite components that are to be in the hot-zone of the furnace are coated with an h-BN suspension that is stabilised with poly-vinyl pyrrolidone. The

recipe used to make the suspension required 2 g of poly-vinyl pyrrolidone 37 g of h-BN and 100 ml of water⁴⁰. All the ingredients for the suspension were stirred together vigorously using a magnetic stirrer bar until the constituency of the entire suspension was uniform. The suspension was then applied by paint brush to the clean hot ($\approx 80^{\circ}\text{C}$) surface prepared for coating.

The graphite components placed in the hot-zone included the graphite punches, an outer graphite die and insert, and an inner graphite die (sample cell) of a fixed diameter, 20 mm and 13 mm inner diameter dies. All the coated components that were to be placed in the hot-zone were photographed and are presented in figure 3.2.2.

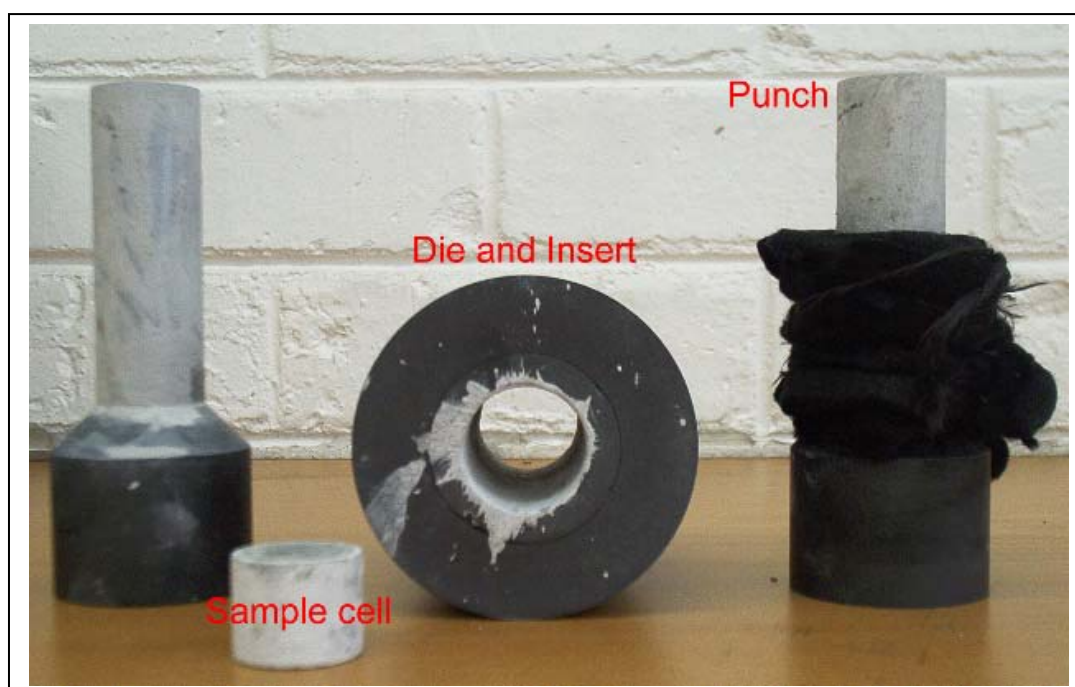


Figure 3.2.2: Hot-zone components used in the uniaxial hot press

A general furnace program was used to make the samples. In this process the hot press was evacuated to pressures less than 100 mtorr and then back filled with argon. Argon was then allowed to flow through the furnace during the furnace temperature cycle. The furnace was heated to 600°C at $20^{\circ}\text{C}/\text{min}$ and held at 600°C for 5 minutes. The soak time here is simply an attempt to allow the liquid phase, which would have formed entirely by 600°C , to infiltrate into the pores. The mechanical load was then applied to the sample and the furnace was heated to 1400°C at $10^{\circ}\text{C}/\text{min}$ and held at

1400°C for 60 minutes. The furnace was then cooled to room temperature at 20°C/min. At temperatures lower than 850°C the furnace temperature lagged behind the programmed temperature. At 600°C the load was removed from the sample. At room temperature the sample cell was removed from between the punches and the sample then removed from the sample cell.

The temperature at which the hot press operates is monitored by an optical pyrometer. An independent calibration of the hot press operating temperature was done using a hot-wire pyrometer. The results are presented in figure 3.2.2.

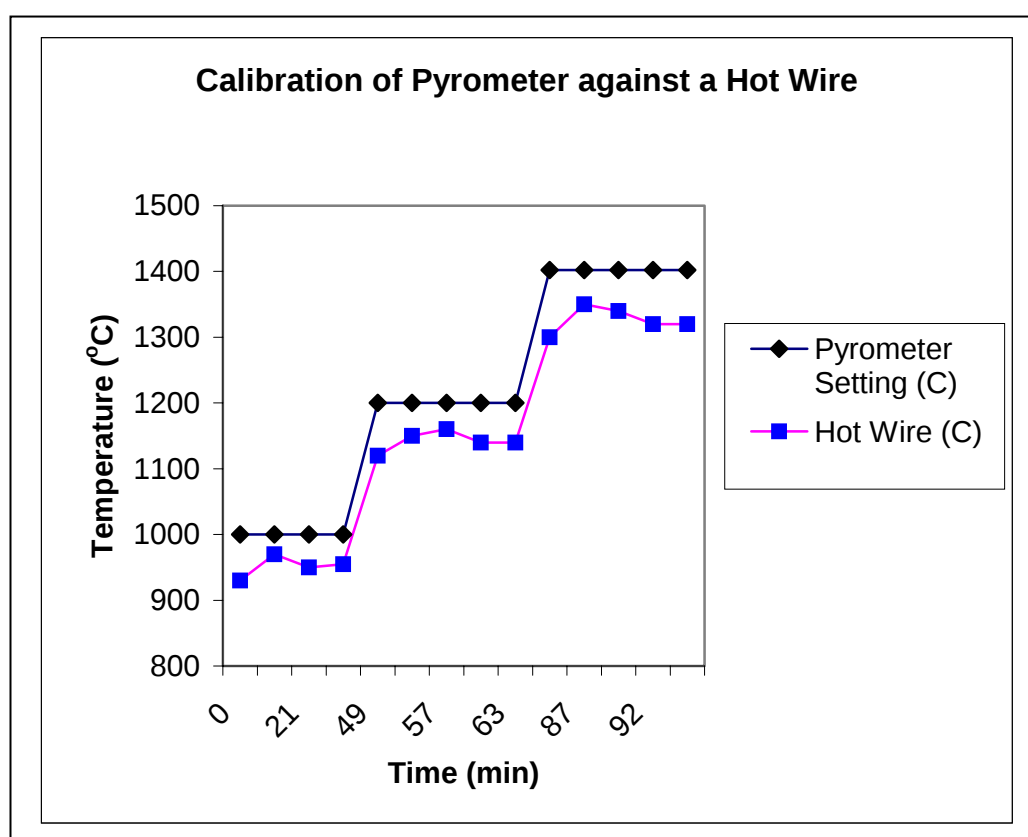


Figure 3.2.2: Calibration of the hot press' optical pyrometer with an hot wire pyrometer

The hot wire pyrometer is on average 35°C lower than the optical pyrometer. The error in using the hot wire pyrometer is much larger than the optical pyrometer due to the process of measurement that is taken when reading the temperature of the hot wire pyrometer. The adjusting of the light intensity to match that of the furnace intensity of

the hot wire is subjective. Thus, the temperature reading from the optical pyrometer of the hot press was assumed to be the temperature of the furnace chamber.

3.2.1.4: Pyrolysis Furnace

A low temperature tube furnace was used for the pyrolysis of organics from those milled starting powders that contained organics. Such organics include stearic acid (surfactant) and paraffin (oxidation barrier) that are added to the elemental powders before milling them.

Pyrolysis of the organics is conducted by heating the furnace to 300°C at 5°C/min and then maintaining that temperature for 60 minutes and then cooling the furnace and contents by shutting the power off to the furnace element under a constant flow of Argon. The pyrolytic temperature was determined by thermo-gravimetric analysis (TGA). The TGA profile for a powder containing Al, Mg, B, stearic acid and paraffin is given in figure 3.2.3.

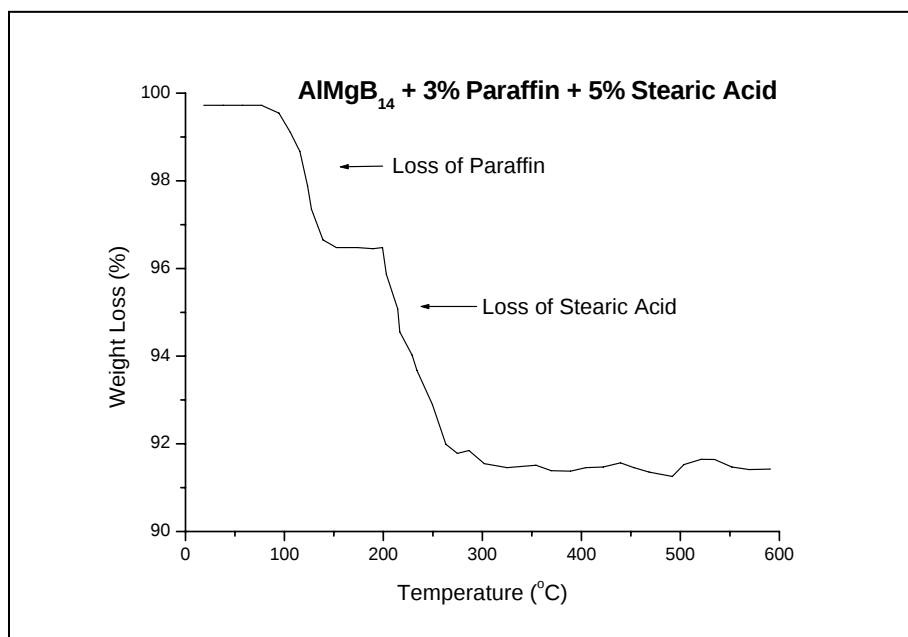


Figure 3.2.3: A thermo-gravimetric profile for AlMgB₁₄ + 3 wt.% Paraffin and 5 wt. % Stearic acid in argon, heating rate 5°C/min

The amount of paraffin and stearic acid weighed out for the TGA profile was greater than that weighed out for the production of samples because the loss of paraffin and stearic acid would then be more pronounced in the profile.

3.2.2: The Planetary Mill

A Fritsch Pulverisette 6 planetary mill was used for all the milling cycles. The milling vessel used inside the planetary mill was a WC-Co lined stainless steel vessel with a capacity of 250 ml. WC-Co ball milling media of 5 or 20 mm diameters was used, and unless otherwise stated the mass ratio of the milling media to powder charge was set at 30:1. The mill was operated at a speed of 200 rpm.

3.3: The Reaction Procedure

This section outlines the procedure that was adopted in order to prepare and sinter the powder mix in an uniaxial hot press.

3.3.1: Preparing the Starting Powders

Elemental powders of Al, Mg and B were weighed out in the ratio required for the experiment concerned. Usually in 1:1:14 mole ratio respectively. Additionally 1 wt.% by mass paraffin and 0.5 wt.% stearic acid was weighed out. The wt.% of paraffin and stearic acid were determined with respect to the final powder charge. The mass of the milling media required was then calculated from the final powder charge and the calculated mass of the milling media was then weighed.

Together with the milling media, 100 ml. of the solvent (usually methanol) was added to the milling vessel. Argon gas was then bubbled through the solvent for 30 minutes in order to displace air from the milling vessel. Stearic acid and paraffin were then added to the solvent. Half of the boron powder was then added to the methanol followed by Al and Mg that were added together and then the remaining boron powder was added. This was done to ensure that the denser metal powders did not settle to the bottom of the milling vessel. Argon gas was bubbled through this mixture for a further 30 minutes. The vessel was then sealed and milled for 2 hours. If longer milling times were required then after 2 hours of milling the milling vessel was removed from the planetary mill and the contents of the milling vessel were flushed with argon for a further 30 minutes. The milling vessel was then resealed and milled

for a further two hours. This process was repeated until the required milling time was achieved.

Once the milling cycle was completed the powder was removed from the milling vessel and the solvent was removed under reduced pressure in a rotary evaporator. The powder was then removed from the rotary evaporator flask and sieved through a 38 μm sieve.

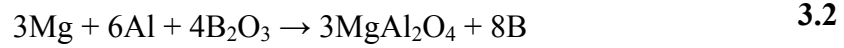
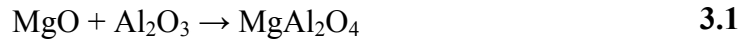
The powder was then weighed out into suitable amounts for green compaction in dies of 13 or 20 mm diameters at a pushing pressure of 5 MPa. The geometric density of the pre-pyrolisis green compacts was then determined. The green compacts were then placed in a quartz tube and the tube was then placed into the pyrolisis furnace. The quartz tube was then evacuated under a rotary vacuum pump for 30 minutes after which the tube was back filled with argon gas. The furnace cycle was then initiated under a constant flow (flow rate 10 mlmin^{-1}) of argon gas. After the pyrolisis treatment the geometric density of the post-pyrolisis green compacts were determined before they were placed into coated graphite sample cells and loaded into the hot press.

3.3.2: Compositions of the Powders

The powder compositions were calculated according to the molar ratio of AlMgB_{14} . As will be seen in chapter 4, section 4.3.4.2 the effect of the composition on the formation of the spinel phase MgAl_2O_4 , which is not desirable, can be reduced by the careful choice of starting composition. The calculation is based on the spinel content determined from a Rietveld analysis that was done on a composition prepared from a 1:1:14 mole ratio of Al, Mg and B respectively. The Rietveld analysis result is presented in Chapter 5, section 5.3.2.1.

A simplifying assumption is made that the formation of the spinel phase is from the metals Mg, Al and the semi-metal B, and not from the processing atmosphere. Chapter 5 shows that spinel formation is not only related to the presence of MgO and Al_2O_3 but also a result of the presence of B_2O_3 . However, Chapter 5 also gives a method to minimise the amount of B_2O_3 in the starting boron powders and so the

formation of MgAl_2O_4 from either B_2O_3 or MgO and Al_2O_3 or a combination of both the relevant reactions 3.1 and 3.2 results in the loss of Mg and Al.



This is used in the calculation of the starting compositions to additionally minimise the spinel formation. That is Mg contributes MgO and Al contributes Al_2O_3 . The reaction product thus formed from the two metal oxides is the spinel, MgAl_2O_4 . The second assumption is that the formation of the spinel results from the reaction of the respective oxides present in the starting powders and is not determined from the oxidation of the metals during the reaction.

In order to compensate for the formation of the spinel phase, MgAl_2O_4 , two methods can be employed. Firstly, less boron powder can be added to react with the Al and Mg metals present in the Al and Mg starting powders. Secondly, more Al and Mg powder can be added to a fixed amount of boron powder to ensure that there is sufficient Al and Mg metal to react with the boron powder. The approach adopted here was to use the first method thus adding less boron powder to the Mg and Al starting powders.

To determine the amount of the starting powders to use it was assumed that 10 wt.% spinel was present in the metal powder. It was further assumed that the only phases present in the final sintered compact are MgAl_2O_4 and AlMgB_{14} . Therefore the calculated mole ratios of the samples are thus $(\text{AlMgB}_{14})_{0.8634}(\text{MgAl}_2\text{O}_4)_{0.1367}$. Thus the mole ratio of boron to be added would be 12.088 instead of 14.

The stoichiometry of the final product is expected to be:



This yields mass ratios for Al, Mg and B of 0.1915, 0.1363 and 0.6722 respectively.

3.3.3: Sintering the Green Compacts

Uniaxial hot pressing of the green compacts was carried out as described in section 3.2.1.3. After hot pressing, the sintered compacts were removed from the sample cells and the surface layers of the sintered compact were removed by grinding on a diamond wheel. The Archimedes density of the sintered compacts was then determined in hexane. The density determination procedure is described in section 3.4.1 After determining the sintered density of the compact the compact was then cut into suitable pieces with a diamond saw. A few of the cut pieces were then mounted and polished in order to look at the microstructure and to perform hardness measurements. Additional pieces of the compact were kept in order to perform additional measurements as required, e.g. X-ray diffraction (XRD).

3.4 Analytical Procedures

3.4.1: Density Determination

The density of samples was determined using the Archimedes method. Samples were immersed in hexane and the hexane was boiled for three hours in order to displace air from the pores in the sample. The ASTM method suggests boiling the sample for 5 hours but it was found that there was no significant change in the value of the density for samples boiled for 3 hours. After boiling the sample for three hours in hexane the boiled solvent containing the sample is allowed to cool overnight to ambient temperature.

The density of the material is calculated by determining the mass of the boiled sample in hexane (m_i). The sample is then removed from the solvent and lightly dried to remove excess hexane from the surface of the sample. The wet mass (m_w) is then determined. This is done quickly so as to limit the evaporation of hexane from the pores of the sample. Finally the sample is dried in an oven and then cooled to ambient temperature and the dry mass measured (m_d). Each mass is determined three times in order to calculate a mean and standard deviation and those mean values are then used to determine the density (ρ) and the porosity (P_o) of the samples. The standard deviations of the mass measurements was used to compute the error in the corresponding density and porosity calculation.

The equation used for the determination of the density is given in equation 3.4 and the porosity in equation 3.5.

$$\rho = \frac{m_d \rho(\text{hexane})}{(m_i - m_w)} \quad 3.4$$

$$^{41}\rho(\text{hexane}) = 0.6603 \text{ gcm}^{-3}$$

$$P_o = 100\% * \frac{(m_i - m_d)}{(m_i - m_w)} \quad 3.5$$

3.4.2: Porosity by Image Analysis

The determination of the porosity by the Archimedes method is not valid for closed porosities. Therefore the determination of the porosity for samples that exhibit closed porosity can only be done by image analysis. Samples that exhibited closed porosity were polished as detailed in section 3.4.3. A light microscope equipped with a digital camera was used to take images of the polished surface at 20 times magnification. These images were then converted to black and white bitmap images. Using a custom programmed image analysis software package the percentage area occupied by the pores in the image was then determined and reported as the porosity of the material.

3.4.3: Polishing of the Samples

Samples to be polished were first mounted in a hot mounting press in Lucite™ powder and then lapped for 30 minutes on a standard lapping wheel using 350 µm diamond grit. Samples were then lapped further with 120 µm diamond grit for 20 minutes in order to remove the scratches on the surface of the samples caused by the 350 µm diamond grit.

By experimentation the best polishing procedure is as follows. Metallographic polishing proceeded after the lapping. Mounted samples were polished for 25 minutes with 9 µm diamond grit at 300 rpm followed by 20 minutes with a 6 µm diamond grit at 400 rpm then 15 minutes with a 3 µm diamond grit at 450 rpm and finally

15 minutes with a 1 μm diamond grit at 600 rpm. Successively smaller diamond grits were used only after microscopic scrutiny of the surface confirmed that no scratches from the previous diamond sized grit were present on the surface.

3.4.4: X-Ray Diffraction

Powder X-ray diffraction was performed on a PW1710 Philips, powder diffractometer using monochromatic Cu K α radiation (40 kV and 20 mA). Diffractograms were collected over a range of 2θ between 10-116°. Depending on the accuracy required of the measurement, a step size of between 0.01 and 0.04° 2θ was used together with count times of between 1 and 10 seconds per step. General identification of the phases was usually done from 10-70° 2θ , step size 0.04° with a count time 5 s per step. More accurate scans as those required for the results presented in chapter 4 were done at step sizes of 0.01° 2θ and count times of 10 seconds per step.

Si was used as an internal standard for the calibration of the peaks used in chapter 4. The addition and purity of the silicon added is discussed in Chapter 4, section 4.2.2.

Diffraction data for pure phases, obtained from the ICSD database, was used to identify what phases were present in the appropriate samples. Phase analysis was done by importing simulated scans from the JCPDS cards for the pure phases found in the ICSD database and were then layered underneath the diffractogram obtained by XRD for that sample. Each simulated scan will be labelled by phase and JCPDS number.

3.4.5: Particle Sizing

A mastersizer (Malvern instrument SB 20) was used to measure the volume median diameter. The accuracy of the instrument is $\pm 4\%$ (volume median diameter). Particle sizes in the range 0.1-80 μm were sized using a 45 mm focal length lens. Calgon was used as a dispersant in water and the mixture of calgon water and particles was homogenised using a stirrer set at a pump speed of 40% of its maximum and the ultrasonics were adjusted to 80% of its maximum.

3.4.6: Scanning Electron Microscopy

A JOEL scanning electron microscope (SEM) equipped with a field emission gun operating between 8-20 kV was used to assess the microstructure of the polished samples. Element analysis was done using an energy dispersive spectrometer (EDS) analyser.

3.4.7: Transmission Electron Microscopy

A Phillips CM 200 transmission electron microscope (TEM) equipped with a field emission gun operating at 20 kV was used. An EDS analyser was used to analyse the elemental composition of the various phases in the material. Sample preparation is discussed in more detail in Chapter 5.

3.4.8: Inductively Coupled Plasma Analysis

Inductively coupled plasma analysis (ICP) was done on samples in order to determine the elemental composition of samples. A Spectrociros CCD ICP analyser equipped with an end on plasma and a coupled charged detector was used to do the analyses. The plasma was operated at 1200 W. Samples were digested in a solution containing 5 ml HNO₃ (55%), 2 ml HCl (32%) and 3 ml HF (40%) by microwave digestion in a Multiwave 3000 SOLV analytical sample preparatory microwave supplied by Anton Paar. Digestion was done at 1400 W for 1.5 hours. Calibration of the CCD ICP analyser was done from elemental standards obtained from Merck.

3.4.9: Hardness and Fracture Toughness Testing

Polished samples were analysed by Knoop and Vickers microhardness testers. The microhardness was determined for constant loads. The loads varied between 100 and 10 000 g. The hardness reported in chapter 6 will be reported as H_{Kx} or H_{Vx} where K and V represent Knoop and Vickers respectively and x is the load at which the hardness was determined.

Fracture toughness was evaluated using Palmqvist cracks from the Shetty⁴² formula where it is not necessary to know the materials' elastic modulus (E). The formula is given in equation 3.6;

$$K_{IC} = 0.0889 * \sqrt{\frac{H_v * P}{4 * l}} \quad 3.6$$

H_v = Vickers hardness

P = Indentation load and

$l = c - a$ where, 2a is the indentation diagonal and 2c is the length of the full crack.

3.4.10: Thermal Analysis

Thermogravimetric analysis (TGA) was done on a Perkin Elmer TGA 1. Samples of less than 100 mg were loaded into Pt sample holders and the samples were heated under a constant flow of argon gas (UHP) and the mass was continuously monitored against the heating cycle.

Differential thermal analysis (DTA) was performed on a Perkin Elmer DTA 7. Samples of no more than 10 mg were loaded in to a platinum cup. Alumina of mass less than 10 mg (used as a reference material) was loaded in a second platinum cup. The two samples were placed into the DTA in contact with two separate thermocouples and then heated. The temperature differential was measured against either the time or temperature of the DTA furnace program.