

ON THE PLASTIC DEFORMATION MECHANISMS OF WC-Co ALLOYS AT HIGH TEMPERATURE

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering.

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Signature of candidate)

_____ day of _____ (year) _____

ABSTRACT

This dissertation reports systematic work aimed at determining the plastic deformation mechanisms that led to strains at fracture as high as 4.7% in WC-Co alloys at 1000°C when subjected to 3-point bending tests. The three grades investigated have a Co content of 15wt% and WC grain sizes of 1.3, 0.35 and 0.3µm respectively and were received after they were tested in bending.

Fractography, macrostructural and microstructural investigations were carried out in attempts to identify the mechanisms leading to the large strains. Techniques used included light microscopy, scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and quantitative image analysis.

Through comparisons of the results from the three grades at various temperatures, it was possible to establish that the large strain at 1000°C are mainly due to cracking and cobalt drift. During the fractographic investigations it was found that the grades which contained VC as a grain refiner exhibited steps on the WC grains and that fracture propagated preferentially along the stepped WC grain boundaries.

To

my wife: Feng Zhang

my parents: Yushan Han, Wen Hu

For

their love and support

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1 INTRODUCTION

Tungsten carbide cobalt (WC-Co) alloys are the most widely used cemented carbides, which are a range of very hard, refractory, wear-resistant alloys made by powder metallurgy techniques. WC-Co alloys consist of hard but brittle WC grains bonded by tough cobalt as the binder. Their outstanding properties, such as hardness, wear-resistance and corrosion resistance, lead to their wide and continuous usage in different applications.

One of the main applications of WC-Co is cutting tools, which can reach temperatures of up to 1000°C in service. At such high temperatures, WC-Co undergoes plastic deformation. The deformation mechanisms and microstructural changes at high temperatures are not yet completely understood. Therefore, a study of WC-Co samples that were tested at high temperature is important and may lead to improvements in the material.

S. Luyckx [Luyckx et al., 1998] and Yu. V. Milman [Milman et al., 2002] carried out 3-point bending tests on WC-Co alloys with different compositions at temperatures of up to 1000°C. They reported that grades with a high cobalt content (15wt%) exhibited a strain at fracture at 1000°C of up to 4.7%. This implies that substantial plastic deformation must have occurred. The specimens tested by Luyckx and Milman are examined in this project in the attempt of determining the plastic deformation mechanisms and the role of each phase (WC and Co) in the deformation.

Light microscopy and scanning electron microscopy including field emission SEM were used in the examination of the outer faces and the fracture surfaces of

specimens that exhibited the highest strains. The plane outer faces of the samples were examined in an attempt to identify grain boundary sliding and other changes in the microstructure. The fracture surfaces were examined in an attempt to observe plastic deformation in the binder and, possibly, in the carbide.

The dissertation has the following structure. The motivation for this research is presented in this chapter. Chapter 2 reviews basic literature on WC-Co and in particular results from other researchers on WC-Co deformation mechanisms. The literature survey is followed by Chapter 3 where the method, the samples and the techniques are described. In Chapter 4, the results obtained are reported and in Chapter 5 the results are discussed and conclusions are drawn.

2 LITERATURE SURVEY

2.1 Structure, Properties and Manufacture of WC-Co

2.1.1 Introduction

Cemented carbides (or hardmetals) are a range of quite hard, refractory, wear-resistant alloys made by powder metallurgical techniques [Brookes, 1998]. From a technical point of view, cemented carbides are one of the most successful and most widely used composite materials at present [Exner, 1979].

WC-Co (tungsten carbide cobalt) alloys are the most widely used cemented carbides. WC-Co alloys are sintered materials consisting of brittle tungsten carbide crystals bonded by a tough cobalt-based binder [Luyckx, 2000]. Fig. 2.1 shows a typical microstructure of WC-Co.

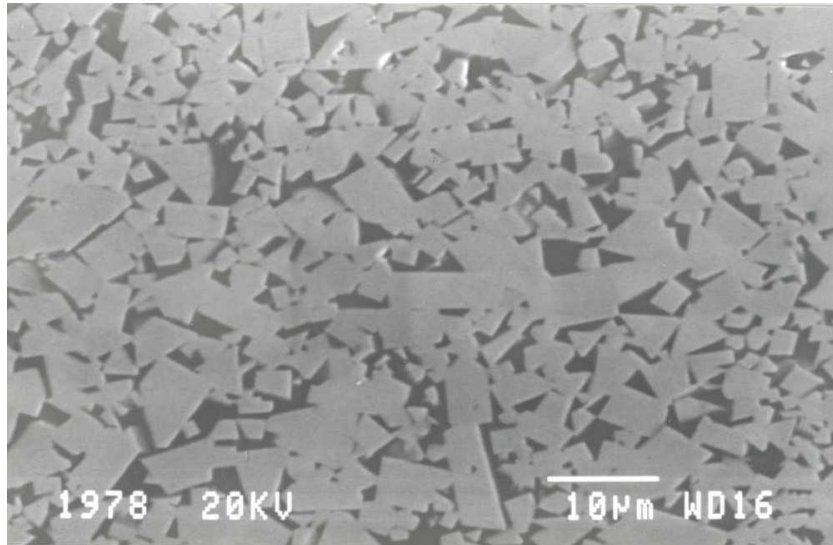


Fig. 2.1: A typical microstructure of WC-12wt%Co. The white angular particles are WC grains and the dark material between the WC grains is cobalt.

2.1.2 Structure and Applications of Tungsten

Tungsten (W) is defined as the element whose nucleus contains 74 protons ($z=74$). Tungsten has a stable BCC (body-centered cubic) structure with two atoms per unit cell [Yih, 1979].

Unalloyed tungsten is widely used in electrical and electronic applications.

2.1.3 Structure and Properties of Tungsten Carbide

It is well established that tungsten forms two hexagonal carbides, the monocarbide WC and the subcarbide W_2C . Only the monocarbide of tungsten is suitable for making satisfactory hardmetals [Exner, 1979].

Tungsten monocarbide WC prevails in cemented carbides as the hard phase. More than 98% of the hardmetals contain WC and more than 50% of those hardmetals are pure WC-Co alloys. [Exner, 1979]

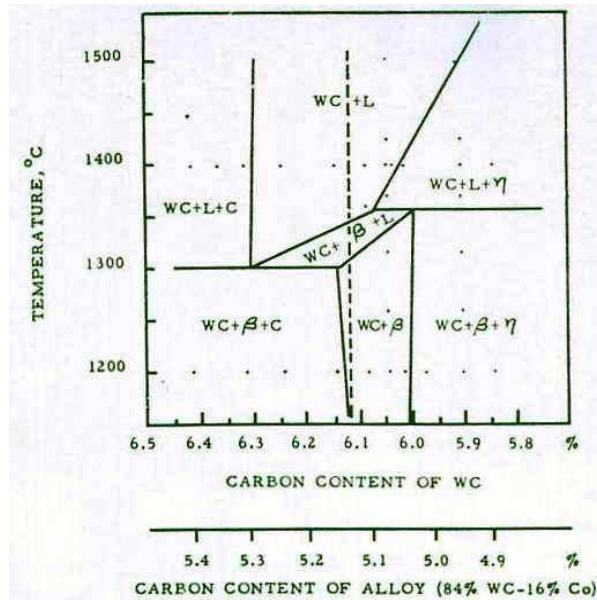


Fig. 2.2: Vertical section through ternary diagram W-Co-C at 16 wt% Co. [Gurland, 1954]

WC has a very small range of homogeneity. Fig. 2.2 is a vertical section through the ternary diagram at 16 wt% Co. The theoretical carbon content of stoichiometric WC is 50 at% or 6.12 wt%. ‘Eta (η) phase’ can be found in substoichiometric WC-Co (carbon content less than 6.12 wt%). ‘Eta phase’ is a complex carbide of tungsten and cobalt having the formula $\text{Co}_{3-x}\text{W}_{3+x}\text{C}$, with x ranging from 0 to 1 [Johansson, et al., 1978]. The properties of ‘eta phase’ are different from those of WC and Co. In a scanning electron microscope (SEM), ‘eta phase’ could be recognized by its less regular shape and other characteristics, e.g. cobalt deficiency and micropores surrounded by dissolution steps in WC, which are steps parallel to crystallographic planes. The ‘eta phase’ is a possible site of fracture initiation [Luyckx, 1981]. If the carbon content is higher than 6.12

wt%, graphite clusters appear, which may be weak points in the material as well [Luyckx, 1967].

Tungsten carbide, WC, has a simple hexagonal structure, with $a = 0.2900\text{nm}$ and $c = 0.2831\text{nm}$, i.e. $c/a = 0.976$. In the simple tungsten atoms lattice, the carbon atoms are either all at $1/3, 2/3, 1/2$ or at $2/3, 1/3, 1/2$ void positions [Luyckx, 1967]. There are two atoms per unit cell, as shown in Fig. 2.3. The shape of equilibrium crystals is shown in Fig. 2.4. The crystals are prisms which have a triangular shape, two equilateral $\{0\ 0\ 0\ 1\}$ faces and three $\{1\ 0\ \bar{1}\ 0\}$ prismatic sides and truncated corners. The reason why there are two sets of three equivalent $(1\ 0\ \bar{1}\ 0)$ planes rather than six equivalent $(1\ 0\ \bar{1}\ 0)$ planes is that the different spacing of the tungsten and carbon planes in the $[1\ 0\ \bar{1}\ 0]$ direction causes the crystal planes of $(1\ 0\ \bar{1}\ 0)$ -type to be highly polar prism [Exner, 1979].

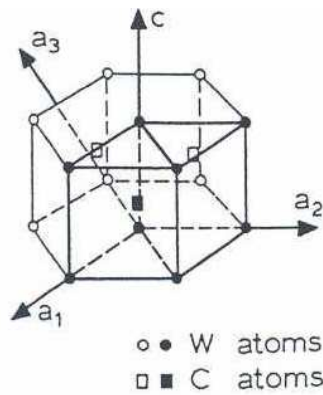


Fig. 2.3: Structure of WC and the position of C atoms. Heavy lines outline a unit cell [Exner, 1979].

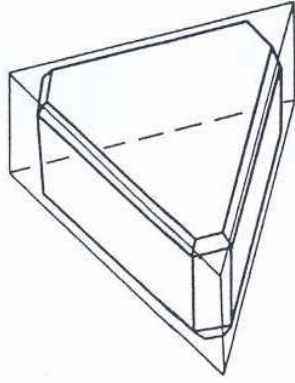


Fig. 2.4: Schematic shape of equilibrium WC crystals [Exner, 1979].

The slip system of WC is $\{1 \bar{1} 0 0\} \langle 1 1 \bar{2} 3 \rangle$, i.e. slip occurs along the $\{1 \bar{1} 0 0\}$ planes [Luyckx, 1970] (which usually happens in hexagonal crystals with ratio $c/a < 1$ [Luyckx, 1967]) and in the $\langle 1 1 \bar{2} 3 \rangle$ directions.

The microhardness of WC is different when measured on different crystallographic planes. The hardness of the $\{0 0 0 1\}$ planes and the $\{1 \bar{1} 0 0\}$ planes is about 2200HV1 and 1100HV1 respectively [Luyckx et al., 1992]. Different hardness data can be obtained when the hardness is measured on the remaining planes.

On polycrystalline WC samples, the hardness satisfies the Hall-Petch relationship:

$$H_{WC} = H_{0WC} + K_{0WC} d^{-1/2} \quad (1)$$

Where H_{WC} is the hardness of polycrystalline WC, d is the mean grain size of the randomly oriented WC grains, H_{0WC} is the average hardness of a WC crystal (over all possible crystallographic planes), and K_{0WC} is the Hall-Petch coefficient, related to the ease of slip transfer across WC/WC grain boundaries. At room temperature, $H_{WC} = 1330 \text{ kgfmm}^{-2}$ [Luyckx, 2000].

WC has an extremely high modulus of elasticity ($E=696 \text{ GN m}^{-2}$), second only to diamond. The high E of WC, accompanied by the high thermal conductivity ($1.2 \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$) and a low coefficient of thermal expansion ($5.2 \times 10^{-6} \text{ K}^{-1}$), are advantages of WC compared to most other materials [Exner, 1979].

Fig. 2.5 shows the classification of WC grain sizes in WC-Co alloys according to the Fachverband für Pulvermetallurgie, which is widely accepted and regarded as an effective standard [Brookes, 2005].

Grain size	Designation
< 0.2 μm	Nano
0.2 - 0.5 μm	Ultrafine
0.5 - 0.8 μm	Submicron
0.8 - 1.3 μm	Fine
1.3 - 2.5 μm	Medium
2.5 - 6.0 μm	Coarse
> 6.0 μm	Extra coarse

Fig 2.5: Classification of WC grain sizes according to the Fachverband für Pulvermetallurgie [Brookes, 2005].

2.1.4 Structure and Properties of Cobalt

The binder phase of cemented carbides is the metal component which binds the carbide grains. The metals are selected from group VIII in the periodic table [Almond, 1983] and the most common metal used as a binder is cobalt (Co), followed by nickel (Ni) and iron (Fe) [Exner, 1979].

In cemented tungsten carbides, cobalt is used almost exclusively and accounts for more than 95% of production. Its excellent wetting and adhesion with its

advantageous mechanical properties explains its popularity [Exner, 1979]. The cobalt content in commercial grades of WC-Co is between 5 and 25 wt-%, corresponding to 8.5-37.2% vol.-%Co [Gurland, 1970].

Cobalt powder used in cemented carbides is usually produced by hydrogen reduction of cobalt oxide. Powders are produced hydrometallurgically [Brookes, 1998]. The typical particle shape of Co is a chain-line arrangement of small rounded particles sintered during reduction. The typical cobalt specific surface area is in the order of $1 \text{ m}^2\text{g}^{-1}$ with a crystallite size of approximately 50nm [Exner, 1979].

Cobalt has two kinds of allotropic modifications at different temperatures. Below 417°C, cobalt has a HCP (hexagonal close pack) structure; while at higher temperatures up to the melting point (1495°C) cobalt is stable with a FCC (face centered cubic) structure [Luyckx, 1967].

In sintered alloys containing WC, the cobalt binder phase has mostly a cubic lattice, even at room temperature. The cubic lattice is not transformable by annealing. Because cobalt in the WC-Co alloy is a solid solution containing 2-10wt% tungsten depending on the carbon content and processing conditions [Gurland, 1970], the reason for the cubic structure is that dissolved tungsten and carbon can stabilize the cubic modification [Luyckx, 1967].

The hardness of pure cobalt has been reported to be between 140 and 240HV [Luyckx, 2000]. The data varies due to different methods of sample preparation. Depending on the composition, a solid solution with W and C in cobalt can be up to 100% harder than pure cobalt. The hardness of the cobalt binder in WC-Co also satisfies a Hall- Petch type relationship:

$$H_{Co} = H_{0Co} + K_{0Co}\lambda^{-1/2} \quad (2)$$

where H_{Co} is the hardness of the cobalt, λ is the thickness of the cobalt layer, usually called ‘the cobalt mean free path’, H_{0Co} is the mean hardness of cobalt, and K_{0Co} is the Hall-Petch coefficient, related to the ease of slip transfer [Luyckx, 2000].

2.1.5 Manufacture of WC-Co Alloys

Fig. 2.6 shows the process of WC-Co production.

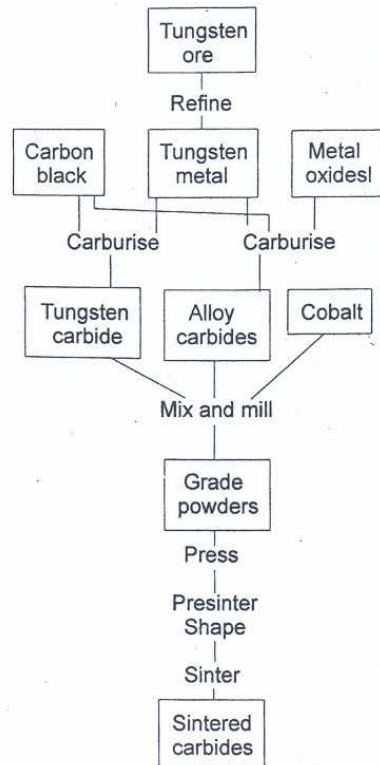


Fig. 2.6: Schematic flow chart for WC-Co production [Brookes, 1998].

2.1.6 WC-Co and its Properties

Since WC is brittle and hard while cobalt is soft and ductile, neither of them alone satisfies tool materials requirements. However, when combining these two constituents, WC provides hardness and wear resistance and cobalt contributes to the necessary toughness. Therefore WC-Co is both hard and tough.

2.1.6.1 Interaction between WC and Co

As mentioned above, WC is soluble in Co at high temperatures and its solubility affects the properties of Co in WC-Co. Co, however, is not soluble in WC.

At high temperature in the reaction $W + C = WC$, there seems to exist an equilibrium constant, which represents a reciprocal relationship between the dissolved tungsten[W], and the dissolved carbon[C] in cobalt, i.e. $[W] \cdot [C] = \text{constant}$. The amount of tungsten dissolved in cobalt is greatly reduced when WC precipitates during cooling from the sintering temperature, especially during slow cooling. Besides the cooling rate and the carbon content, the size of the cobalt domains also determines the tungsten content in the cobalt binder [Exner, 1979].

2.1.6.2 Main Properties of WC-Co

In tool materials, hardness is a measure of resistance to penetration and abrasion, and toughness is the ability to absorb energy by deformation without cracking. Hardness in WC-Co is mainly contributed by WC and toughness mainly by cobalt [Gurland, 1970].

2.1.6.2.1 Hardness

There are many factors affecting the hardness of WC-Co. The cobalt content and the WC grain size are the most important ones. The hardness of WC-Co can be varied from about 800HV to more than 2000HV with different combinations of cobalt content and WC grain size. The hardness of WC-Co decreases with increasing cobalt content at all carbide grain sizes and decreases with increasing grain size at all cobalt contents [Luyckx, 2000].

Lee and Gurland expressed the relationship between the hardness of WC-Co, its microstructure and its composition by the equation:

$$H_{WC-Co} = CV_{WC}H_{WC} + (1 - CV_{WC}) H_{Co} \quad (3)$$

where H_{WC-Co} is the hardness of the alloy, H_{WC} and H_{Co} are the hardness of the WC and Co phases, which can be obtained from equations (1) and (2), V_{WC} is the volume fraction of the WC phase, C is the ‘contiguity’, which is defined as the ratio of the grain boundary area and the total surface area of the carbide phase. $CV_{WC} = V_c$, and V_c is the ‘continuous carbide volume’ or ‘volume fraction of the carbide skeleton’. The definition of V_c is the volume fraction occupied by that part of the WC grains which are involved in forming infinitely long chains of connected particles. Those grains which are totally surrounded by the cobalt binder do not contribute to V_c . Equation (3) agrees with experimental results [Luyckx, 2000].

Makhele-Lekala et al. worked on the relationship between the hardness, grain size and mean free path of WC-Co further. They obtained an empirical formula and a theoretical model, both of which did not reproduce high hardness WC-Co values. They then modified and derived the following semi-empirical formula for the hardness of WC-Co:

$$H_{WC-Co} = 4100 \left[k' \left(\frac{\lambda}{2d^{1/2}} \right)^{1/2} + 1 \right]^{-1} - 130 \quad (4)$$

where $k' = 22.3 \text{ mm}^{-1/4}$, fitting all the results well [Makhele-Lekala et al., 2001].

The contiguity C decreases with increasing cobalt content. It also decreases when increasing sintering time and sintering temperature. At constant sintering conditions, contiguity is independent of carbide crystal size. When varying both cobalt content and sintering conditions, Exner reported the following relationship:

$$d = \lambda (1 - C) (1 - V_{Co}) / V_{Co} \quad (5)$$

where d is the mean linear size of WC, λ is the mean linear intercept of Co, V_{Co} is the volume fraction of the binder phase and $V_{Co} = 1 - V_{WC}$ [Exner, 1979].

The effect of temperature on hardness is important because in most applications WC-Co is used at temperatures up to 900-1000°C. The knowledge of this effect contributes to suitable materials selection and material properties improvement.

According to Milman et al., the hardness of WC-Co decreases with increasing temperature and the hardness of WC-Co with coarser grain size decreases more rapidly than that of finer grain size grades [Milman et al., 1997]. At all temperatures, the following Hall-Petch type relationship between hardness and grain size has been found:

$$H_{WC-Co} = H_0 + K_y d^{-1/2} \quad (6)$$

where

$$H_0 = H_{0WC} V_{WC} C + H_{0Co} (1 - V_{WC} C) \quad (7)$$

and

$$K_y = K_{0WC} V_{WC} C + K_{0Co} (1 - V_{WC} C) B^{-1/2} \quad (8)$$

with

$$B = (1 - V_{WC}) / [V_{WC} (1 - C)] \quad (9)$$

since from equation (5):

$$\lambda = (1 - V_{WC}) d / [V_{WC} (1 - C)]$$

The softening of WC-Co with increasing temperature is expected to be due to the intrinsic softening of the component phases (WC and Co) up to about 600°C while above 600°C the softening is expected to be controlled by the ease of slip transfer across grain boundaries (WC/WC, Co/Co, WC/Co) [Milman et al., 1999]. Above $\pm 800^\circ\text{C}$ other mechanisms may contribute to the decrease in hardness, e.g. grain boundary sliding.

Other factors, such as grain size distribution, binder composition, carbon content, porosity may affect the hardness of WC-Co in different ways.

2.1.6.2.2 *Strength and Toughness*

“Strength” generally means fracture stress in tension or bending. Toughness is regarded as a measure of the energy absorbed before fracture. In the case of cemented carbides, these two concepts are often used interchangeably. In practice, the transverse bend test (TRS) has been widely used to evaluate both strength and toughness of cemented carbides [Gurland, 1970].

The fracture toughness of WC-Co is increased by raising the Co content and increasing the WC grain-size [O’Quigley et al., 1996] (see Fig. 2.7).

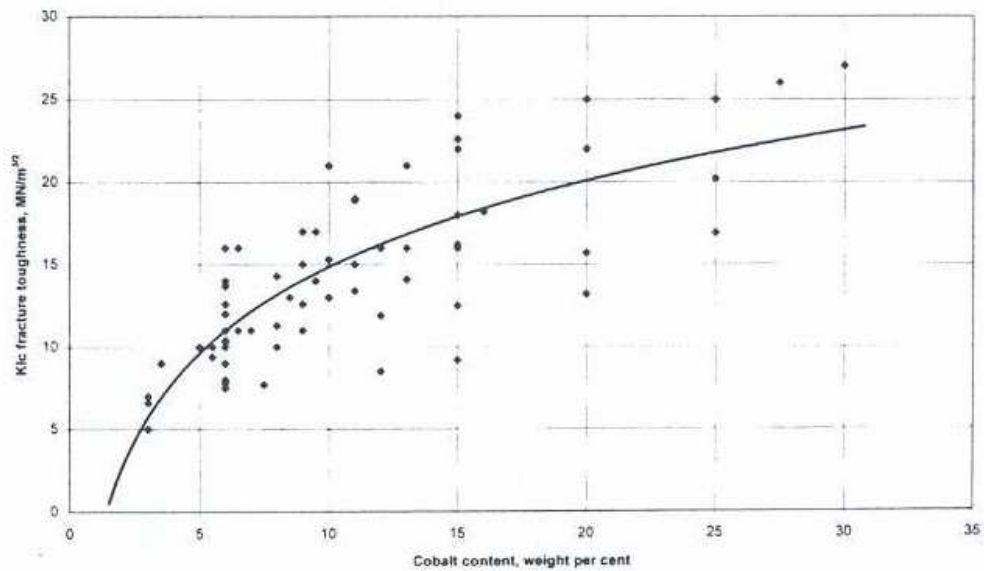


Fig. 2.7: Fracture toughness K_{IC} of commercial WC-Co hardmetals as a function of cobalt content. The scatter is mainly due to variations in grain size [Brookes, 1998].

Compressive strength and yield stress vary similarly to hardness, i.e. decrease with increasing cobalt content and WC particle size.

When the WC grain size is constant, the transverse rupture strength and tensile strength increase with increasing cobalt content and reach a maximum value, which depends on grain size [Gurland, 1970]. When the cobalt content is fixed, the transverse rupture strength also shows a maximum at intermediate grain sizes (see Fig. 2.8).

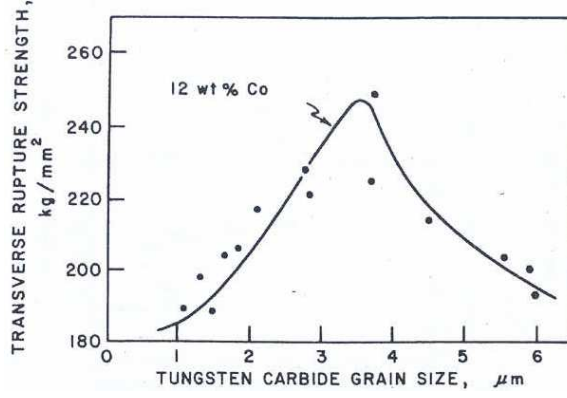


Fig. 2.8: Effect of grain size on transverse rupture strength of cemented tungsten carbide [Yih, 1979].

In order to express the effect of both cobalt content and WC particle size, the mean free path in cobalt is often used. ‘Nominal’ mean free path is the average distance in the cobalt between carbide particles:

$$\lambda_n = d \frac{V_{Co}}{1 - V_{Co}} \quad (10)$$

where λ_n is the ‘nominal’ mean free path, d is the mean linear intercept particle size of WC, and V_{Co} is the volume fraction of cobalt. Fig. 2.9, which presents the transverse rupture strength as function of cobalt mean free path, describes this relationship. The ‘nominal’ mean free path is based on an idealized structure in which all particles of WC are regarded as non-contiguous. It is related to the ‘true’ mean free path by:

$$\lambda = \frac{d}{1 - C} \frac{V_{Co}}{1 - V_{Co}}$$

which takes the contiguity C into account [Gurland, 1970]. The ‘true’ mean free path describes the material more precisely because in practice WC grains are contiguous.

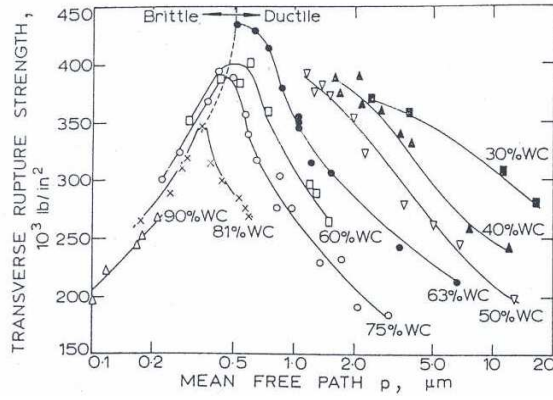


Fig. 2.9: Transverse rupture strength vs. mean free path [Gurland, 1970]

2.1.6.2.3 Relationship between Hardness and Fracture Toughness

When keeping the WC grain size constant, the relationship between hardness and fracture toughness is linear:

$$H_{WC-Co} = -a(d)K_{IC} + b(d) \quad (11)$$

where $a(d)$ and $b(d)$ are functions of the WC grain size [O'Quigley et al., 1996].

When the WC grain size also changes, the reciprocal relationship between the hardness and the toughness of WC-Co is more complex [Luyckx, 2000].

2.1.6.3 Relationships between Some Microstructural Parameters

The relationship between d , λ , C and the cobalt volume fraction V_{Co} (see equation 5), indicates that each of the four parameters depends on the other three parameters. However, Luyckx and Love [Luyckx and Love, 2003] found that λ and the d are directly proportional when V_{Co} is constant and

$$m = \lambda / d = 0.214 - 0.691 V_{Co} + 5.975 V_{Co}^2 \quad (12)$$

with m a dimensionless function of Co content. Equation (5) can be rewritten as:

$$C = 1 - \frac{V_{Co}}{(1-V_{Co})\lambda/d} = 1 - \frac{V_{Co}}{(1-V_{Co})(0.214 - 0.691V_{Co} + 5.975V_{Co}^2)} \quad (13)$$

Therefore equation (12) and (13) allow one to get the microstructural parameters of a WC-Co alloy of known composition by measuring only one parameter.

2.1.7 Applications

The manufacture of tips and inserts for cutting tools is by far the most important part of the hardmetal industry. Cutting tool applications include turning, facing, milling, boring, reaming, threading, filing, broaching, shearing, and glass cutting [Yih, 1979]. Metalcutting utilizes perhaps two-thirds of hardmetal production. Almost every kind of tool can be obtained with carbide cutting edges [Brookes, 1998].

Apart from metalcutting; mining, oil-industry and masonry tools represent up to a quarter of hardmetal tonnage for the purpose of rock-drilling and stone-cutting. Hardmetals are also used for metalforming tools (e.g. carbide rolls), pressing dies (e.g. wire-drawing dies, blanking and shearing dies, dies for the production of synthetic diamond or cubic boron nitride manufacture, etc.), structural components (e.g. rotating seals, compressor plungers, lathe jaws, boring bars, grinding spindles, pulverizing pins and bearing journals), wear parts (e.g. nozzles, guides, plungers, balls, etc.) and abrasive grits. Since World War II, tungsten carbide has been used in projectile cores for armor-piercing weapons [Brookes, 1998].

2.2 Plastic Deformation and Fracture Mechanisms of WC-Co

2.2.1 Plastic Deformation of WC

The study of plastic deformation of WC started in the mid 1960s. The observations of slip bands and dislocation network formations proved wrong the assumption that WC was as brittle as ceramics. As in most crystalline materials, there is dislocation movement in WC during plastic deformation [Östberg, 2005]. WC grains deform by slip and as introduced in section 2.1.3, the slip system of WC is $\{1 \bar{1} 0 0\} \langle 1 1 \bar{2} 3 \rangle$, i.e. slip occurs along the $\{1 \bar{1} 0 0\}$ planes and in the $\langle 1 1 \bar{2} 3 \rangle$ directions [Luyckx, 1970]. Dislocations and stacking faults may be introduced during the milling process and survive through the sintering treatment [Roebuck and Almond, 1979].

2.2.2 Plastic Deformation of Co

In WC-Co the Co-based binder phase has a heavily faulted FCC structure [Almond, 1983]. Partial dislocation movement is the most important plastic deformation mechanism [Rettenmayr et al., 1988]. The intersections of stacking faults in the cobalt binder are possible void nuclei [Sigl and Fischmeister, 1988].

2.2.3 Plastic Deformation and Fracture of WC-Co at Room Temperature

2.2.3.1 Plastic Deformation at Room Temperature

At room temperature, plastic deformation of WC-Co under tensile or compressive conditions was studied by means of bending tests, indentation tests and scratch tests [Bartolucci and Schlössin, 1966]. All these tests show plastic deformation of WC grains in the form of slip lines. Cracks were generated at the intersections of slip planes in WC grains or of slip planes and WC/WC interfaces, which led to transgranular or intergranular cracks.

2.2.3.2 Fracture Propagation

Apart from the initiation of cracks as a result of slip, fracture often starts from pores, inclusions or ultra-large WC grains at room temperature [Luyckx, 1975]. These flaws lead to stress concentrations in the surrounding area and are always the most possible fracture origin location.

After the initiation of cracks in either WC grains or at WC/WC grain boundaries, or from flaws, ductile tearing of cobalt occurs. WC-Co alloys of different composition and different WC grain sizes fracture similarly [Hong and Gurland, 1983].

There are four possible fracture paths [Almond, 1983]:

- a) transgranular fracture of WC;
- b) fracture across Co binder region;
- c) interfacial fracture along WC/Co boundary;
- d) interfacial fracture along WC/WC boundary.

A schematic crack tip region in WC-Co is shown in Fig. 2.10.

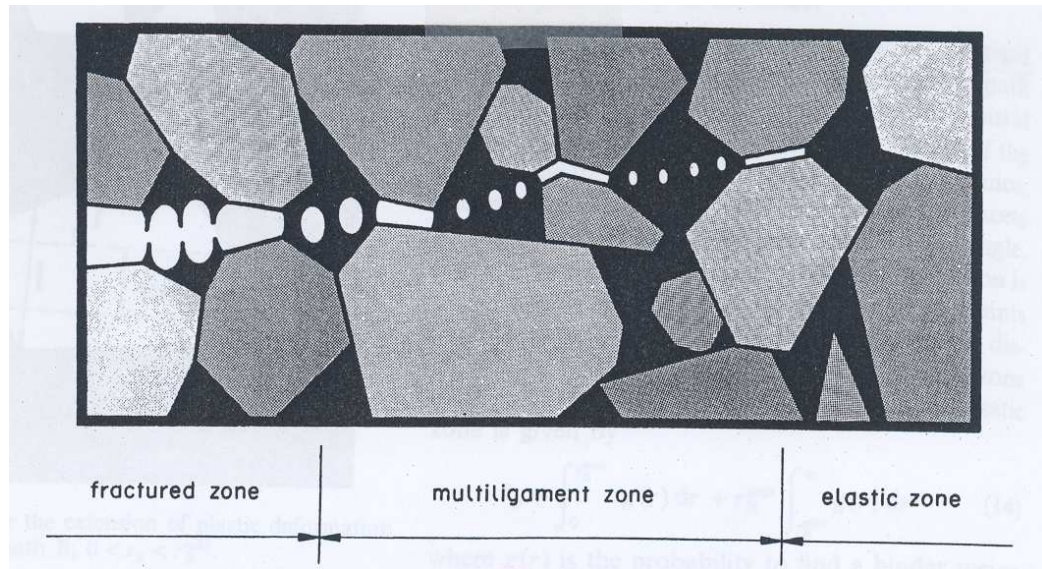


Fig. 2.10: A schematic crack tip region in WC-Co [Sigl and Fischmeister, 1988].

The cleavage or debonding of WC grains puts the cobalt phase under tensile stress and therefore the cobalt stretches. Since the cobalt volume is constant and cobalt is continuous with the WC grains, cobalt ligaments contract during the elongation process. In the mean time, the crack tip blunts and voids form inside the ligament. With the increasing stress, the blunted crack tip and the internal voids gradually grow and coalesce. The cobalt ligament finally fractures and the crack moves on. The crack tip region in Fig. 2.10 is divided into three zones: elastic zone where materials suffer only elastic deformation; the multiligament zone, where ligaments have formed but not yet fractured and fractured zone where the cobalt ligament have fractured. The multiligament zone is a steady zone where the cobalt ligaments bridge the crack path [Sigl and Fischmeister, 1988].

2.2.3.3 Fractographic Features

WC grains that undergo transgranular or intergranular fracture look different on a fracture surface. The transgranularly fractured WC grains may exhibit river patterns, which are typical of cleavage fracture. The intergranular cracks or debonding of WC/WC boundaries show smooth non-matching WC grains on each side of the fracture surfaces [Hong and Gurland, 1983].

WC-Co fracture may propagate in a stable or unstable manner. Stable fracture surfaces from fatigue or high stress static loading tests are characterized by step-like features in the cobalt, as shown in Fig. 2.11. These features seem to be due to brittle rather than ductile fracture. They are believed to be the result of FCC $\rightarrow$ HCP transformation in cobalt under stress and to be a combination of cleavage microcracks [Erling et al., 2000].

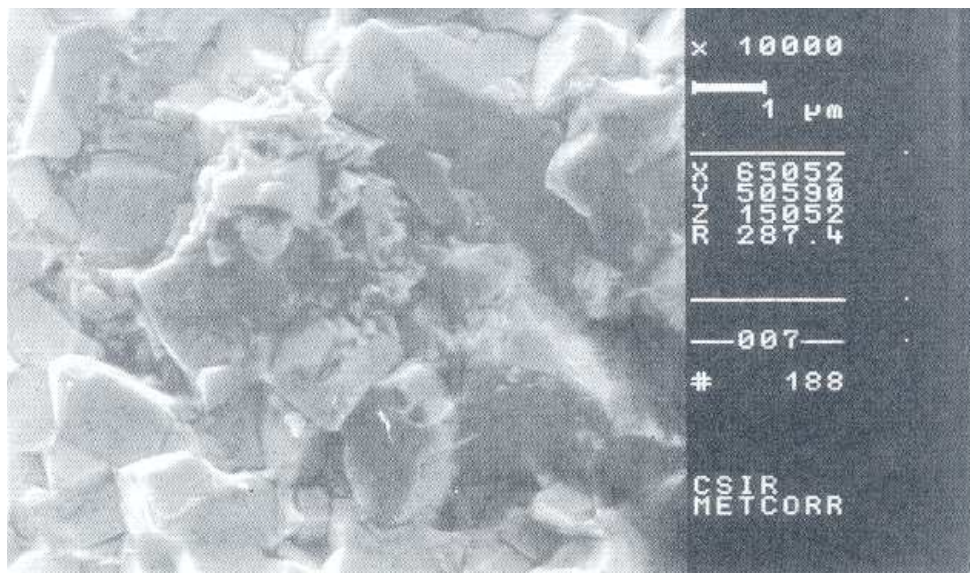


Fig. 2.11: Scanning electron micrograph of the stable fracture surface of a WC-10wt%Co sample tested in 4-point bending fatigue [Erling et al., 2000].

Ridges and dimples in cobalt are the characteristics of unstable fracture surfaces (see Fig. 2.12). Ridges result from a microscopic necking process in the cobalt layers after cracks initiated. Thus ridges on one fracture surface should be matched by ridges, not grooves, on the mating fracture surface. Dimples appear as microscopic hollows outlined by ridges and correspond to dimples on the matching fracture surface. Dimples indicate the presence of microvoids. Void nucleation is the controlling factor in dimple development [Sigl and Fischmeister, 1988] and results from possible cavitation during sintering, possible cavities around solute particles and volume changes in FCC $\rightarrow$ HCP in cobalt under stresses [Luyckx, 1977].

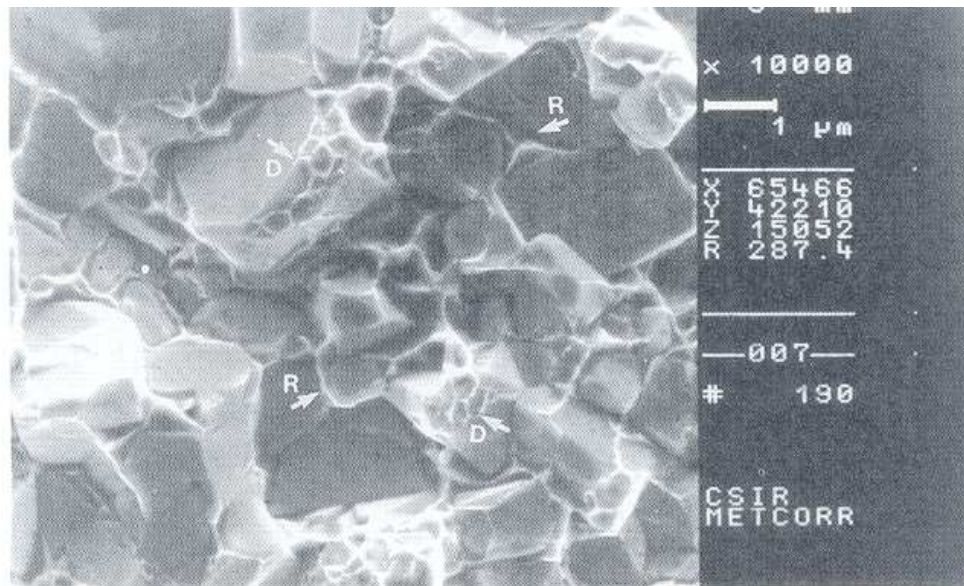


Fig. 2.12: Scanning electron micrograph of the unstable fracture surface of a WC-10wt%Co sample. The binder exhibits a large number of dimples (as “D” indicated) and ridges (as “R” indicated) [Erling et al., 2000].

At a macroscopic level, WC-Co fracture surfaces often exhibit fracture mirrors, which are smooth, circular areas surrounding the fracture origins under tensile conditions [Luyckx and Sannino, 1983]. Hong and Gurland studied the fracture

process of WC-Co alloys, classified and compared the fracture appearances according to different compositions and WC grain sizes [Hong and Gurland, 1983].

2.2.4 High Temperature Performance of WC-Co

2.2.4.1 High temperature performance of WC

Plastic deformation of single WC grains at room temperature and at 1000°C was studied by means of micro-indentations [Hibbs et al., 1983]. It was concluded that at room temperature, the WC slip system is the same as presented in section 2.2.1. It was also concluded that at 1000°C, the slip system of WC is the same as that at room temperature.

Rowcliffe further studied the indentation damage on the basal plane of WC single crystals at increasing temperatures (from room temperature to 1000°C) and under increasing loads (up to 450N). His results agreed with those of Hibbs's and showed the hexagonal pattern of slip lines caused by plastic deformation above room temperature instead of the triangular pattern obtained at room temperature [Rowcliffe, 1983].

According to Mari [Mari et al., 1999], few dislocations have been found in the WC grains at 900°C, even in deformed ones, but this is not the general case.

2.2.4.2 High Temperature Performance of Co

Partial dislocations bordering stacking faults, which are common in cobalt at room

temperature, become mobile above about 600°C. The stacking faults shrink and the network becomes loose. At high temperature, recombined perfect dislocations make up the cobalt microstructure [Mari et al., 1999].

Compression testing at temperatures between 1100 and 1200°C was carried out to study the high temperature plastic flow in a Co-9WC alloy (see Fig. 2.13).

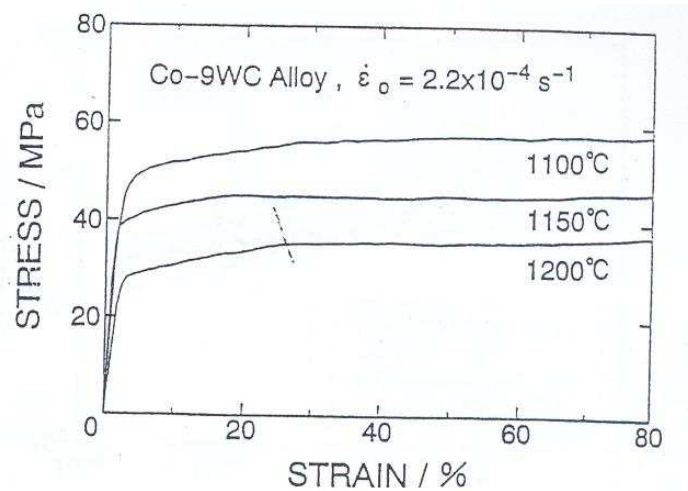


Fig. 2.13: Stress-strain curves in the Co-9WC solid solution alloy at an initial strain rate of $2.2 \times 10^{-4} \text{ s}^{-1}$ [Lee, 1996].

It was suggested that the deformation in a Co-9WC alloy in this temperature range is controlled by a single deformation mechanism: dislocation creep [Lee, 1996].

2.2.4.3 High Temperature Hardness of WC-Co

High temperature hardness, defined as the resistance to plastic deformation, is a useful property to provide information on high temperature plastic deformation.

The hardness of polycrystalline WC, WC-Co, and different surfaces of WC single crystals was investigated [Lee, 1983] and the results are shown in Fig. 2.14.

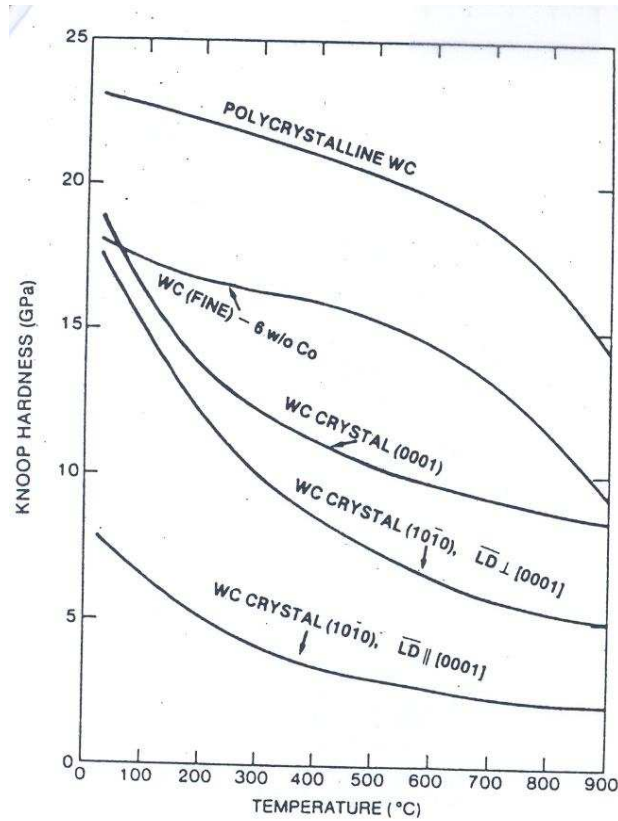


Fig. 2.14: High temperature Knoop hardness curves of polycrystalline WC, WC-Co, and different faces of WC single crystal (9.81N test load). LD refers to Load Direction [Lee, 1983].

As shown in Fig. 2.14, the hardness of different surfaces of single WC crystals decreases in a similar way with increasing temperature. The hardness of polycrystalline WC is higher than that of WC-Co. It can also be noticed that polycrystalline and single WC crystals soften with increasing temperature at different rates.

Co rich W-Co-C alloys were also investigated (Fig. 2.15).

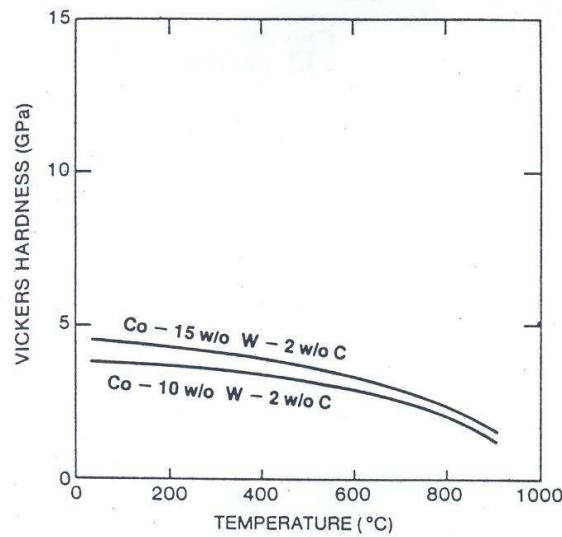


Fig. 2.15: High temperature Vickers hardness of ternary W-Co-C alloys with varying compositions (9.81 N test load) [Lee, 1983]. When the amount of tungsten increases, the hardness of the ternary alloys increases.

Milman et al. measured the hardness of WC-6wt%Co in the temperature range -196 to 900°C [Milman et al., 1997]. Their results agree with those of Lee's. They further suggested that below 600°C, the softening is due to the softening of WC and the binder phase, while above 600°C, the ease of slip transfer across grain boundaries plays a major role [Milman et al., 1999].

2.2.4.4 High Temperature Strength of WC-Co

The transverse rupture strength behavior of WC-10wt%Co was investigated by 3-point bending in the temperature range 25 to 1000°C [Acchar et al., 1999]. Results are shown in Fig. 2.16.

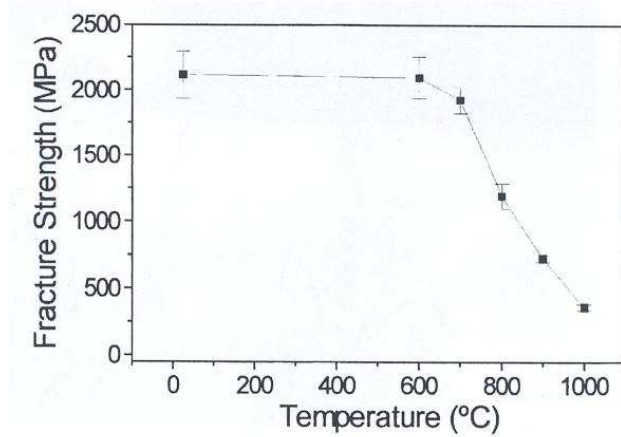


Fig. 2.16: Transverse rupture strength (fracture strength) of WC-10wt%Co as a function of temperature [Acchar et al., 1999].

As seen in Fig. 2.16, below 600°C, the TRS is constant, while above 600°C, severe decline of TRS occurs with increasing temperature. At 1000°C, the TRS is only about one seventh of that at 600°C. Fractographic analysis showed significant oxidation at high temperature, which may contribute to the strength degradation [Acchar et al., 1999].

Luyckx et al. and Milman et al. carried out a broader investigation on the TRS of different grades with different cobalt content and different WC grain size. Fig. 2.17 and Fig. 2.18 are the TRS results:

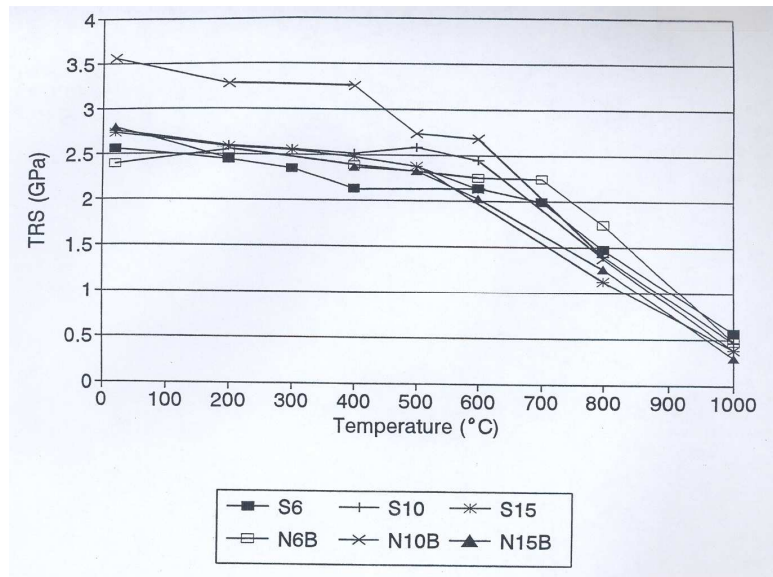


Fig. 2.17: A comparison of the TRS values obtained from S (micron) grades, whose grain size is $1.3 \mu\text{m}$, and NB grades (submicron, grain size $0.35 \mu\text{m}$ and containing 0.4wt%VC) at increasing temperature [Luyckx et al., 1998].

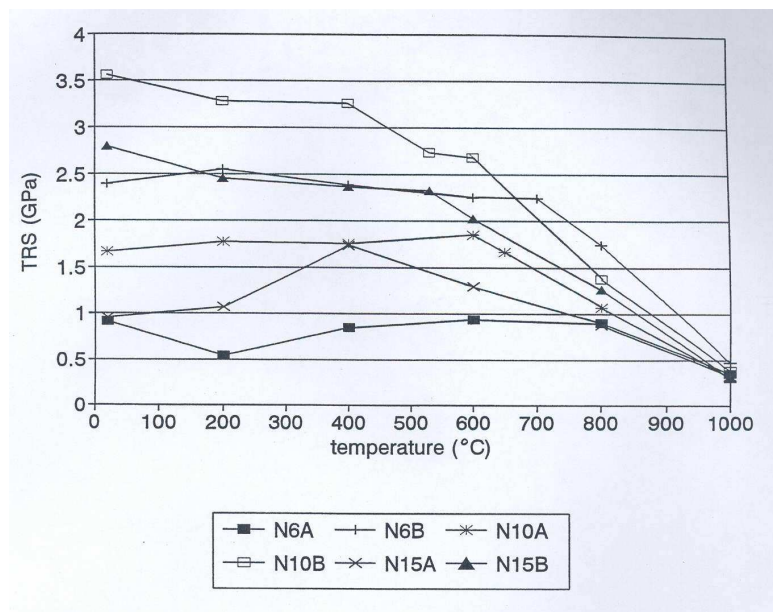


Fig. 2.18: A comparison of the TRS values obtained from NB grades (submicron, grain size $0.35 \mu\text{m}$ and containing 0.4wt%VC) and NA grades (submicron, grain size $0.30 \mu\text{m}$ and containing 0.8wt%VC) at increasing temperature [Luyckx et al., 1998].

The TRS values decrease slowly with increasing temperature up to 600°C and decrease more rapidly at higher temperatures. The TRS values of the S and NB grades are comparable (Fig. 2.17) while the TRS values of the NA grades are lower than that of the NB grades (Fig. 2.18).

The ductility at fracture of the S and NB grades is shown in Fig. 2.19, and of the NA and NB grades in Fig. 2.20.

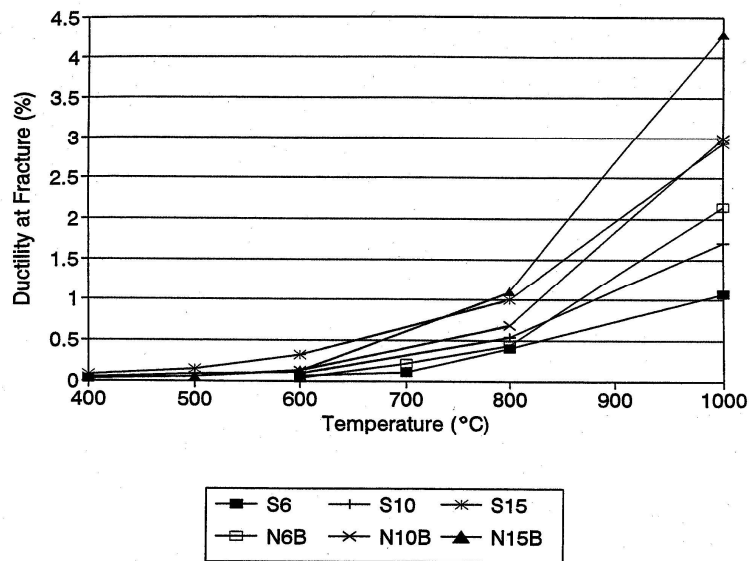


Fig. 2.19: A comparison of the ductility at fracture of the S and NB grades [Luyckx et al., 1998].

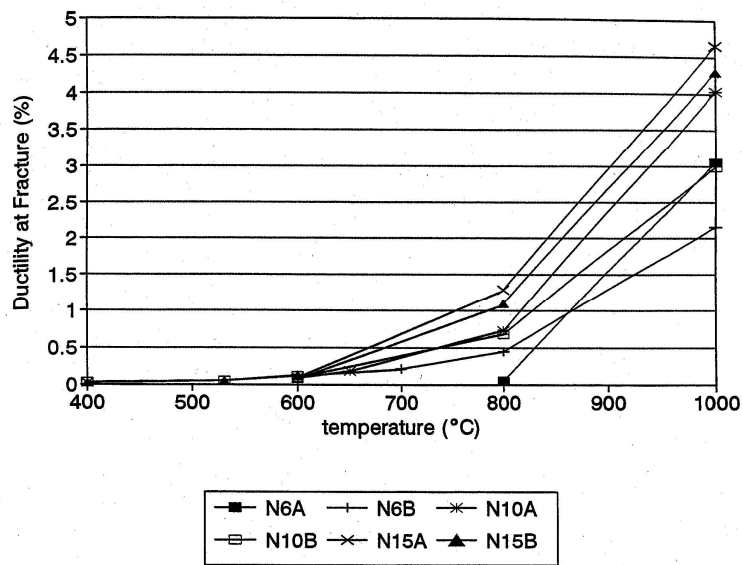


Fig. 2.20: A comparison of the ductility at fracture of the NA and NB grades [Luyckx, et al., 1998]

From Fig. 2.19 and Fig. 2.20, it is shown that above about 600°C, the amount of plastic deformation increases rapidly and at 1000°C, the finer the grain size, the higher the ductility at fracture.

The samples of the N15A, N15B and S15 grades in the above figures are those investigated in current project.

2.2.4.5 High Temperature Plastic Deformation of WC-Co

Apart from the plastic deformation of the WC grains and Co binder phase, WC-Co is expected to deform plastically at high temperature by means of a) grain boundary sliding and b) diffusion [Östberg, 2005].

Grain boundary sliding (GBS) is defined as “plastic shearing of a grain in relation to another grain, parallel to the interface plane and if the interface is comparably

thin the grains can be considered as two rigid blocks of materials gliding against each other” [Östberg, 2005]. GBS occurs at temperatures higher than $0.4T_m$ and always occurs with grain boundary migration (GBM) and dislocation movement [Östberg, 2005]. There are three ways in which GBS can be accommodated (see Fig. 2.21).

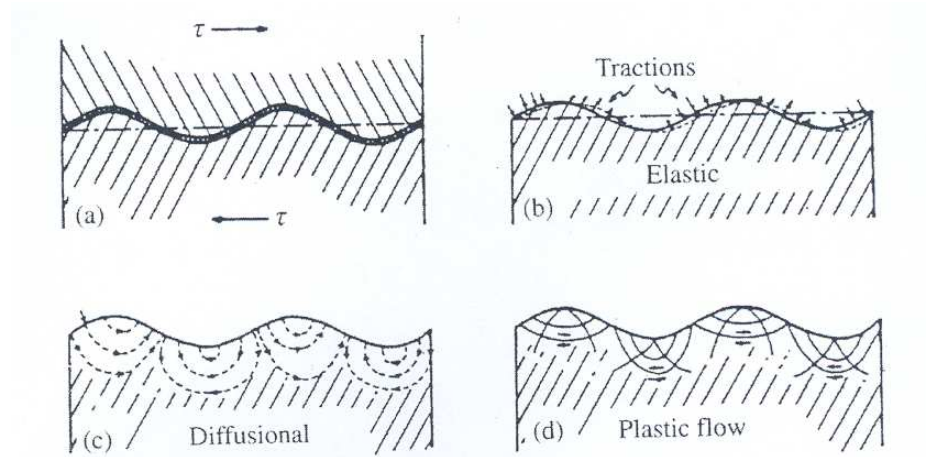


Fig. 2.21: Illustration of the different accommodation processes for grain boundary sliding. A shearing stress is applied (a). The resulting movement is first elastically accommodated (b). At higher temperatures accommodation can be achieved by diffusional movement of material along the boundary from compressive to tensile regions (c). Accommodation may also occur by plastic flow through movement of lattice dislocation (d) [Sutton and Balluffi, 1995].

Efforts have been put into detecting grain boundary sliding of WC-Co at high temperatures. One successful example is a photolithographic technique applied by Mari et al. [Mari et al., 1992]. A very fine chromium grid was deposited on the surface of the samples. The samples were then subjected to 3-point bending tests at 900°C . The examination afterwards detected WC grain debonding (see Fig. 2.22) and grain boundary sliding (see Fig. 2.23) by means of the grid lines displacements. No deformation of the WC grains up to 900°C was observed.

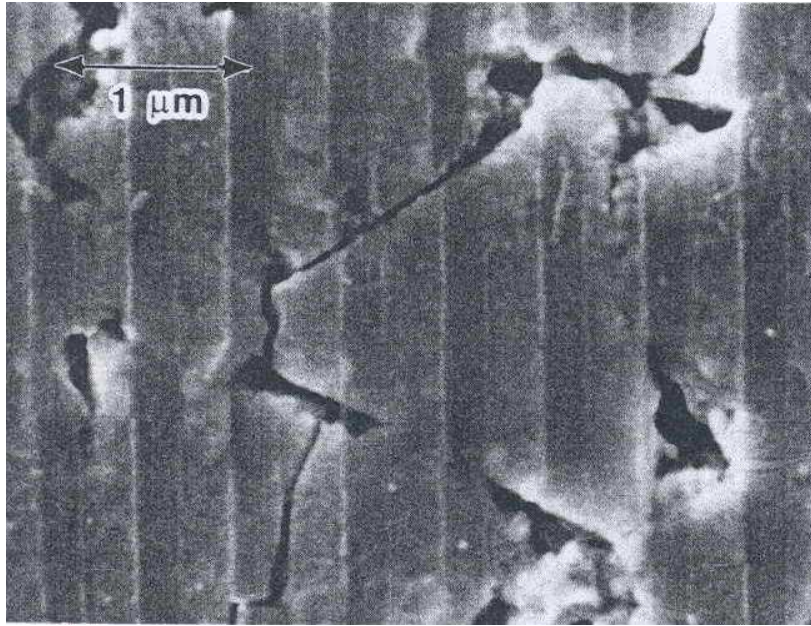


Fig. 2.22: An example of the debonding of the WC grains. The grit lines are 0.5μm. Debonding of the WC grains is detectable through grit displacement [Mari et al., 1992].

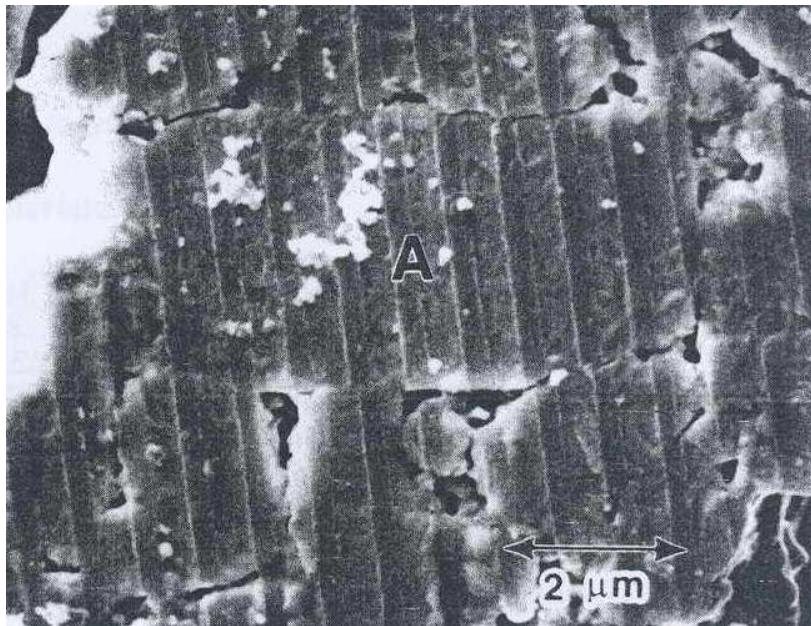


Fig. 2.23: Example of grain boundary sliding. The sliding of the upper and lower grain boundaries of the WC grain A can be observed [Mari et al., 1992].

According to Schaller [Schaller, 2000], the brittle-to-ductile transition temperature in WC-Co is associated with grain boundary sliding, as well as dislocations and faults. According to Östberg, diffusion, whose rate increases with temperature, including interstitial diffusion, substitutional diffusion and grain boundary diffusion, play an important role in assisting GBS [Östberg, 2005].

2.2.5 Plastic Deformation Mechanisms of WC-Co

Three temperature domains have been defined by Mari according to the different mechanical behavior of WC-Co [Mari et al., 1999]:

- a) domain I: $T < 800\text{K}$ (527°C), the deformation is elastic;
- b) domain II: 800K (527°C) $< T < 1100\text{K}$ (827°C), limited plasticity occurs;
- c) domain III: $T > 1100\text{K}$ (827°C), extended plastic deformation is observed.

According to Mari, in domain I, the material is brittle and the deformation is elastic, although other researchers have observed plastic deformation in WC-Co at temperatures $< 800\text{K}$ [Luyckx, 1968]. In domain II, as indicated in section 2.2.4.2, partial dislocations in cobalt become mobile. The dislocation density of WC grains in deformed WC-Co does not seem to increase much in domain II. In domain III, grain boundary sliding (GBS) occurs. GBS takes place with the assistance of grain boundary diffusion and lattice diffusion. Cobalt seems to contribute to increasing the WC skeleton strain rate at low stress because the infiltration of cobalt atoms into the grain boundaries enhances GBS. While at higher stresses, GBS is accommodated by WC deformation [Mari et al., 1999].

Milman et al. [Milman et al., 2002] also suggested three temperature ranges for

WC-Co with different plastic deformation mechanisms. The temperature ranges are similar to those defined by Mari:

- a) low temperature range: $t < 600-800^{\circ}\text{C}$, only Co binder plastic deformation possibly takes place;
- b) middle temperature range: $600-800^{\circ}\text{C} < t < 1000^{\circ}\text{C}$; both Co binder and WC skeleton deform plastically;
- c) high temperature range: $t > 1000^{\circ}\text{C}$ (or $t > 800^{\circ}\text{C}$ for submicron grades), GBS is the plastic deformation mechanism.

Östberg studied the plastic deformation of WC-Co at high temperature in tool-cutting. A model from Östberg (see Fig. 2.24) helps to visualize the mechanisms of deformation of WC-Co at high temperature. In an area under stress, tensile or shear stresses can be induced according to the orientation of WC grains. WC grains slide over each other under shear stresses or separate under tensile stresses. Since it is generally energetically favorable for WC grains to form two WC/Co boundaries rather than two free surfaces, cobalt diffuses into the boundary at the same time as the WC grains separate. This infiltration of Co may be explained by the geometry in Fig. 2.25. At high temperatures (above 1000°C), where “diffusion” happens fast, the binder phase will easily penetrate along the WC boundaries [Östberg et al., 2005].

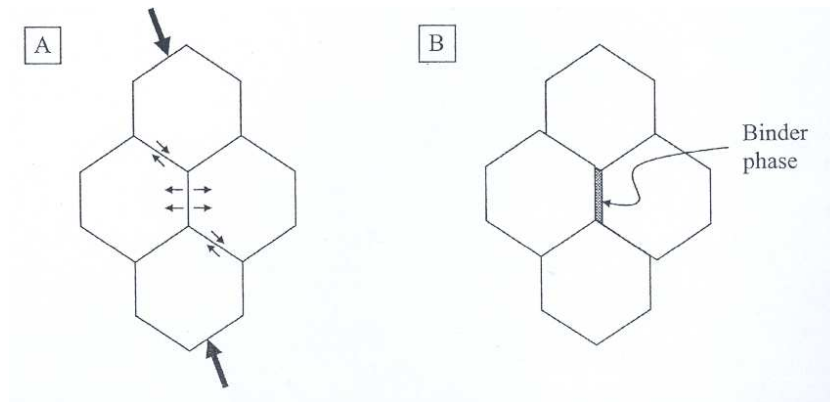


Fig. 2.24: A schematic model for visualizing the formation of a binder phase layer between two WC grains [Östberg et al., 2005].

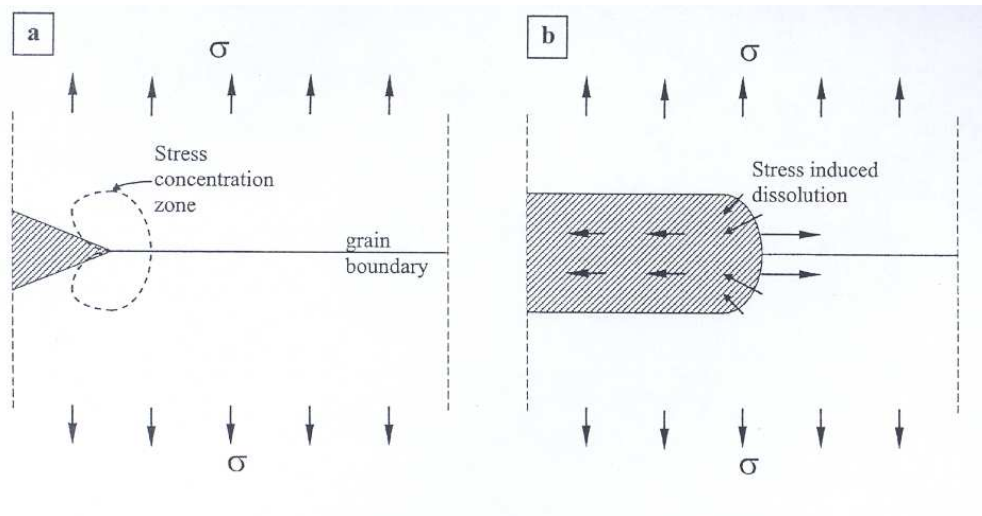


Fig. 2.25: Geometry of a model for grain boundary infiltration by binder phase in a boundary subjected to a tensile stress at high temperature [Östberg et al., 2005]

Cobalt, as layers and as pockets, was observed by Mari at interfaces between WC grains (see Fig. 2.26). This agrees with the findings of Östberg. However, Mari did not show that the layers and pockets were not there before deformation.

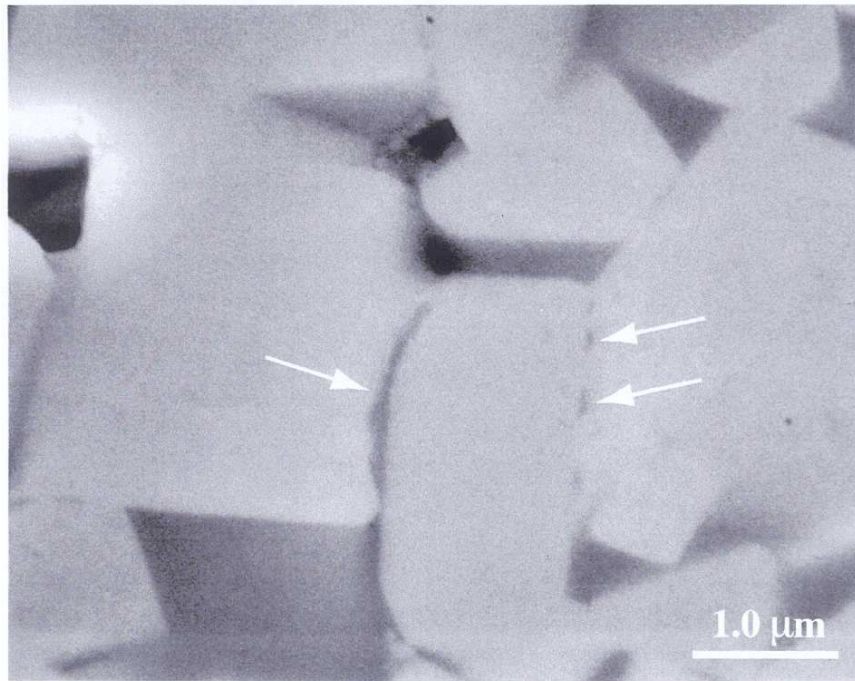


Fig. 2.26: SEM micrograph of a WC-17wt%Co after deformation at 1000°C. A Co layer and pockets between WC grains are indicated by arrows [Mari et al., 1999]

Movement of WC grains is made easier with fully or partly infiltrated cobalt and GBS occurs under shearing and tensile stresses. Östberg also points out that lattice diffusion in adjacent WC grains or dislocation movement is required to accommodate GBS [Östberg et al., 2005].

The major controlling mechanism of WC-Co plastic deformation at high temperature is proposed to be infiltration of cobalt and dissolution of WC grains, which assist GBS [Östberg et al., 2005]. Östberg provided some evidence for both, although the evidence for cobalt infiltration was not totally convincing.

2.3 Formation of Steps on WC Grains

The addition of a small amount of VC is effective to inhibit the grain growth of WC in WC-Co alloys. It has been found that there are fine faceted interfaces or multistep formed along the WC-Co interfaces when VC is added. This phenomenon has been shown to be due to the precipitation of (V,W)C particles at the WC/Co interfaces [Egami et al., 1993] [Lay et al., 2001].

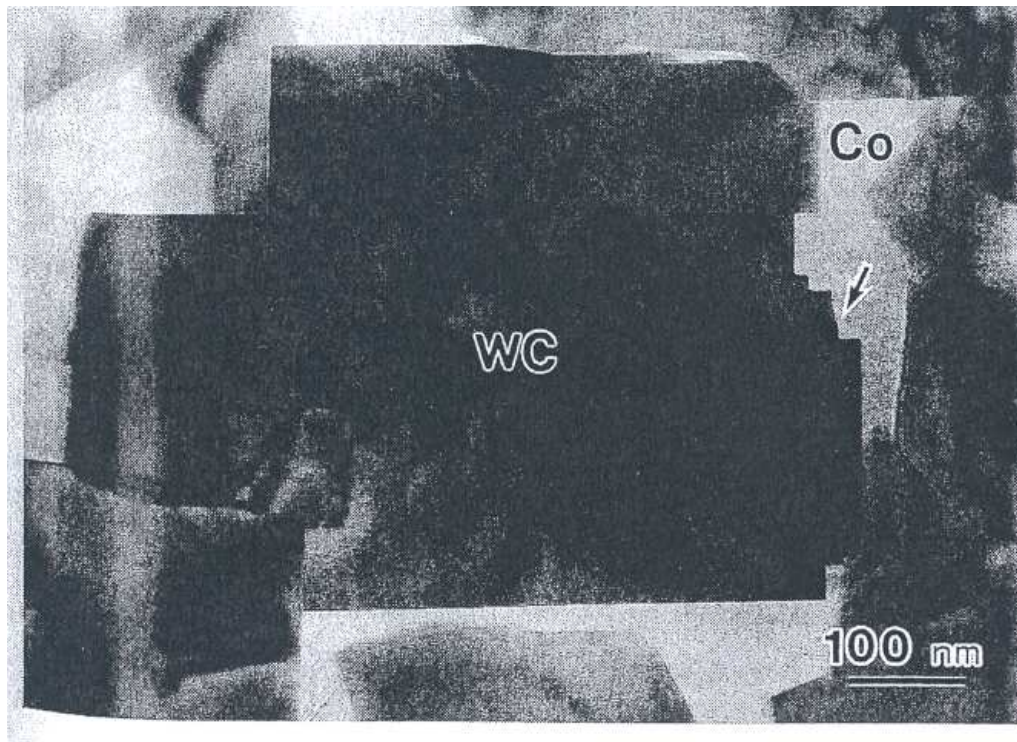


Fig. 2.27: A typical WC grain having a multistep interface in WC-12wt%Co-0.5wt%VC [Jaroenworarluck et al., 1998].

Apart from the addition of VC, carbon content may also lead to changes in the WC grain shape. Faceted steps were reported by Kim et al. (Fig. 2.28) [Kim et al., 2003]. WC-30wt%Co was the fundamental composition to which different amount of carbon (from 0.1wt% to 1.0wt%) was added and steps on WC grains

were observed at the lower carbon contents.

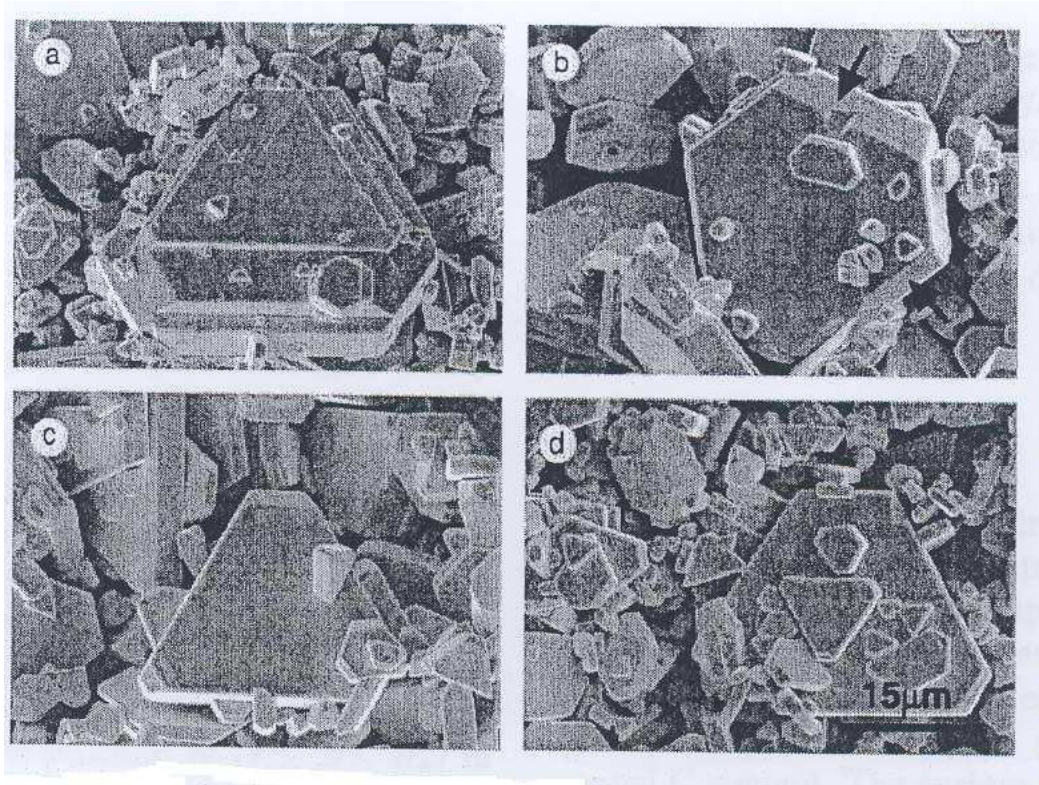


Fig. 2.28: The morphology of WC grains of the WC-30wt%Co alloys with different C contents of (a) 0.1%, (b) 0.3%, (c) 0.7%, and (d) 1.0% [Kim et al., 2003].

Dissolution steps were reported (see Fig. 2.29) [Luyckx, 1984] on the inner surface of a large pore in a material containing eta phase, i.e. with low carbon content, which confirms the results of Kim et al.

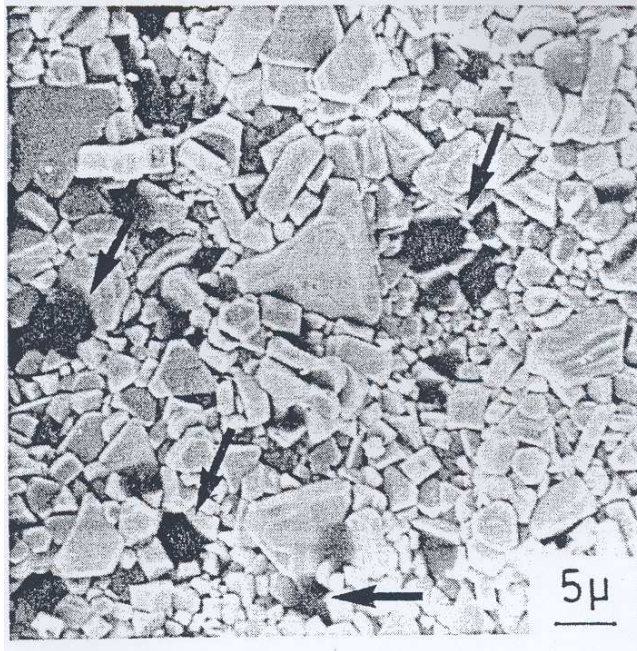


Fig. 2.29: Scanning electron micrograph of the inner surface of a pore in a WC-Co sample. Many WC grains exhibit dissolution steps. The features indicated by arrows are micropores, i.e. small empty cavities [Luyckx, 1984].

During sintering, the outer layers of WC grains dissolve in the liquid cobalt, with the formation of dissolution steps. The dissolution steps disappear when W and C in cobalt reprecipitate as WC at decreasing temperatures. If carbon content is substoichiometric, the W and C react with cobalt to form “eta phase” and dissolution steps are left on the grains [Luyckx, 1984].

3 METHODS, MATERIALS AND TECHNIQUES

Details of the experimental procedures, materials, techniques and apparatus applied in the project are presented in this chapter.

The purpose of the current project was to explain the large strain of the three grades at 1000°C (see Table 3.1 and Fig. 3.1). The strain could be due to:

- a) plastic deformation in the WC grains;
- b) plastic deformation in the Co, considering that at 15wt% Co, the WC skeleton is not continuous;
- c) sliding of the WC grains relative to each other.

In order to look for possible evidence of the above phenomena, the outer surfaces of the specimens were first examined by using light microscopes at low magnification. Depending on the flatness of the surfaces, reflected light or stereo microscopes were chosen. After the macrostructure, the fractography and microstructure were studied by means of electron microscopy at high magnification. When cobalt movement was discovered through fractography, qualitative analysis of the elements was done by EDS microanalysis in different areas. Microstructural parameter (such as cobalt mean free path) measurements were also carried out as an attempt to explain the deformation phenomena by means of linear analysis.

3.1 Materials

This project continues the research of Luyckx [Luyckx et al., 1998] and Milman

[Milman et al., 2002] on submicron and micron WC-Co grades. Table 3.1 lists the three grades investigated in the current project and some of the information and results obtained by Luyckx and Milman.

Table 3.1: Co content, grain size, VC addition and strain at fracture of the three WC-Co grades investigated in this project.

Grades	Co content (wt%)	WC grain size (μm)	VC content (wt%)	Strain at fracture %(at 1000°C)
S15	15	1.30	0	2.9
NYA15	15	0.30	0.8%	4.7
NYB15	15	0.35	0.4%	4.3

The specimens with the original size: $35 \times 4.5 \times 1.2 \text{ mm}^3$ were subject to 3-point bending tests at temperatures ranging from 20 to 1000°C [Milman et al., 2002]. Fig. 3.1 shows the temperature dependence of the strain at fracture. At 1000°C, the strains at fracture of all the three grades were much higher than those at lower temperatures and the finer the grain size, the higher the strain at fracture (not always at lower temperatures).

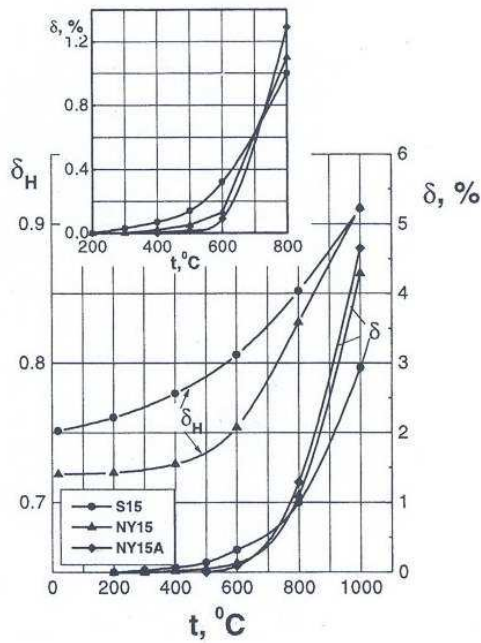


Fig. 3.1: The temperature dependence of the strain at fracture δ and the plasticity characteristic δ_H for the grades investigated in this project. Plasticity characteristic δ_H is determined by the hardness measurement method and is the ratio of the plastic deformation during indentation to the total deformation [Milman et al., 2002]. δ_H will not be discussed here.

After bending, most of the specimens were broken into two or more pieces. Different surfaces of the fragments were investigated for different purposes. A sketch of a specimen fragment with surface names used in this project is shown in Fig. 3.2.

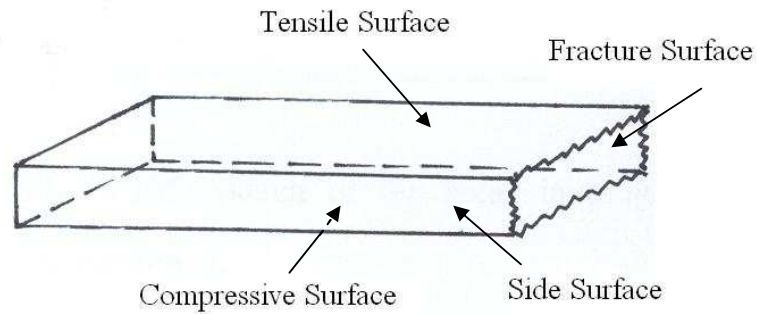


Fig. 3.2: Surface names defined for the specimens in this project

3.2 Specimen Preparation

3.2.1 Specimen Cleaning

Specimens without mounting, especially for fracture surfaces observations were immersed in acetone and cleaned in the BRANSONIC 3510E-MT ultrasonic cleaner for at least 15 minutes. Specimens were stored in a desiccator before use.

3.2.2 Metallographic Specimen Preparation

Specimens were prepared for optical microscopy, electron microscopy and X-ray microanalysis investigations in the metallurgical laboratories. Side surfaces (see Fig. 3.2) were prepared for the purpose of crack identification, microstructural parameter measurement, cobalt concentration investigation and microstructural

observation. Microcracks and other features may be concealed by grooves on the surfaces of the specimens and can not be identified without metallographic preparation. The apparently flat side surfaces were not microscopically flat enough for microstructural analysis.

The specimens were first mounted in a thermosetting bakelite resin in the LECO PR-25 heat and pressure mounting press. Preliminary grinding was carried out manually after the specimen was removed from the press. The specimens were then ground on silicon carbide paper followed by successive grinding on Struers 80, 120, 220, 1200 pans in the Struers PEDEMAX-2 grinding machine to obtain flat surfaces. The specimens were ground on each grade of pans until all the scratches from the preceding operation had been removed. Running water was applied throughout the preliminary grinding stage to remove debris and avoid heat accumulation. Polishing was done by holding the specimen against a rotating lap on the BUEHLER METASERV Universal Polisher. IMP 1 μm synthetic diamond spray with lubricant fluid was used for polishing. Finally, the specimens were cleaned under running water, then with alcohol and finally wiped with cotton wool. The specimens were blown dry quickly to avoid staining and stored in a desiccator.

3.3 Light Microscopy

An investigation of a specimen usually starts with low magnification by a reflected light optical microscope.

3.3.1 Reflected Light Microscope

Light microscopes were used first to observe the specimen surfaces at low magnification. Since WC-Co is opaque, the material must be examined under a microscope with light incident from above [Bradbury and Bracegirdle, 1998], i.e. in a “metallurgical microscope”. A “metallurgical microscope” differs from a microscope with transmitted light in having the objective to act as its own condenser [Bradbury and Bracegirdle, 1998]. A Carl Zeiss Axiotech 25HD binocular reflected light microscope (see Fig. 3.3) was used to observe the flat specimen surfaces. Those flat specimen surfaces include the side surfaces, as well as some flat tensile and compressive surfaces (see Fig. 3.2) of samples tested at low temperatures. A Carl Zeiss AxioCam MRcolour digital camera is installed on the microscope and digital pictures can be taken and analyzed with the software AxioVision 3.1.2.1 linked to the microscope.



Fig. 3.3: The reflected light microscope used in this project

The reflected light microscope was used only for flat surfaces because its depth of field is small. The fracture surfaces are rough and hard to focus and some specimens were fractured and bent after bending tests, therefore a stereo microscope was used to observe these rough surfaces.

3.3.2 Stereomicroscope

The stereomicroscope produces a 3-dimensional picture of the object. It has a long working distance and considerable depth of field.

A Nikon SMZ 1500 stereomicroscope with a Nikon digital camera DXM 1200 was used in this project (see Fig. 3.4). The digital camera is linked to a computer and digital pictures were taken by the software Nikon ACT-1 (Version 2.20).



Fig. 3.4: The stereomicroscope used in this project

For strain calculations, digital pictures were first taken in the stereomicroscope. Then the pictures were copied to the computer linked to the reflected light microscope, calibrated and measured by the AxioVision software mentioned above.

However, the stereomicroscope does not have the same power of magnification or resolution possessed by the ordinary light microscope [Tribe et al., 1975]. The investigation of rough surfaces at high magnification was carried out by SEM.

3.4 Electron Microscopy

In light microscopy, the depth of field is unsatisfactory, especially at high magnification. The stereomicroscope provides good 3-dimensional images but the magnification that one can get is very low (below 200× in practice). The SEM permits nearly 3-dimensional representation of the object on a 2-dimensional picture over a wide range of magnifications.

Specimens of all grades were investigated in detail by electron microscopy.

3.4.1 SEM (Scanning Electron Microscope)

The SEM has been designed after the TEM (transmission electron microscope) for direct examination of fractures and other surfaces without a need for replica techniques. Since the depth of field is improved 300 times, the resolution at least ten times and magnification is much higher than in the light microscope, the SEM is a powerful instrument in physical and chemical research for examination of rough fractures and other surface contours [Ohnsorge and Holm, 1978].

A JEOL JSM-840 SEM (see Fig. 3.5) was used in this project. Fig. 3.6 shows the schematic cross section of it.

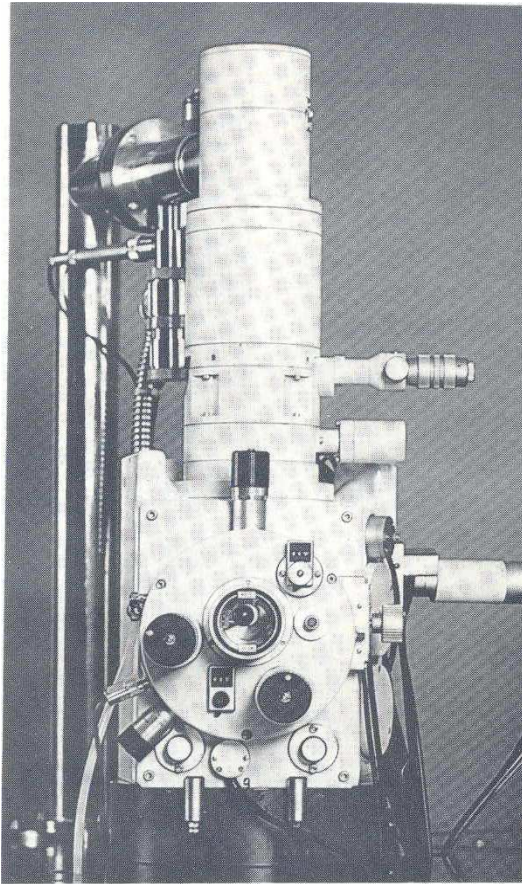


Fig. 3.5: The JEOL JSM-840 scanning electron microscope [Gabriel, 1985].

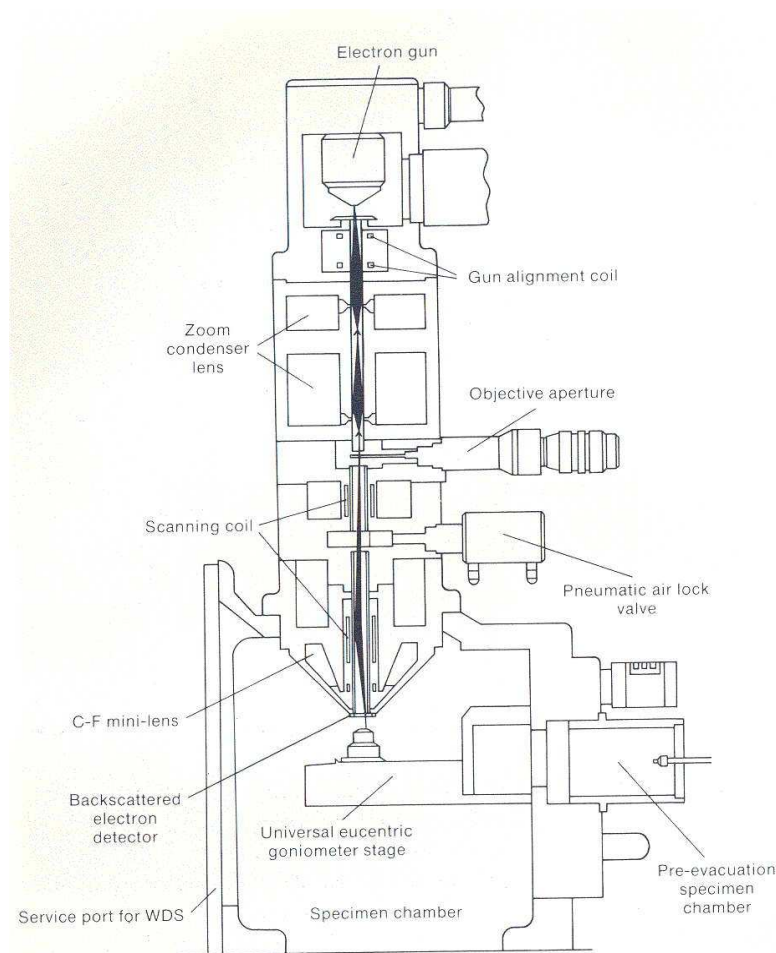


Fig. 3.6: Schematic cross section of the JEOL JSM-840 SEM [Gabriel, 1985].

The SEM fundamentally composes of four parts [Gabriel, 1985]:

- 1) The illuminating/imaging part: comprises an electron gun (produces the electron beam) and an imaging system (includes several magnetic lenses to direct the electron beam onto the sample);
- 2) The information part: consists of the specimen (with different signals resulting from the interaction between the imaging beam and the specimen) and different signal detectors for different data signals;
- 3) The display part: includes the screen of a CRT (cathode-ray tube) for observing and a camera for photographing;
- 4) The vacuum part: consists of equipment for obtaining and maintaining

necessary vacuum environment in SEM.

A tungsten hairpin filament is used in the JEOL JSM-840 SEM as the electron gun.

A Nikon F-301 camera is connected to the SEM to record the image.

When the electron beam produced by the electron gun (called “primary electron beam”) hits the specimen, interactions between them occur and different signals are generated (see Fig. 3.7). In one case, the primary electron beam may strike an electron in the orbit of a specimen atom and knock the orbital electron out of the atom. This collision reduces the energy of the incident beam electron therefore it is a type of inelastic scattering. The specimen electrons which are close to the surface of specimen, liberated by inelastic scattering escape from the material and are known as secondary electrons (SE). Alternately, the beam electron may strike the nucleus of a specimen atom and rebound without appreciable energy loss (elastic scattering). The same beam electron enters and exits the specimen, so it is called a backscattered electron (BSE) beam.

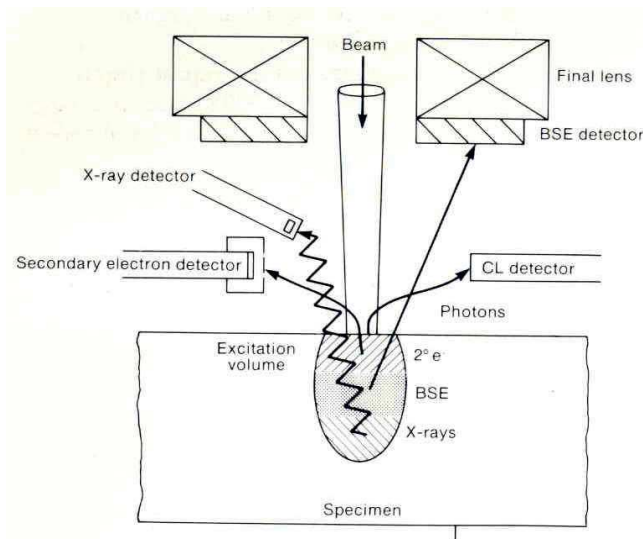


Fig. 3.7: Different signals originated from the interactions between electrons and the material [Gabriel, 1985].

Since the secondary electrons are close to the surface of the specimen, the SE imaging reveals the topography of the specimen and was suitable for observing rough surfaces (especially for the morphology of fracture surfaces) in current project. BSE imaging distinguishes components of different atomic number within an alloy material because of different contrast level each component shows. The probability of a backscattering event from a higher atomic number component is higher than lower atomic number component. So high atomic number components release more BSEs and in consequence appear brighter than from low atomic number components. So BSE imaging provides both topographic and compositional information.

3.4.2 FESEM

Since some of the grain sizes of the materials investigated in this project are very fine (classified into “ultrafine” or “submicron” grades), SEM with tungsten filament as electron gun is not always adequate. Therefore a LEO 1524 FESEM (Field Emission Scanning Electron Microscope) was used for higher resolution and higher magnification.

In the FESEM, to improve the quality of the SEM image, the electron gun has undergone considerable development so as to attain the highest resolution. The process of field emission overcomes some disadvantages of thermoionic emission [Chapman, 1986]. Fig. 3.8 shows the schematization of a field emission electron gun [Goldstein et al., 1981]. An extremely fine single crystal tungsten rod tip (100nm diameter or less) is needed. By means of a very high electric field (at least 10^7 V/m), which is generated between the tip and the first anode, electrons are

drawn from the tip, without the filament heating in a conventional electron gun. The potential difference between the second anode and the tip then accelerates the electrons down the column, in the same way as in a conventional SEM.

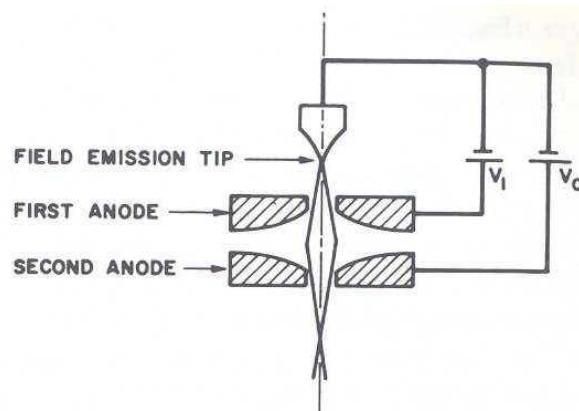


Fig. 3.8: Schematization of a field emission electron gun [Goldstein et al., 1981].

The electron gun brightness (current density per solid angle unit) [Ohnsorge and Holm, 1978] is about 1000 times higher than that of a conventional tungsten hairpin filament. In a SEM, the brightness is an important measure of the resolution obtainable because the higher the brightness, the higher the current density. The very bright source allows very smaller beam spot sizes and in turn improved depth of field and higher resolution.

With the improvement of quality, ultrahigh vacuum system (10^{-8} Pa or lower) is needed for contamination prevention and stable emission.

3.4.3 EDS (Energy-dispersive Spectroscopy)

When the electron beam strikes the surface of the specimen, a number of interactions between electrons and the material occur (see Fig. 3.7). Besides secondary electrons (SE) and backscattered electrons (BSE) mentioned above (in

section 3.4.1), there is also some emissions of X-rays, lightphotons (cathodoluminescence), etc. The X-rays generated are very useful because by measuring their characteristic energy, one can get compositional information on the specimen.

During the interactions, an incident electron may hit an atom and eject one of its inner-shell electrons. An out-shell electron then falls into the vacancy to balance ground potential again and the atom emits an X-ray which has equal energy to the energy difference between the two shells. Since the energy of the emitted X-ray is related to the difference in energy between the uniquely defined levels of the atom, it is called a characteristic X-ray. By measuring the energy or the wave-length of the X-rays, it is possible to qualify and quantify the element. The X-ray microanalysis used in this project in conjunction with SEMs is energy-dispersive spectroscopy (EDS), while electron microprobes typically associate with wavelength-dispersive spectroscopy (WDS) [Goldstein et al, 1981].

In EDS, a Si(Li) solid state detector converts the X-ray quanta to voltage pulses whose weight is proportional to their energy. These pulses are further amplified and passed to a multichannel analyzer (MCA). After some time counting, the energy spectrum of the characteristic X-ray of all elements present in the area hit by the electron beam is obtained [Ohnsorge and Holm, 1978].

A beryllium (Be) window EDS X-ray detector connected to the JOEL JSM-840 SEM was used in microanalysis in this project. Fig. 3.9 shows a typical EDS spectrum obtained in the project. It needs to note that absorption of the X-rays in the Be window degrades the spectrometer resolution at energies below 0.7 keV, so an element having a lower atomic number than sodium (11) is not detectable.

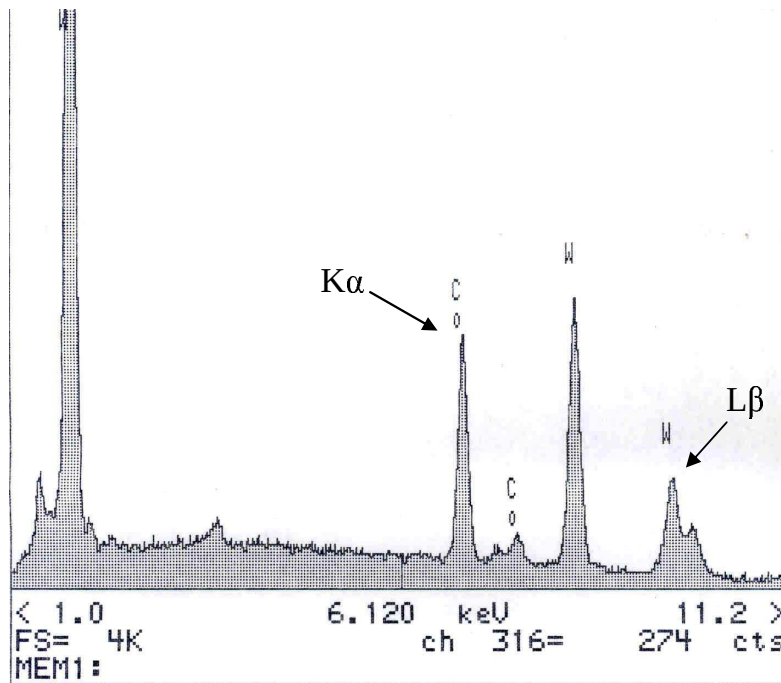


Fig. 3.9 A typical EDS spectrum obtained with current apparatus.

In addition to characteristic X-rays, noncharacteristic X-rays, which forms a “continuum”, are emitted as well. Noncharacteristic X-rays arise from deceleration of beam electrons in the nuclear field of an atom. Their energies are independent of elemental composition and are displayed as background in a spectrum [Gabriel, 1985]. Characteristic X-ray peaks lie above the background so that the background must be subtracted when evaluating the intensity of the peaks. Here, the background was approximately subtracted by drawing a straight line through most of the mean heights of background peaks at high keV, as shown in Fig. 3.10.

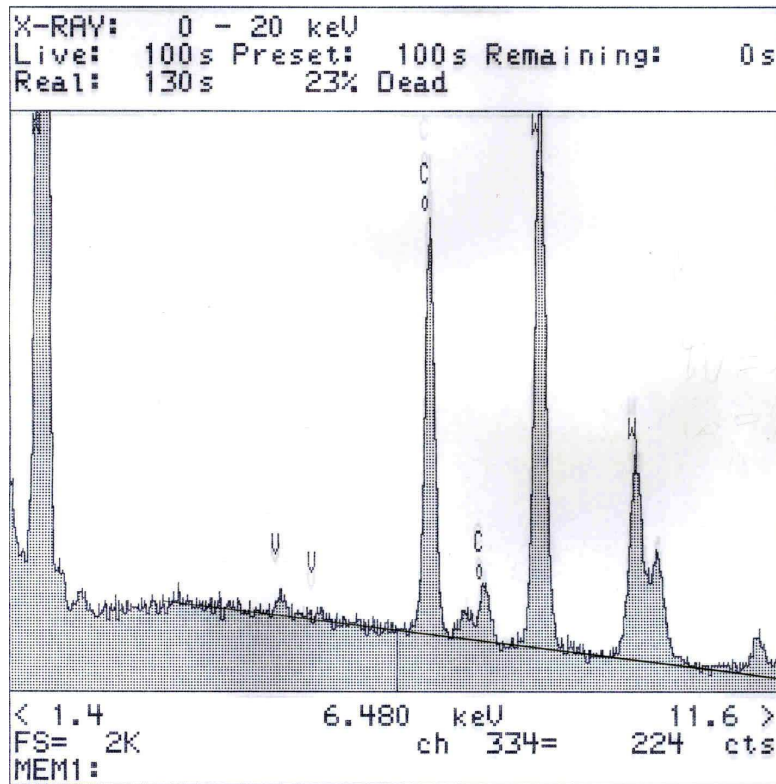


Fig. 3.10 Method to subtract the background used in this project when evaluating the relative intensity of the characteristic peaks.

Since the EDS detector has virtually constant efficiency (near 100%) in the range 3-10 keV, the relative peak heights observed for the families of X-ray lines are close to the values expected for the signal as it is generated in the sample [Goldstein et al., 1981].

In the current project, some fracture surfaces and side surfaces were analyzed by EDS:

- 1) to examine the fracture surfaces, after an ultrasonic acetone bath. General spectra in areas near tensile and compressive sides, at 500× magnification, were obtained.
- 2) to examine the side surfaces after specimens were prepared according to

section 3.2.2. Different areas on the side surfaces, including corners near the tensile and compressive surfaces and areas far from the fracture surfaces, were analyzed, at 500× magnification as well.

- 3) after subtraction of the background, the heights of the W $L\beta$ peaks and the Co $K\alpha$ (see Fig. 3.9) peaks were measured. The ratios of the heights of the Co and W peaks (Co/W) were calculated. The Co/W ratios on the fracture surfaces of specimens tested at different temperatures were compared in order to determine possible changes in cobalt concentration on the fracture surfaces during bending tests and its temperature dependence. The Co/W ratios were also compared with the ratios obtained from the side surfaces of bulk material, to investigate whether cobalt moved from the bulk to the fracture surfaces during testing.

3.5 Microstructure Parameter Measurement

Cobalt mean free path is an important microstructural parameter. In this project its variation at different locations may be valuable to assess the high temperature cobalt deformation. The cobalt mean free path was obtained by linear analysis. Specimens were prepared metallographically, side surfaces were exposed and polished. Micrographs were taken in the JOEL JSM-840 SEM using secondary electron (SE) images. A WACOM sensitive pad interfaced with a desktop was used to analyze the images. Data was generated, transferred and manipulated in Microsoft Excel. The cobalt mean free paths were calculated and data from different areas on the side surfaces were compared.

4 RESULTS

This chapter starts with the description of the specimens studied in the project. Macrostructure and microstructure observation results follow.

4.1 Specimen Description

This project continues research carried out by S. Luyckx [Luyckx et al., 1998] and Yu. V. Milman [Milman et al., 2002] which investigated bending behavior of WC-Co alloys with different compositions in increasing temperature. Only part of the specimens used in the previous research were studied in the current project.

As described in the previous chapter, three grades of specimens have been studied, namely: S, NYB and NYA. The cobalt content of each grade is 15wt%. The average grain size is: S: 1.30 μ m, NYB: 0.35 μ m, NYA: 0.30 μ m, respectively. The specimens were subjected to 3-point bending tests at different temperatures: 20, 200, 400, 600, 800 and 1000°C [Milman et al., 2002]. For convenience, specimens in this project are numbered for example as follows: NYB15-1000C-*, where NYB is the grade, 15 is the cobalt content, 1000C is the temperature at which the specimen was tested and * is the number of the sample.

According to Milman et al., the original size of the specimens were approximately 35 × 4.5 × 1.2 mm. After bending, most of the specimens were broken into two or more pieces. Some specimens tested by Milman at room temperature were not available. The details of all the specimens available are in Table 4.1:

Table 4.1: Summary of specimens studied in this project

Grade	Temp. of testing	Numbers of Specimen(s) received ¹	Fragments of each specimen ²	Matching of fragments or not	Piece(s) missing ³	Specimens fragments name in this text
S15	200°C	2	2	Yes	None	S15-200C-1 S15-200C-2
			2	Yes	None	S15-200C-3 S15-200C-4
	1000°C	2	2	Yes	None	S15-1000C-1 S15-1000C-2
			≥4	Partly ⁴	≥1	S15-1000C-3 S15-1000C-4 S15-1000C-5
NYB	200°C	2	≥3	No	≥1	NYB15-200C-1 NYB15-200C-2
			≥3	No	≥1	NYB15-200C-3 NYB15-200C-4
	400°C	2	2	Yes	None	NYB15-400C-1 NYB15-400C-2
			≥4	No	≥2	NYB15-400C-3 NYB15-400C-4
	530°C	2	≥3	No	≥1	NYB15-530C-1 NYB15-530C-2
			≥3	No	≥1	NYB15-530C-3 NYB15-530C-4

Grade	Temp. of testing	Numbers of Specimen(s) received ¹	Fragments of each specimen ²	Matching of fragments or not	Piece(s) missing ³	Specimens fragments name in this text
NYB	600°C	2	≥3	No	≥1	NYB15-600C-1 NYB15-600C-2
			≥3	No	≥1	NYB15-600C-3 NYB15-600C-4
	800°C	2	2	Yes	None	NYB15-800C-1 NYB15-800C-2
			≥3	No	≥1	NYB15-800C-3 NYB15-800C-4
	1000°C	2	2	Yes	None	NYB15-1000C-1 NYB15-1000C-2
			2	Yes	None	NYB15-1000C-3 NYB15-1000C-4
NYA	20°C	1	≥3	No	≥1	NYA15-20C-1 NYA15-20C-2
	200°C	2	3	Yes	None	NYA15-200C-1 NYA15-200C-2 NYA15-200C-2m ⁵
			3	Yes	None	NYA15-200C-3 NYA15-200C-4 NYA15-200C-4m
	400°C	2	2	Yes	None	NYA15-400C-1 NYA15-400C-2
			≥6	No	≥1	NYA15-400C-3

Grade	Temp. of testing	Numbers of Specimen(s) received ¹	Fragments of each specimen ²	Matching of fragments or not	Piece(s) missing ³	Specimens fragments name in this text
NYA	600°C	2	≥3	Partly	≥1	NYA15-600C-1 NYA15-600C-2
			3	Yes	None	NYA15-600C-3 NYA15-600C-4 NYA15-600C-4m
	800°C	2	≥3	No	≥1	NYA15-800C-1 NYA15-800C-2
			2	Yes	None	NYA15-800C-3 NYA15-800C-4
	1000°C	2	N/A	N/A	None	NYA15-1000C-1 ⁶
			N/A	N/A	None	NYA15-1000C-2 ⁶

Note:

1. “Numbers of Specimen(s) received” is the number which had been subjected to bending tests;
2. “Fragments of each specimen” is not how many fragments received in this project, but is the number of specimen fragments determined according to the matching of fracture surfaces. If two fracture surfaces do not match, at least one fragment between the two fracture surfaces is missing;
3. “Piece(s) missing” is determined by subtracting the real fragment number from the estimated number of fragments;
4. “Fragments partly match” means some fragments are missing but some fracture surfaces of the available fragments match;

5. When a specimen was fractured into three fragments and no piece was missing, the middle fragment is named such as “NYA15-200C-2m”, where “m” refers to “middle”;
6. The two NYA15-1000C specimens were not fractured, so fracture surface matching is not applicable.

The investigation was focused on the lowest and highest temperature specimens because the difference may reveal the impact of increasing temperature on the fracture mechanisms. However, intermediate temperatures specimens were also studied.

4.2 NYA15-1000C-1 Length Measurement

As described above, the specimens of NYA15-1000C did not fracture during 3-point bending tests (one example in Fig. 4.1). The specimens underwent large strain during bending and retained the bent shape after cooling down to room temperature. The length measurement of NYA15-1000C-1 was important for further investigations.



Fig. 4.1: Photograph of the NYA15-1000C-1.

Digital pictures of the specimen were taken in a stereomicroscope (Fig. 4.2). Then the pictures were analyzed and calibrated in the software AxioVision 3.1.2.1.

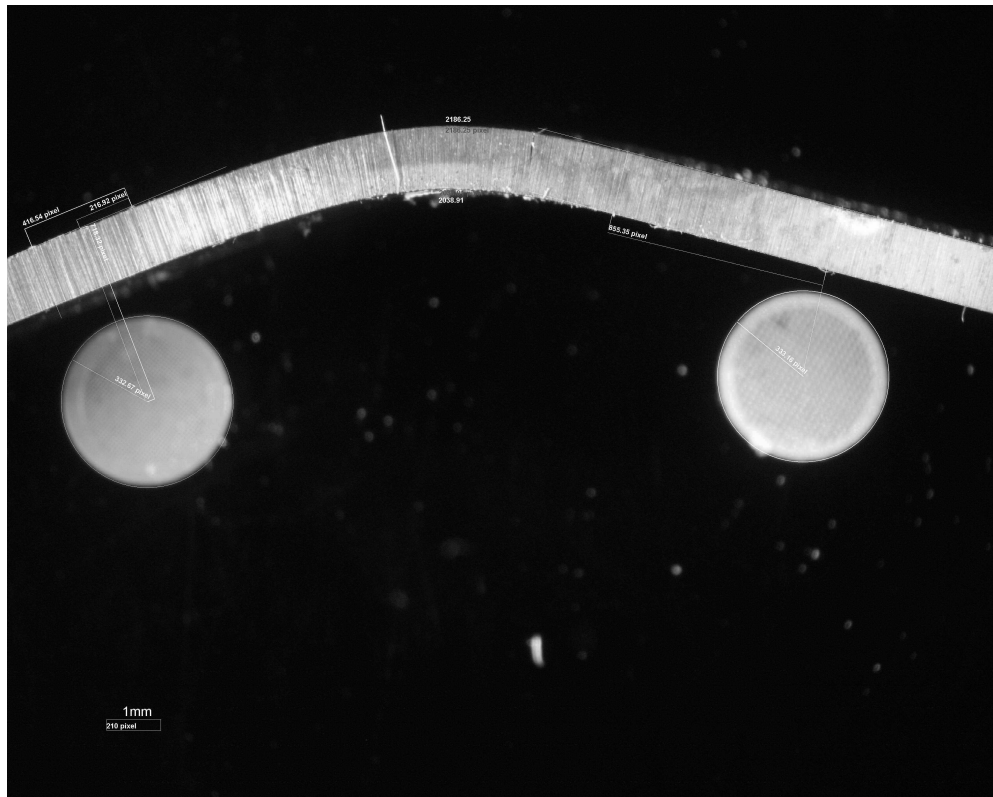


Fig. 4.2: Stereomicrograph for length measurement showing the curved NYA15-1000C-1 specimen. The unfractured parts were cut off and the lengths of the tensile edge and compressive edge were measured.

A digital image is made up by pixels. First the calibration bar was measured in pixels and the ratio microns per pixel was calculated as follows:

$$1\text{mm} = 210 \text{ pixels} \rightarrow 1 \text{ pixel} = 4.76 \mu\text{m}.$$

Then the tensile edge and compressive edge were measured with pixel numbers. The pixel numbers were finally translated to microns again.

The length of the tensile edge was found to be $43182.86\mu\text{m}$, the length of the compressive edge $42402.03\mu\text{m}$. Therefore the tensile edge was $780.83\mu\text{m}$ longer than the compressive edge.

4.3 Macroscopic Observation

Specimens of each grade were first observed in a stereomicroscope and a reflected light microscope. The tensile surfaces, compressive surfaces and side surfaces were studied. The fractographic analysis, i.e. the observation of fracture surfaces from low magnification to high magnification was carried out as well and the results are reported in section 4.4.

4.3.1 Side Surfaces

The side surfaces of S, NYA and NYB grades were investigated under both stereomicroscope and reflected light microscope. The choice of microscope was determined according to the flatness of the surfaces and the magnification required. The results are shown below.

4.3.1.1 Side Surface of NYA15 Grade

Macrocracks, defined in this project as those cracks whose opening is wider than about $3\mu\text{m}$, were found on one side surface of NYA15-1000C-1, detectable even in a low magnification stereomicroscope (see Fig. 4.3). This sample was received unfractured.

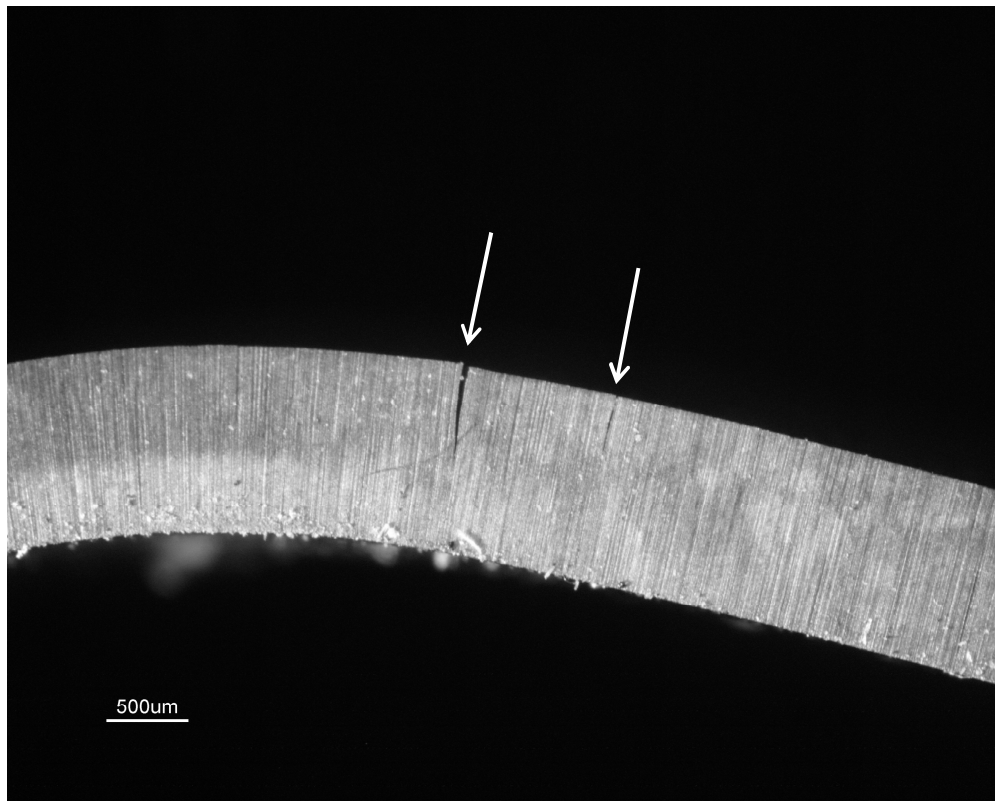


Fig. 4.3: Stereomicrograph showing macrocracks on one side surface of NYA15-1000C-1 (as indicated by arrows).

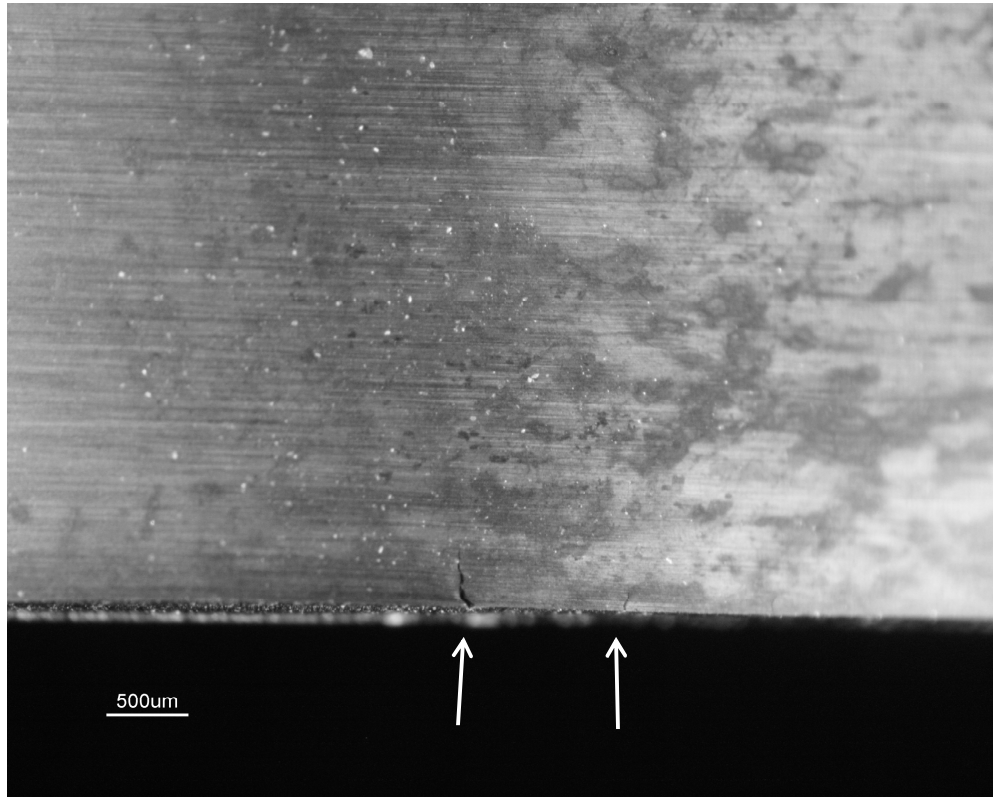


Fig. 4.4: Stereomicrograph: the appearance of the same cracks shown in Fig. 4.3, when observed from the tensile surface of NYA15-1000C-1.

The macrocracks on the side surface of NYA15-1000C-1 were further observed under a reflected light microscope at higher magnifications. The high magnification made the measurement of the crack openings possible (see Fig. 4.5). The total width of the macrocrack openings on one side surface of NYA15-1000C-1 is 100.19 μm . Details of this measurement are given in Appendix A.

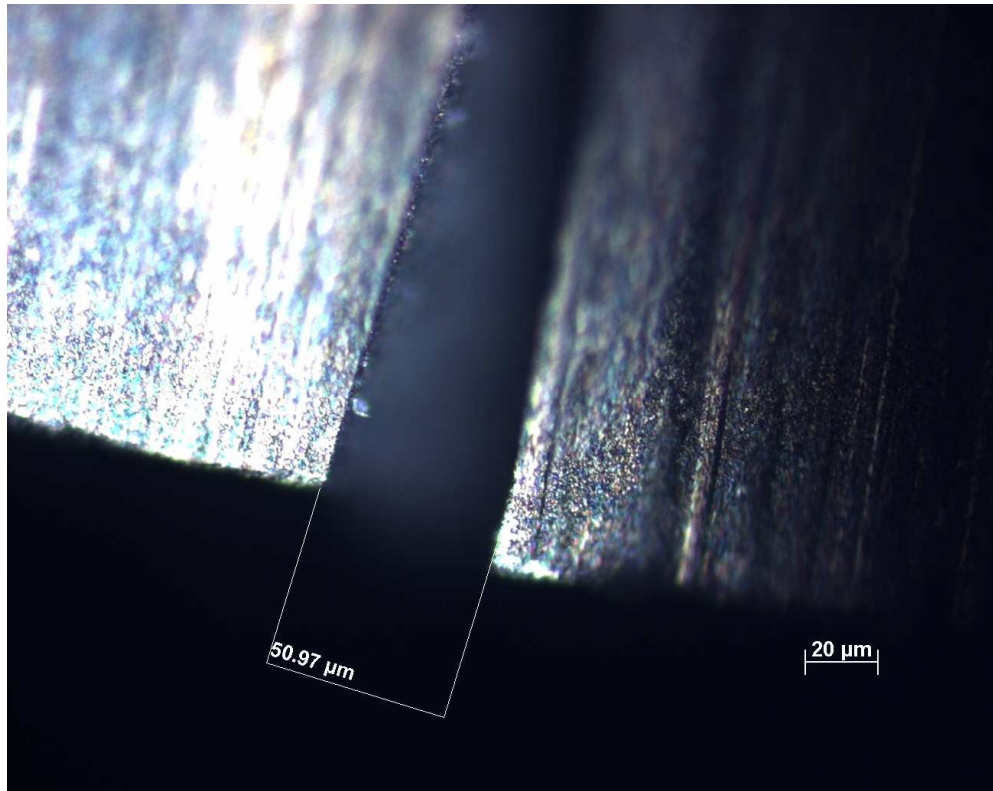


Fig. 4.5: Reflected light micrograph: crack opening width measurement on one side surface of NYA15-1000C-1. A macrocrack wider than 50μm can be seen.

Fig. 4.6 is the stress-strain curve of the NYA grade from which strains due to plastic deformation and due to elastic deformation were determined.

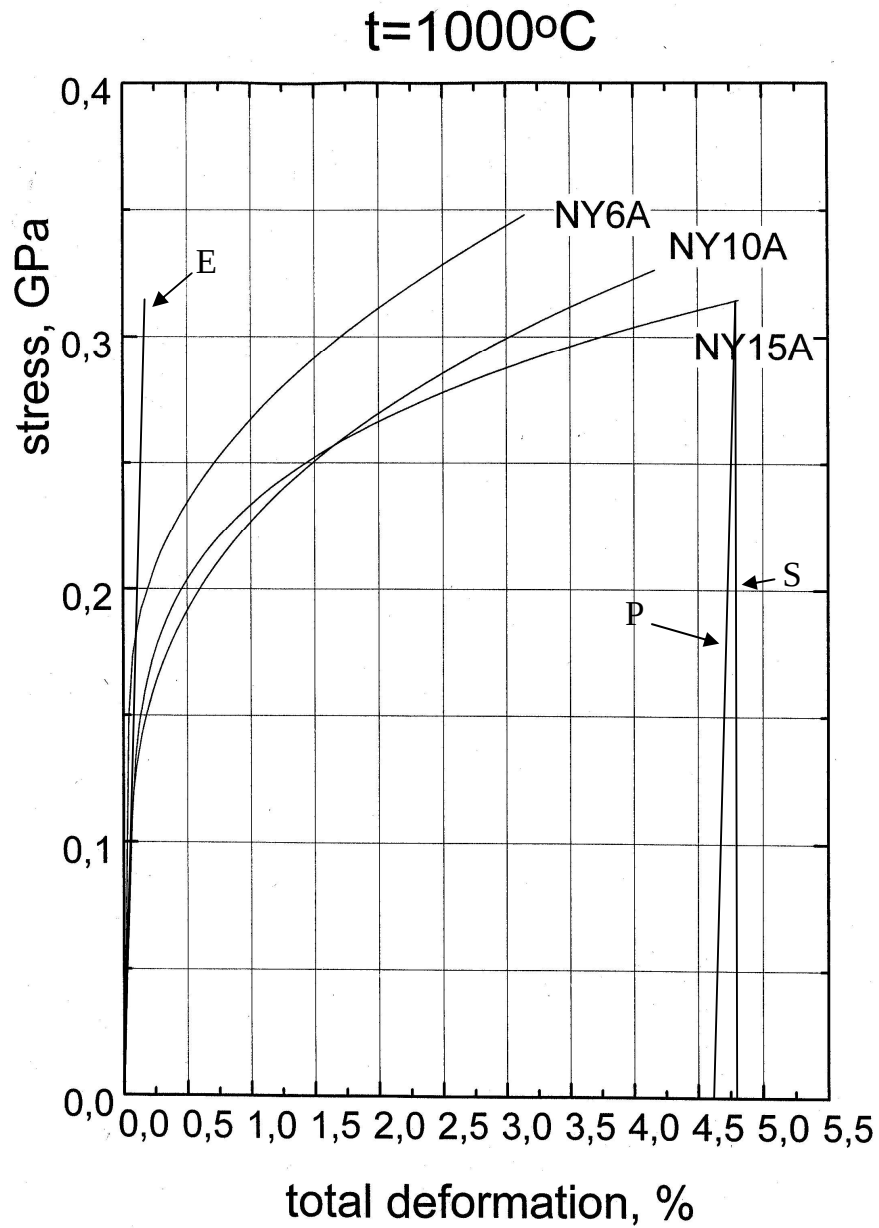


Fig. 4.6: The stress-strain curve of NYA grades. Line E is the extrapolation of the elastic section of NYA15, to determine the Young's modulus of the grade. Line S allows to determine the strain at fracture of the NYA15 grade, which is 4.7%. Line P is parallel to line E and was introduced to evaluate the elastic recovery (by courtesy of Yu. Milman).

It can be read from the points of intersections of lines P and S with the strain axis in Fig. 4.6 that the strain due to plastic deformation is 4.3% and the elastic strain is 0.4%.

Since the order of magnitude of the strain due to cracks is $10^2\mu\text{m}$ (section 4.3.1.1) and the total length of the sample is of the order of $4\times 10^4\mu\text{m}$ (section 4.2), the

$$\text{strain due to crack opening} \approx \frac{1\times 10^2 \mu\text{m}}{4\times 10^4 \mu\text{m}} = 0.25\%$$

Considering the 0.25% strain due to macrocracks out of 4.3% total plastic strain of NYA15-1000C, it is concluded that the macrocracks only account for less than 10% of the total strain. The major strain must be due to other factors, mainly plastic deformation of the material.

It was found that in NYA15-1000C-1, on one side surface (as reported above) there are fewer but wider cracks, while on the other side surface, the cracks were more numerous but narrower (see Fig. 4.7).

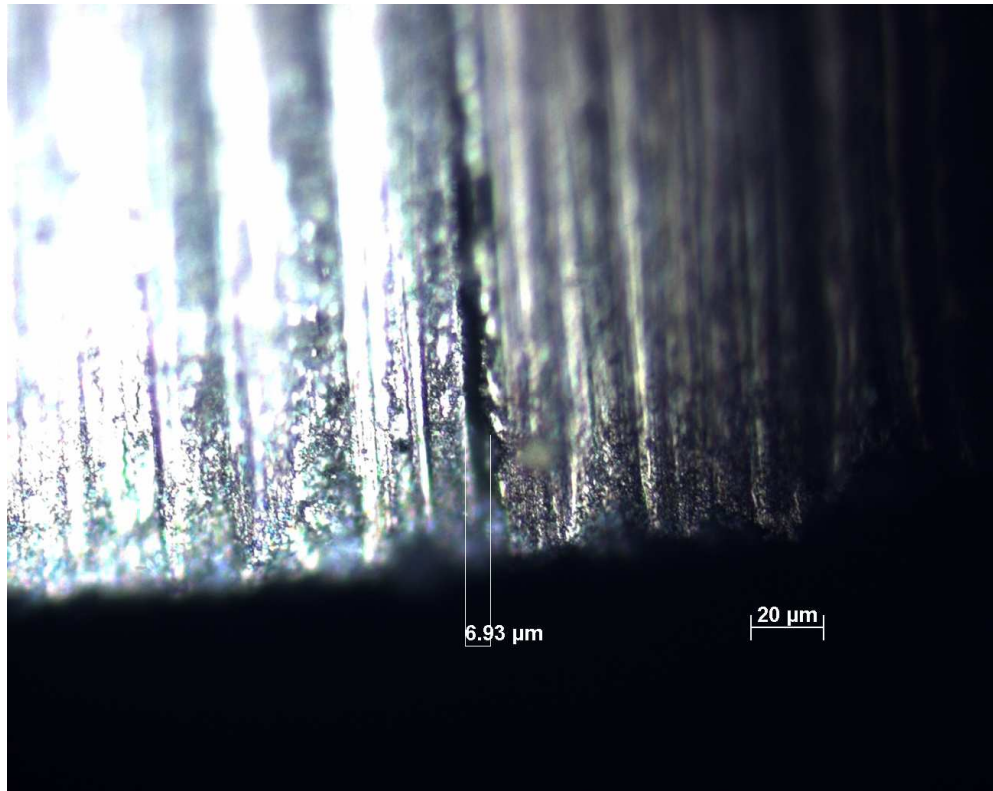


Fig. 4.7: Reflected light micrograph: the widest macrocrack observed on a side surface of NYA15-1000C-1. All the other cracks on this side surface are narrower than 2μm.

Macrocracks are observable in light microscopes. There are also microcracks on the side surfaces, but because of the roughness of the specimen surface, the microcracks are not easy to identify (see Fig. 4.8).

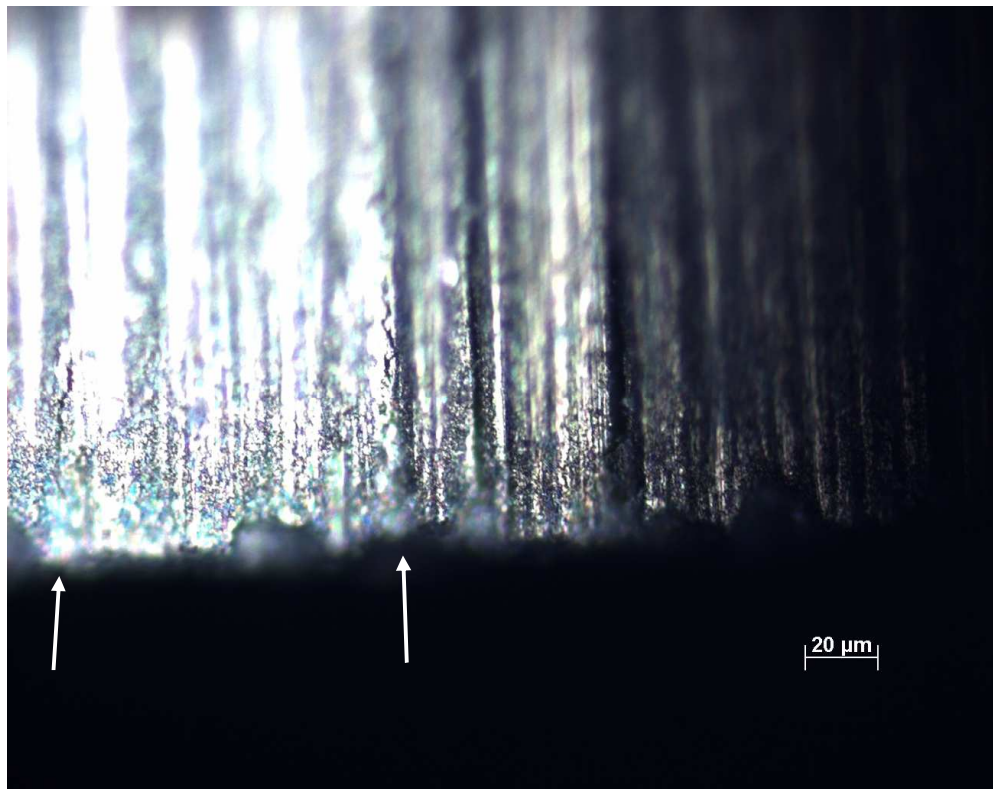


Fig. 4.8: Reflected light micrograph: microcracks (as indicated by arrows) on one side surface of NYA15-1000C-1.

When the side surface was polished, both the macrocracks and microcracks were more easily recognized (see Fig. 4.9).

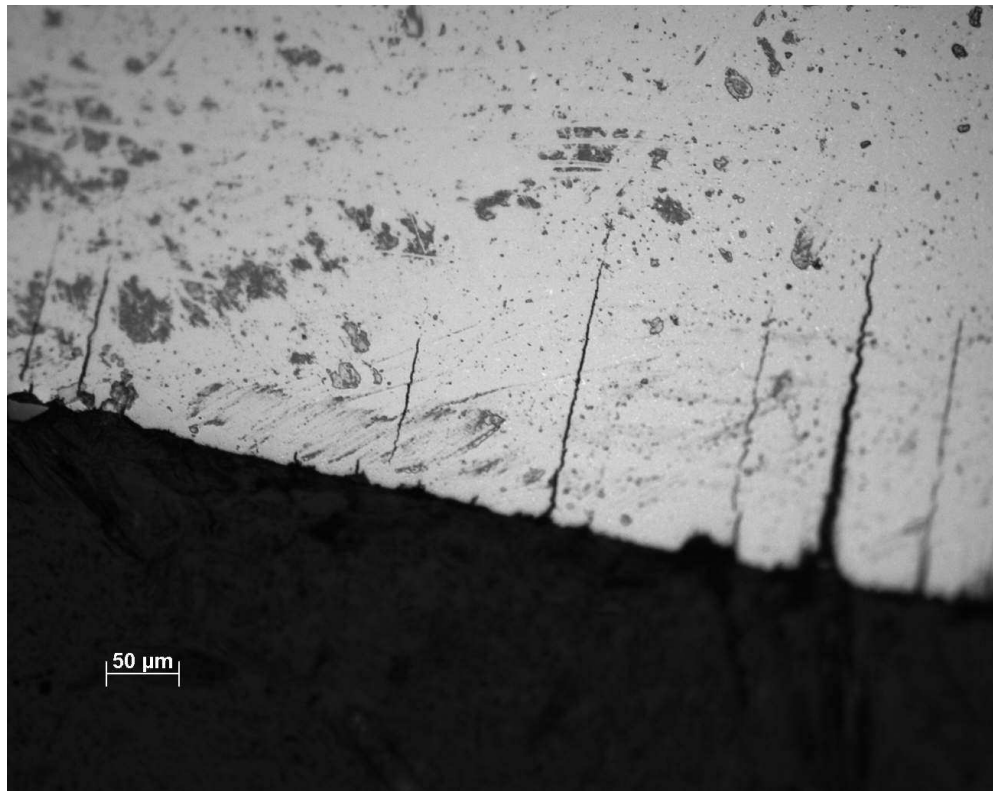


Fig. 4.9: Reflected light micrograph: one macrocrack and some microcracks on the polished side surface of NYA15-1000C-2.

After polishing, it is easier to observe the crack openings and more microcracks appear, but the crack openings at the intersection between the tensile face and side face had been damaged. For this reason, the measurements of crack openings were done on unpolished surfaces.

The side surfaces of 20°C, 200°C, 400°C, 600°C and 800°C specimens of NYA15 grade were investigated. No cracks were identified. However, the rough side surfaces may conceal microcracks, if there are any present.

4.3.1.2 Side Surface of NYB15 Grade

Macrocracks were also found on the side surface of NYB15-1000C-3. There were macrocracks very near (see Fig. 4.10) and not so near the outcrop (see Fig. 4.11) of the main fracture.

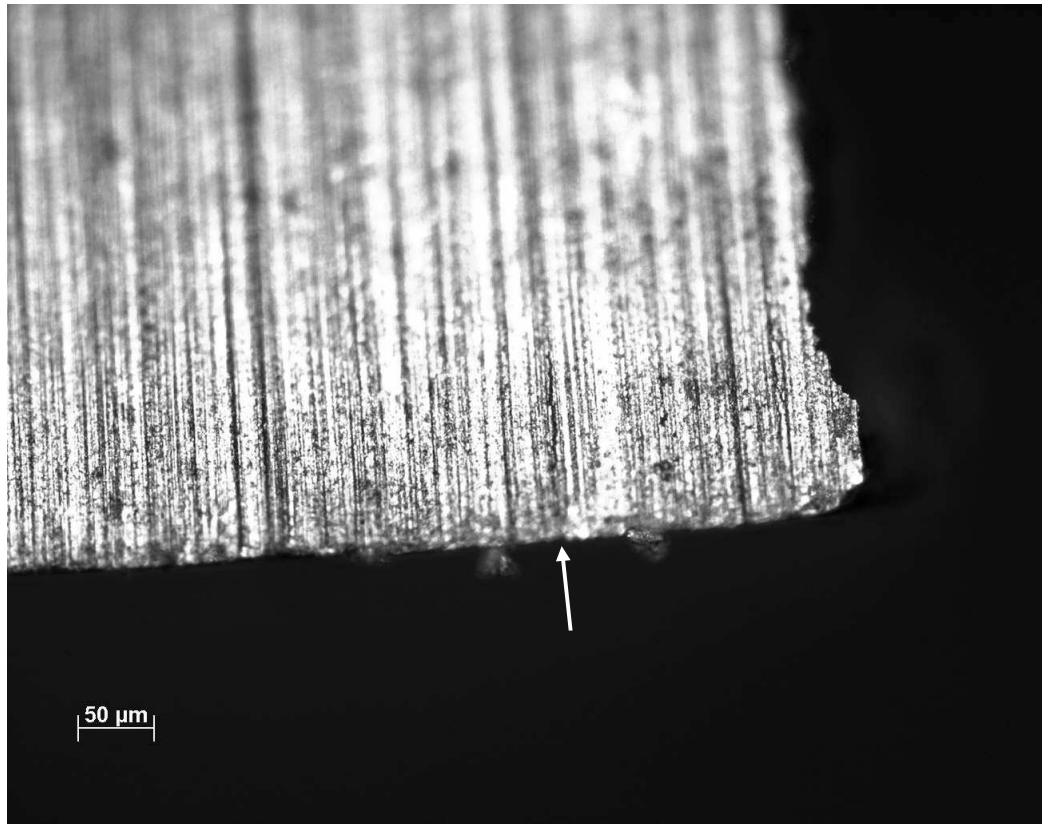


Fig. 4.10: Reflected light micrograph: a macrocrack (as indicated by an arrow) close to the fracture outcrop of NYB15-1000C-3.

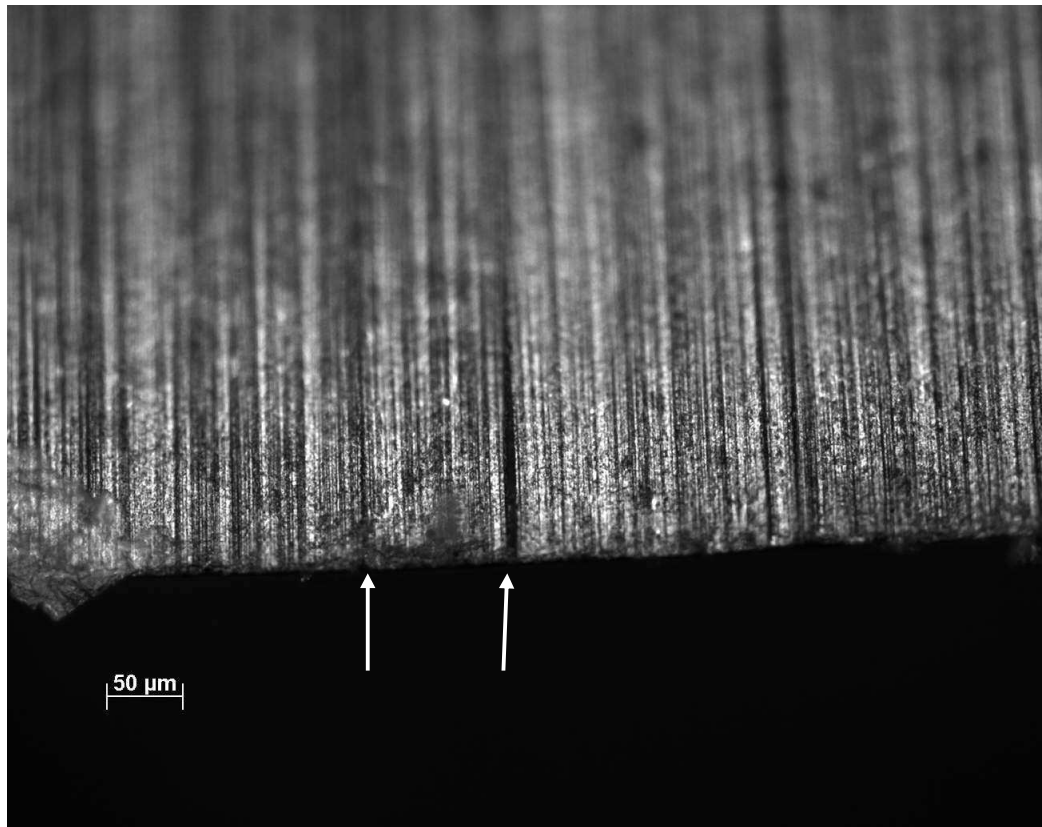


Fig. 4.11: Reflected light micrograph: two macrocracks (indicated by arrows) on one side surface of NYB15-1000C-3.

No cracks were observed on the polished side surface of NYB15-1000C-4.

No cracks were found on the side surfaces of NYB specimens tested at temperatures lower than 1000°C.

4.3.1.3 Side Surfaces of S15 Grade

Few macrocracks could be seen even near the fracture outcrops on the side surfaces of the S15 grade (see Fig. 4.12).

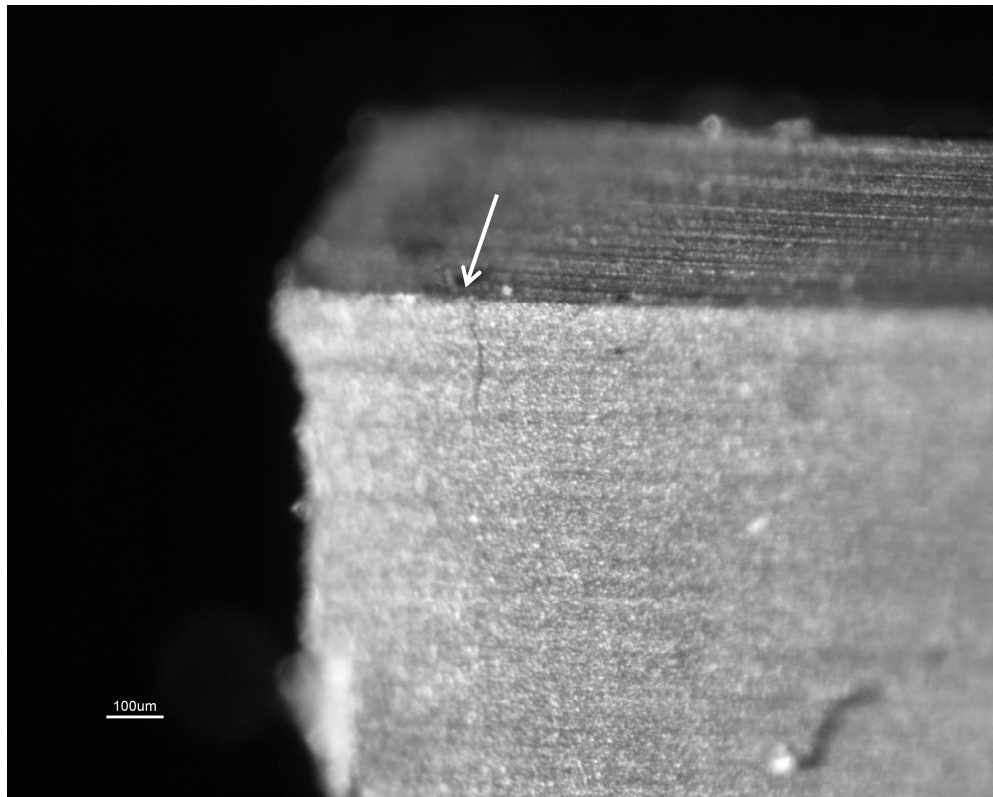


Fig. 4.12: Stereomicrograph: one narrow crack (indicated by an arrow) near the fracture outcrop on the side surface of S15-1000C-1.

No crack was found on the side surface of S15-200C specimens.

4.3.2 Tensile Surfaces and Compressive Surfaces

No cracks were observed on the tensile surfaces and compressive surfaces of all the three grades. However, the same macrocracks on the side surface of NYA15-1000C-1 (Fig. 4.3) can also be noticed on the tensile surface of NYA15-1000C-1 (Fig. 4.4). This stereomicrograph of the tensile surface (Fig. 4.4) is reported in 4.3.1 because it is related to the cracks on the side surface.

4.4 Fracture Surface (Fractography) Observation

During the bending test, the area where the specimens fractured was subjected to a high stress concentration. Observations of fracture surfaces should help to understand the fracture mechanism. Fractography observations started from low magnification under stereomicroscope and optical microscope and continued at high magnification under SEM and FESEM.

4.4.1 Low Magnification

Fracture surfaces of S, NYA and NYB grades were observed and compared under a stereomicroscope. The comparisons can give an idea of the difference between different grades of WC-Co alloys. The comparisons are shown from Fig. 4.13 to Fig. 4.19.

It must be noted that some fracture surfaces of the specimens were contaminated during the bending tests. Before observation, all the specimens were cleaned following the cleaning procedure described in section 3.2. Stains, however, could not be completely removed. Stains can be noticed at both low and high magnification and their existence has been proved by EDS analysis (section 4.4.2.2).

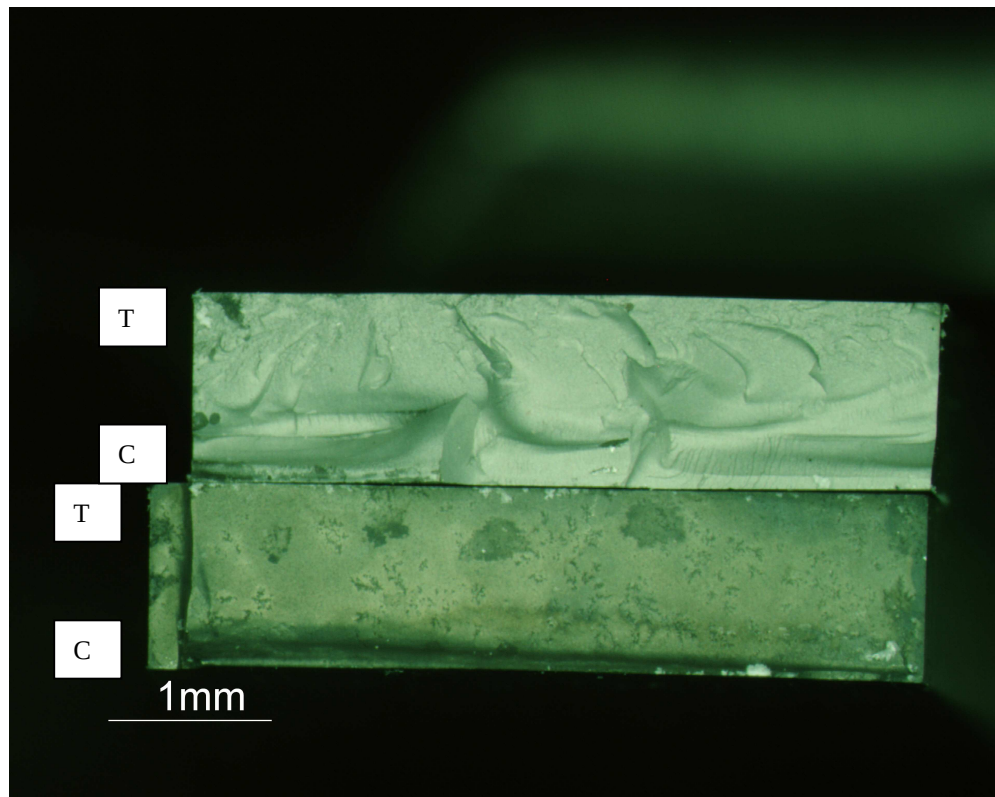


Fig. 4.13: Stereomicrograph: fracture surfaces of NYB15-200C-4 (above) and NYA15-200C-3 (below). “T” represents “tensile”, and “C” represents “compressive”. “T” and “C” indicate the tensile and compressive surfaces of each specimen. The fracture surface of NYA15-200C-3 seems featureless while the fracture surface of NYB15-200C-4 is rough. The fracture origin of NYB15-200C-4 can be easily identified, while the fracture origin of NYA15-200C-3 cannot.

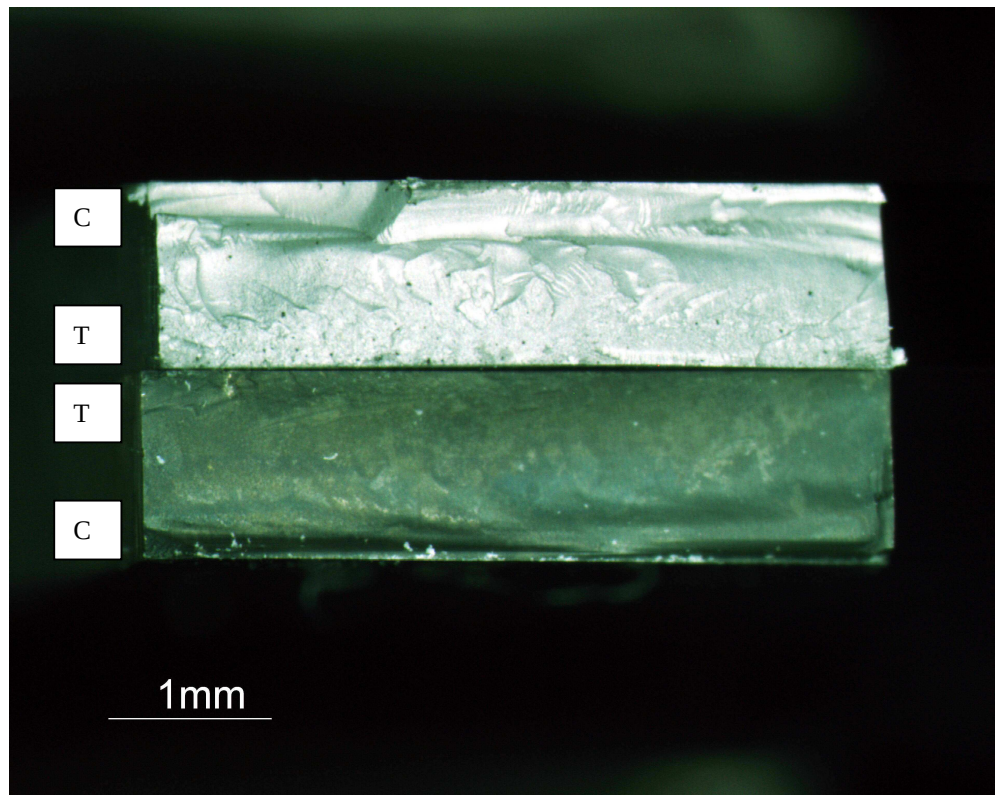


Fig. 4.14: Stereomicrograph: fracture surfaces of NYB15-400C-4 (above) and NYA15-400-2 (below). The fracture surface of NYA15-400-2 is not as featureless as that of NYA15-200C-3 but still not as rough as that of NYB15-400C-4.

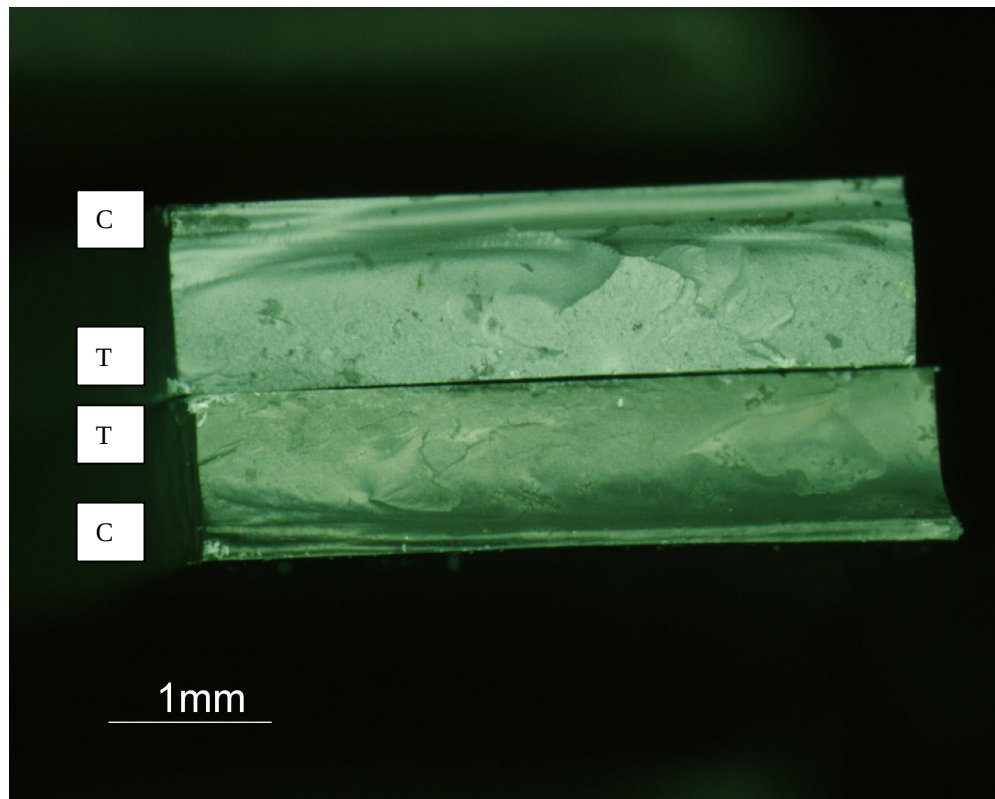


Fig. 4.15: Stereomicrograph: fracture surfaces of NYB15-600C-3 (above) and NYA15-600C-3 (below). Both fracture surfaces are rough with steps near compressive sides.

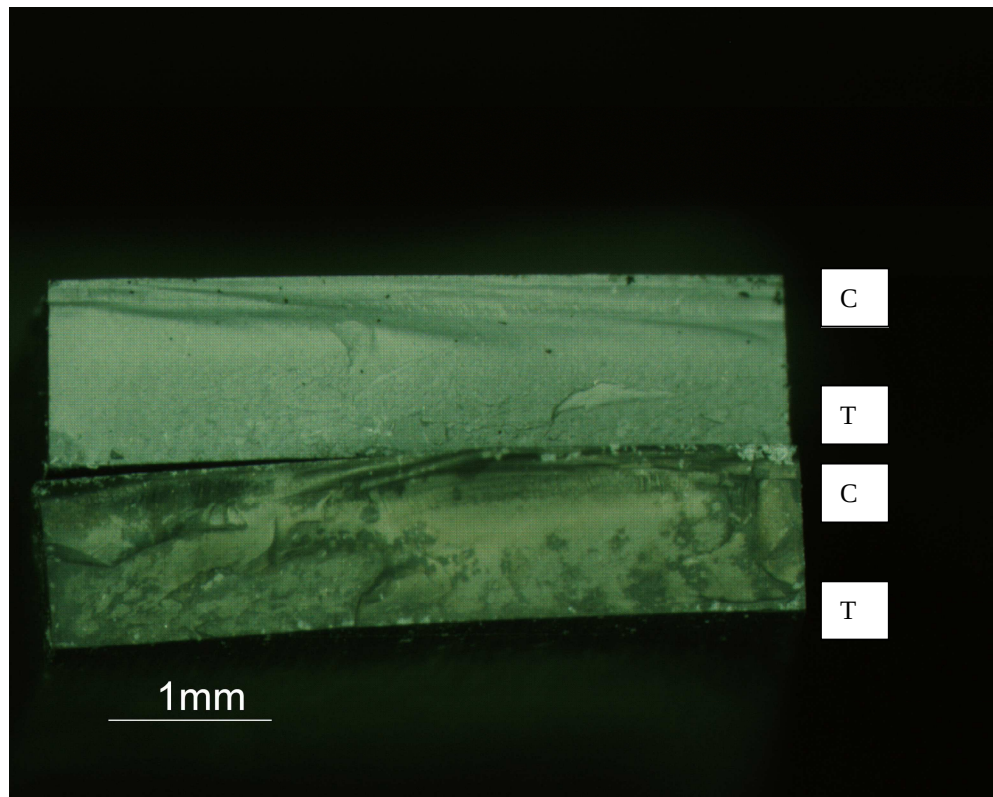


Fig. 4.16: Stereomicrograph: fracture surfaces of NYB15-800C-3 (above) and NYA15-800C-2 (below). The fracture surface of NYA15-800C-2 seems rougher than that of NYB15-800C-2. The fracture origin of NYA15-800C-2 is easier to identify, too. The stains on the surfaces could not be removed by cleaning and must be due to liquids that stained the material during bending tests.

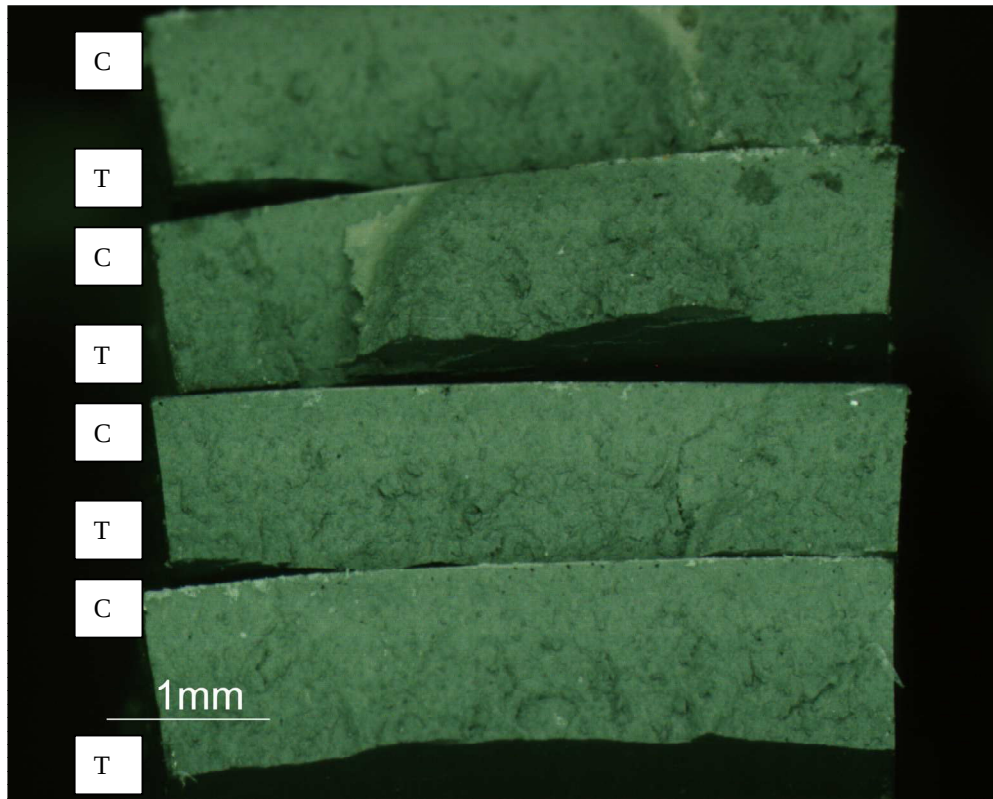


Fig. 4.17: Stereomicrograph: fracture surfaces of NYB15-1000C-1 (top) to NYB15-1000C-4 (bottom). No NYA15 specimen was fractured, so no fracture surface of NYA15 is available. The compressive and tensile sides were determined according to *Theory of Elasticity*: “In considering the upper or lower sides of the bar it is evident that while the curvature of these sides after bending is convex down in the lengthwise direction, the curvature in the crosswise direction is convex upward.” [Timoshenko and Goodier, 1970]

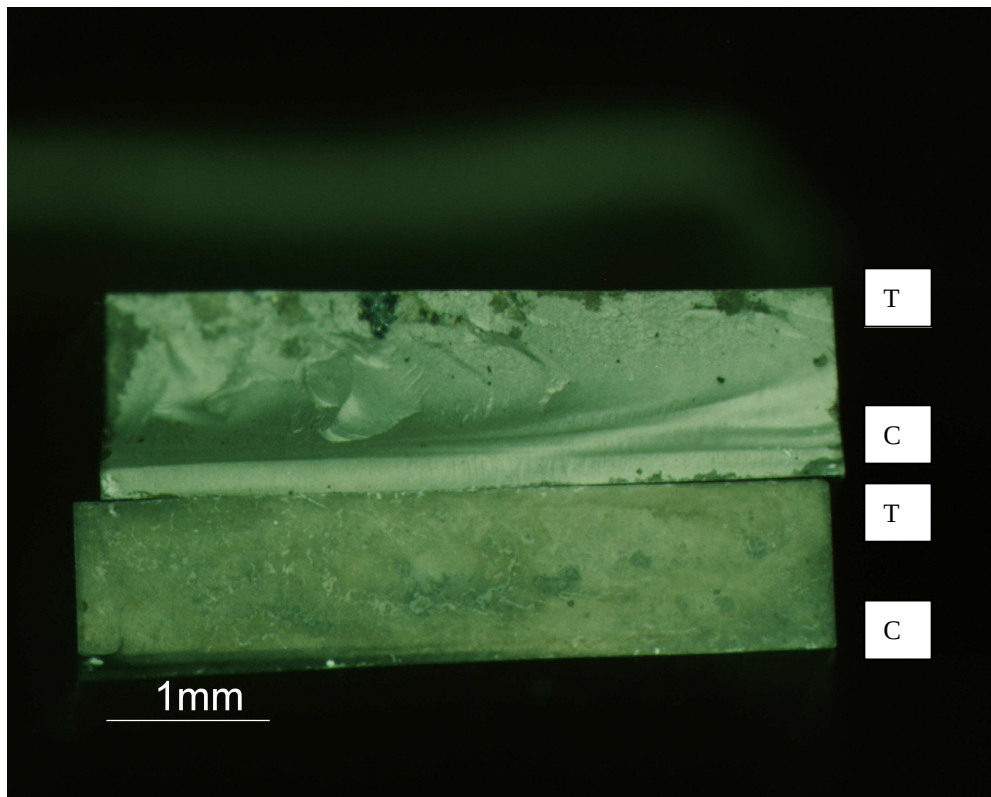


Fig. 4.18: Stereomicrograph: fracture surfaces of NYB15-200C-1 (above) and NYA15-20C-1 (below). The fracture surface of NYA15-20C is not compared to a NYB15-20C because no NYB15-20C specimen was available. The fracture surface of NYA15-20C-1 is even more featureless than that of NYA15-200C-3 (see Fig. 4.13).

It can be noticed that the fracture surfaces of some low temperature (20°C, 200°C, 400°C) NYA specimens are more featureless than those of NYB specimens and those of high temperature NYA specimens.

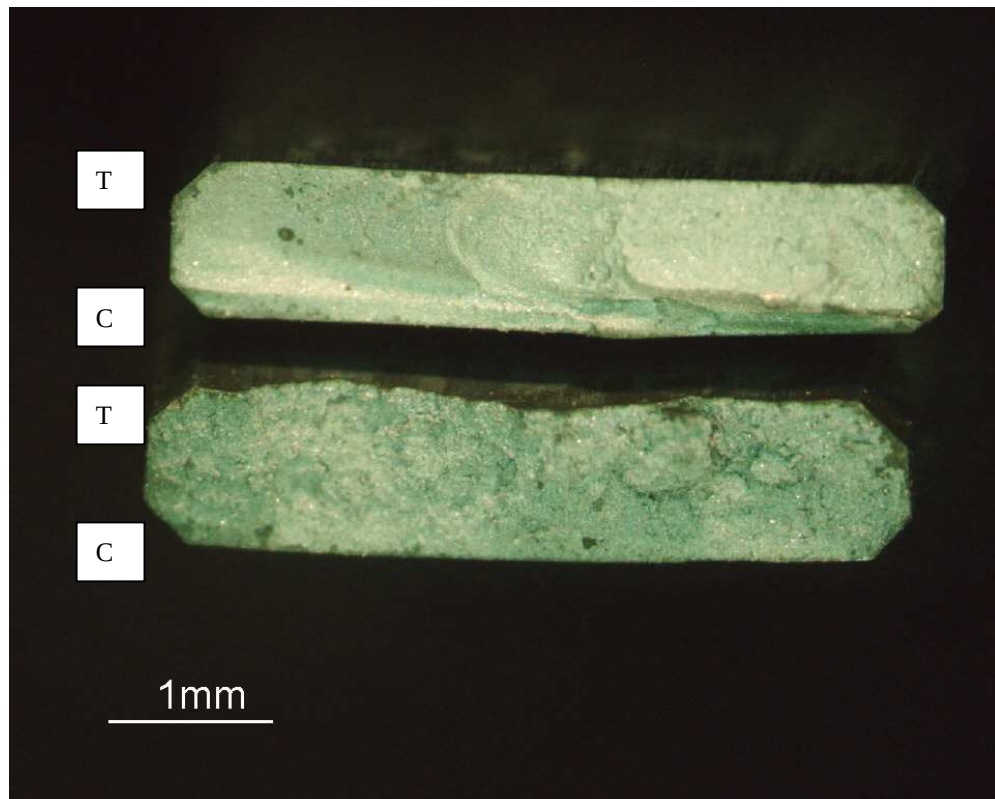


Fig. 4.19: Stereomicrograph: fracture surfaces of S15-200C-1 (above) and S15-1000C-1 (below) were compared. Both of them are rough, but the high temperature fracture surface is much rougher than the low temperature one. Note that these samples were chamfered.

4.4.2 High Magnification

Fracture surfaces of S, NYB and NYA specimens have been examined in an electron microscope. Since the grain sizes of NYA and NYB grades are ultrafine (about 0.3 μ m), a FESEM was used to achieve the required magnification and resolution. FESEM images are shown in this section.

Wherever the fracture origin could be identified, micrographs were taken assuming that interesting features would be found there because fracture always occurs at a point of high stress concentration where plastic deformation is most likely to occur. In some cases, when the fracture origin could not be identified, corners and some other spots near the tensile side on the fracture surfaces, where fracture most likely started from, were examined.

Some fracture surfaces were contaminated and were covered by stains. The specimens were cleaned before use in order to get rid of these stains. However, the stains could not be removed by ultrasonic cleaning in acetone or methanol bath.

The results are divided by features observed, which were steps on WC grains, layers and evidence of cobalt drift.

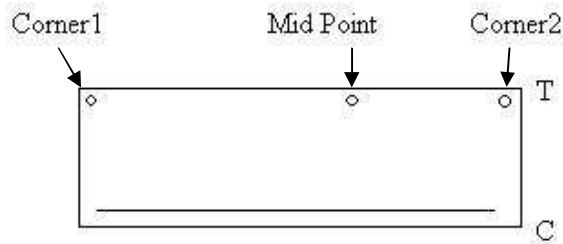
4.4.2.1 Steps on WC Grains

Steps on WC grains on fracture surfaces were observed at all temperatures in the NYA15 grade and in some specimens in the NYB15 grade (NYB15-1000C-3, NYB15-800C-3 and NYB15-400C-3). No steps were found on WC grains on the fracture surfaces of S15 grade specimens.

All the areas examined in the NYA grade were on the fracture surfaces near the tensile side, where the material was subjected to high tensile stresses.

NYA15-20C-1:

The fracture origin could not be identified, so three different areas were observed on the fracture surface of NYA15-20C-1. The three areas are indicated in the sketch below (see Fig. 4.20).



Fracture Surface of NYA15-20C-1

Fig. 4.20: Sketch of NYA15-20C-1 fracture surface with the three areas investigated. “T” represents “tensile” and “C” represents “compressive”. “T” and “C” indicate the tensile and compressive surfaces. Arrows point to where the investigated areas were located (near tensile side or near compressive side) on the fracture surface of the specimen.

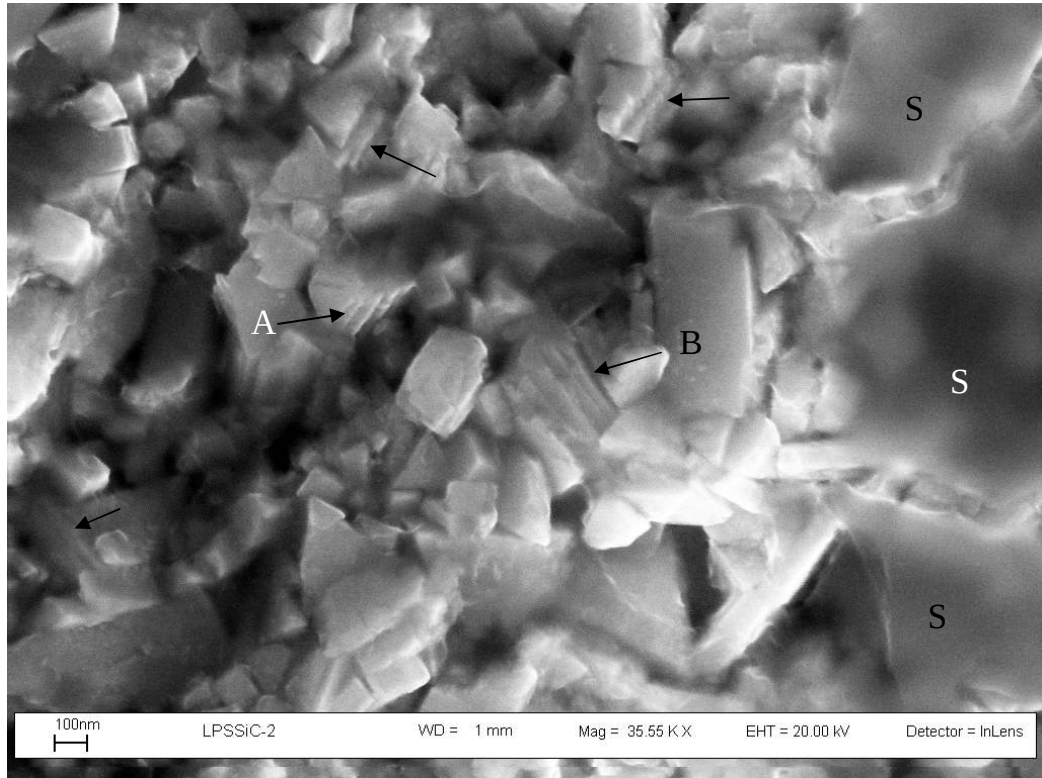


Fig. 4.21: FESEM micrograph of an area of Corner1 on the fracture surface of NYA15-20-1. Several steps on different grains (indicated by arrows) can be seen in this small area which is only several microns long. Details of the steps on grain A and B are shown in Fig. 4.22. The right part of this micrograph (area S) seems to be covered by stains.

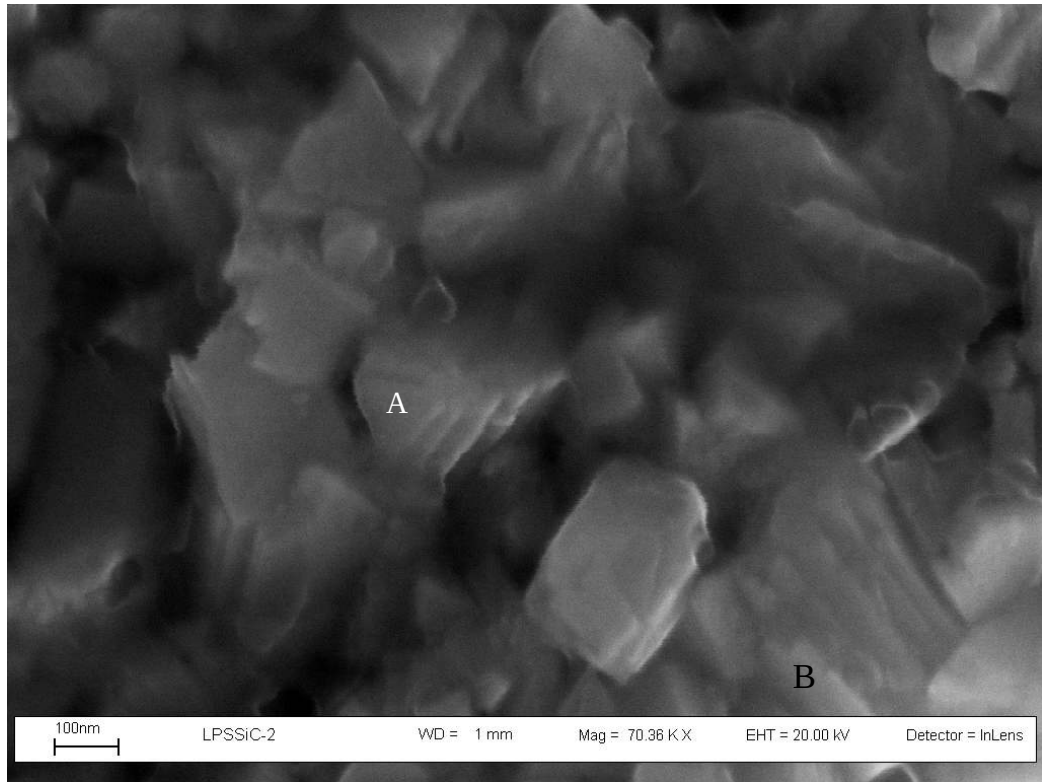


Fig. 4.22: FESEM micrograph: details of the steps on grain A and B in Fig. 4.21.

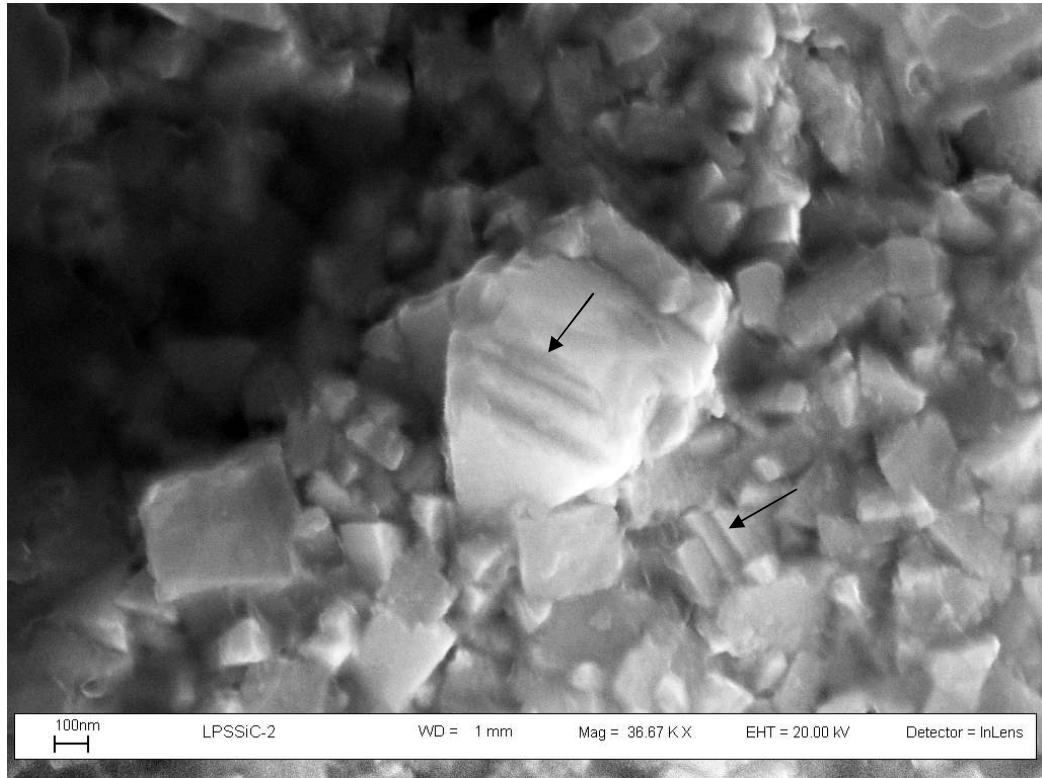


Fig. 4.23: FESEM micrograph of another area of Corner1 on the fracture surface of NYA15-20-1. Steps on different grains (indicated by arrows) can be seen. Details of the steps are shown in Fig. 4.24.

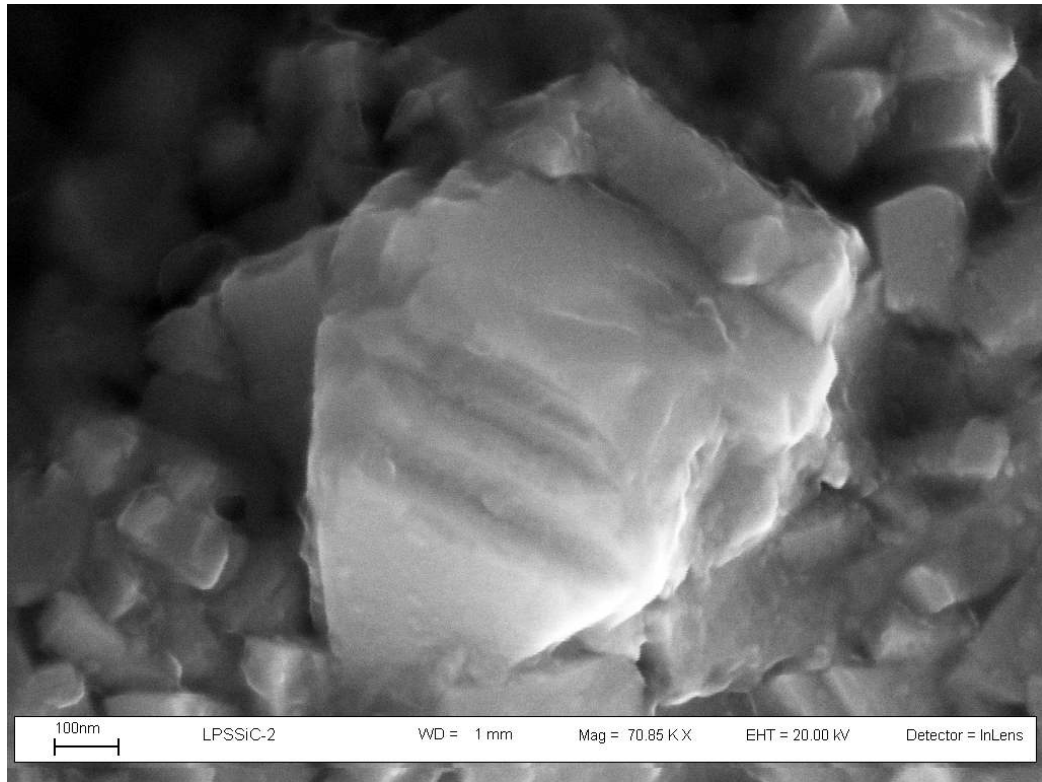


Fig. 4.24: FESEM micrograph: details of the big WC grain in the center of Fig. 4.23.

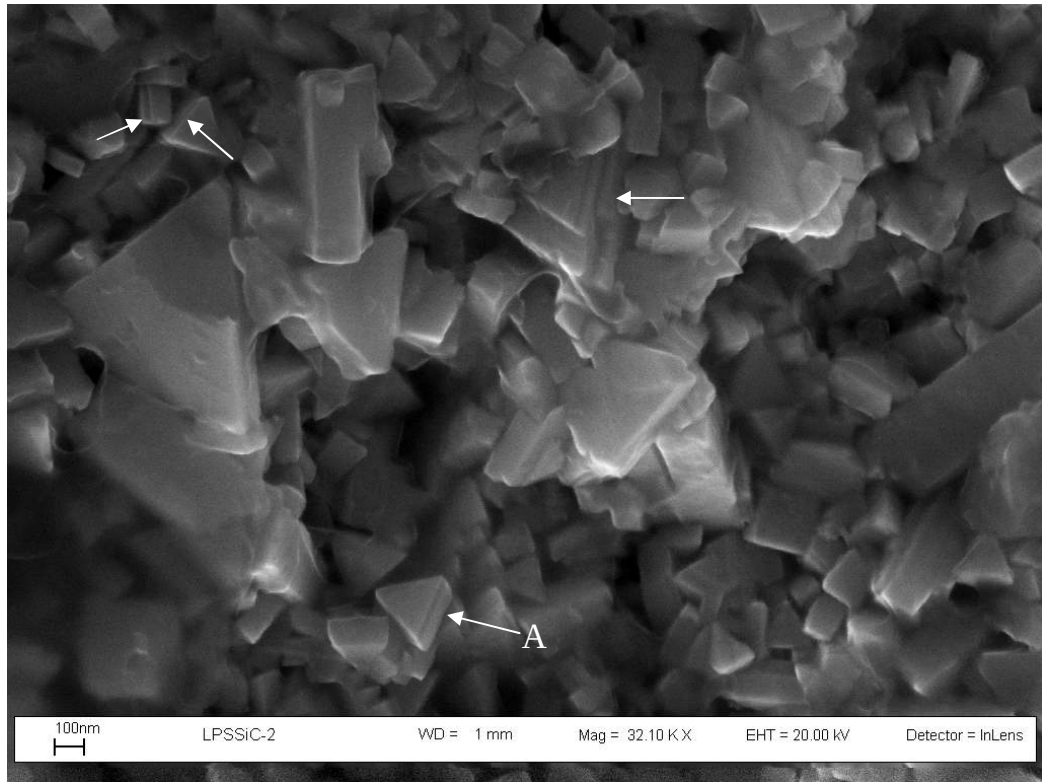


Fig. 4.25: FESEM micrograph of an area of Corner2 on the fracture surface of NYA15-20C-1. Steps can be easily identified (indicated by arrows).

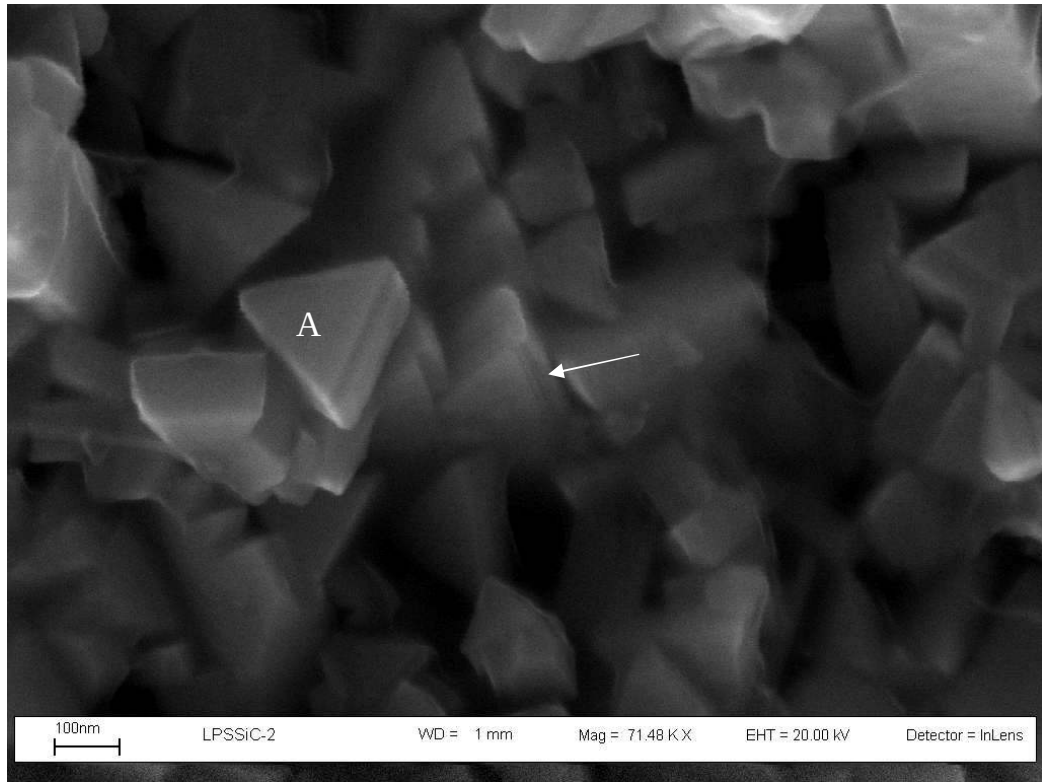


Fig. 4.26: FESEM micrograph: the grain A in Fig. 4.25. At higher magnification, more steps can be identified (as indicated by an arrow).

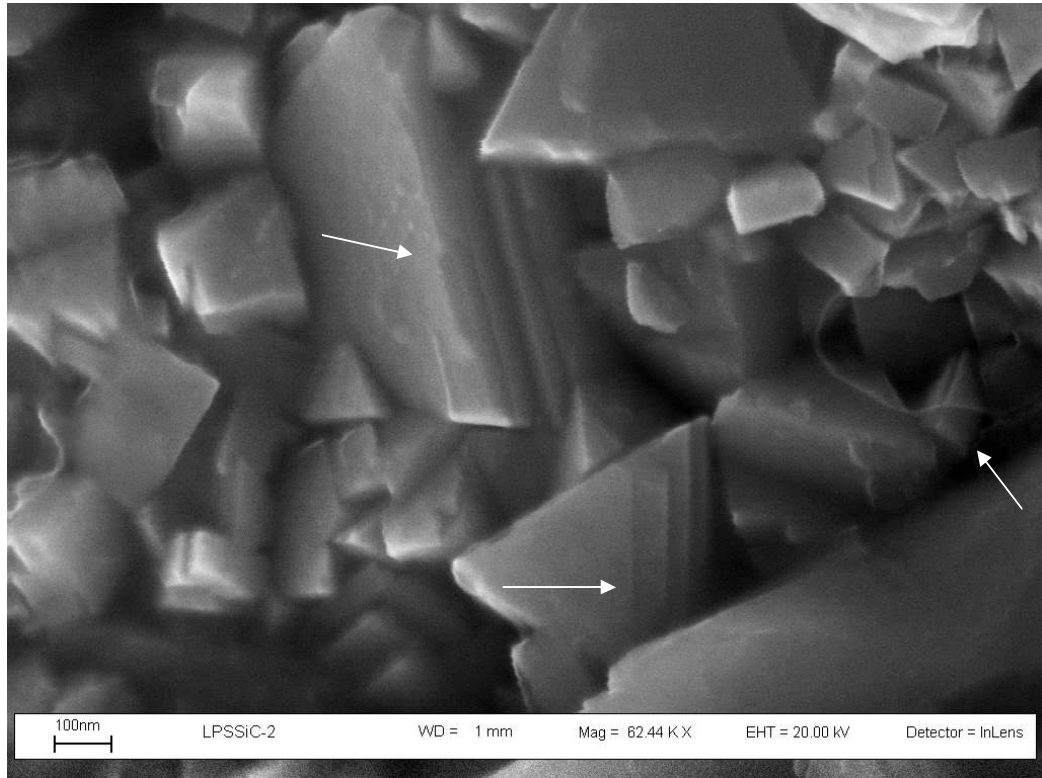


Fig. 4.27: FESEM micrograph of another area of Corner2 on the fracture surface of NYA15-20C-1. Arrows point out the steps.

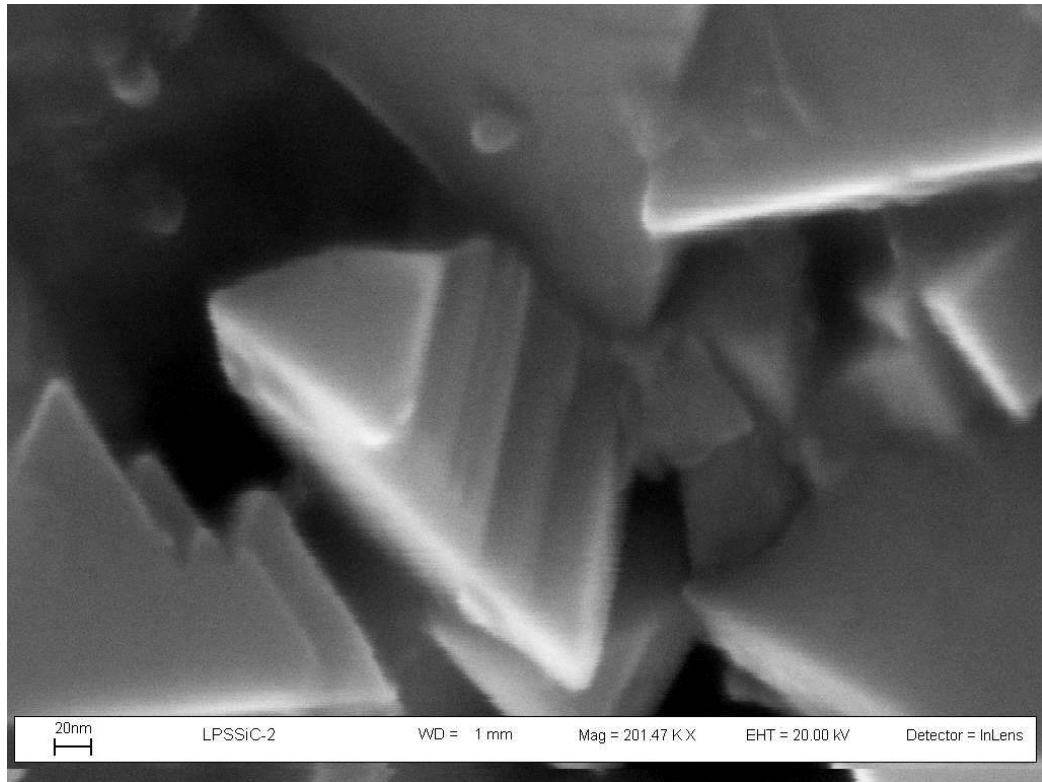


Fig. 4.28: FESEM micrograph of a WC grain in Corner2 area at high magnification (higher than 200,000 $\times$) shows clear steps.

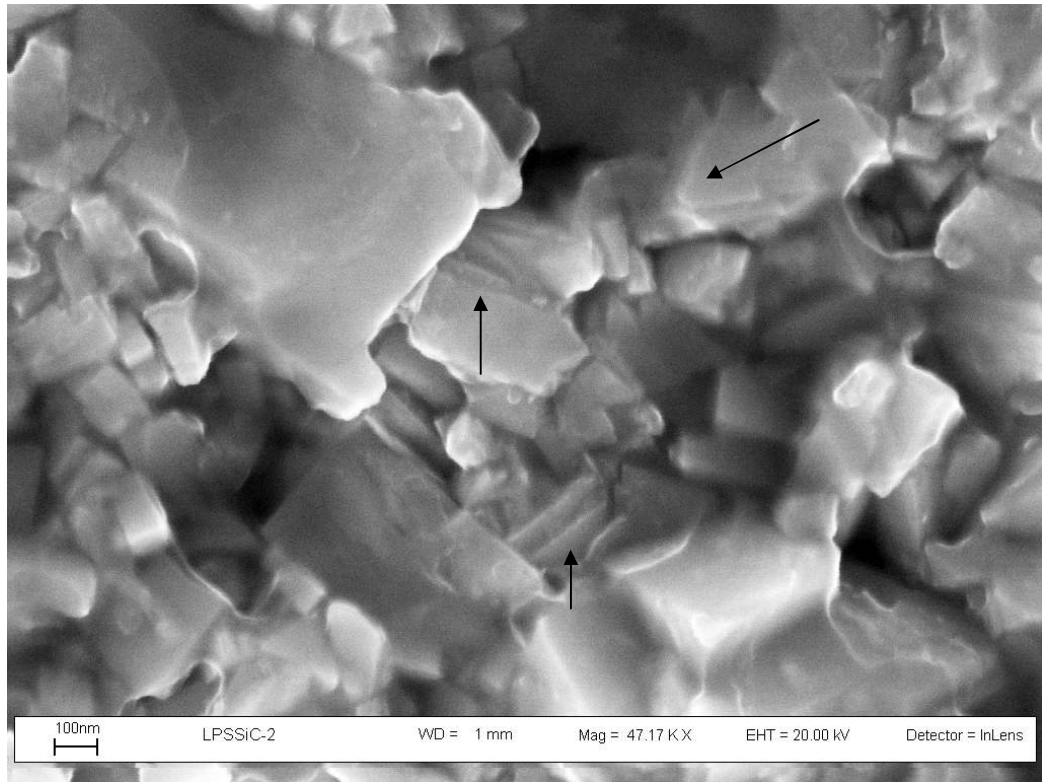


Fig. 4.29: FESEM micrograph of an area of the Mid Point on the fracture surface of NYA15-20C-1. Steps are indicated by arrows. This area seems to be contaminated.

NYA15-200C-3:

The fracture origin of NYA15-200C-3 could not be easily identified. Two areas (see Fig. 4.30) near the tensile side on the fracture surface were observed.

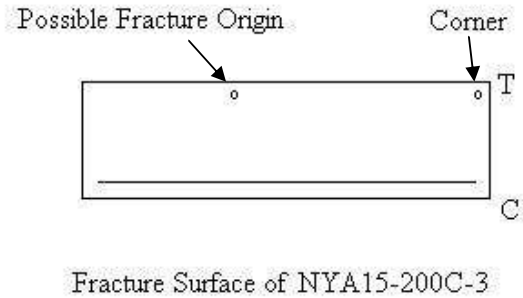


Fig. 4.30: Sketch of NYA15-200C-3 fracture surface with the areas investigated.

When comparing this sketch to Fig. 4.13, it can be seen that these two investigated areas were contaminated. Fig. 4.31 to Fig. 4.35 also prove the contaminations.

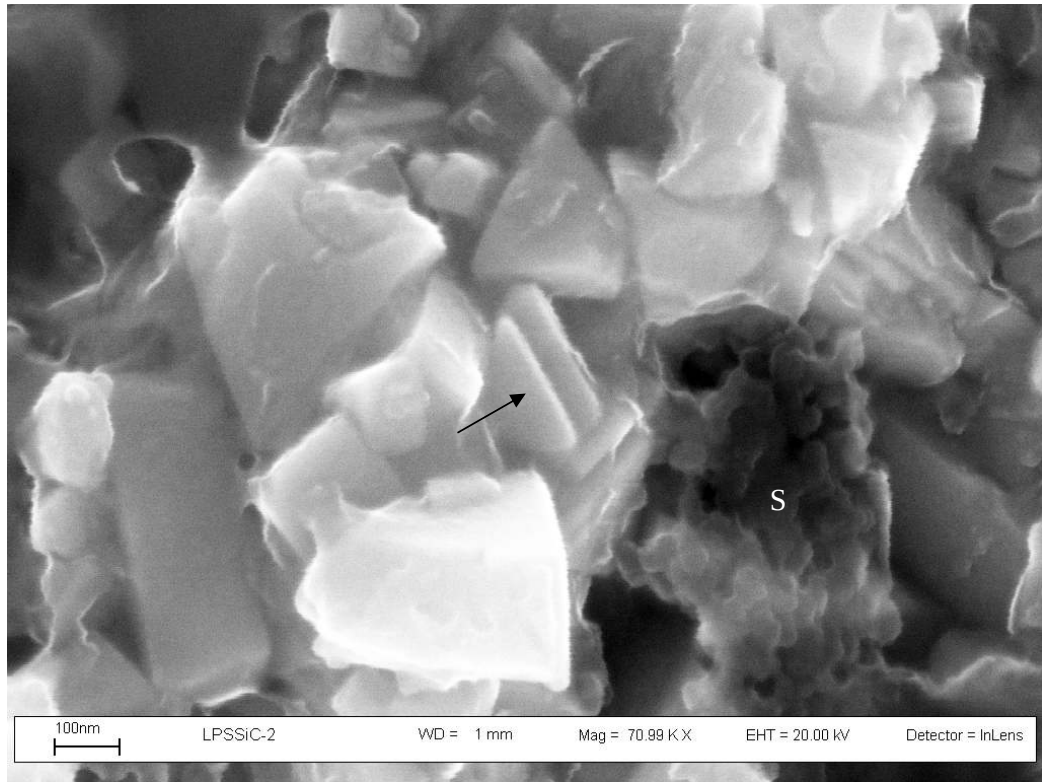


Fig. 4.31: FESEM micrograph of an area of the possible fracture origin on the fracture surface of NYA15-200C-3. The arrow indicates a step. Area S is clearly a stained area.

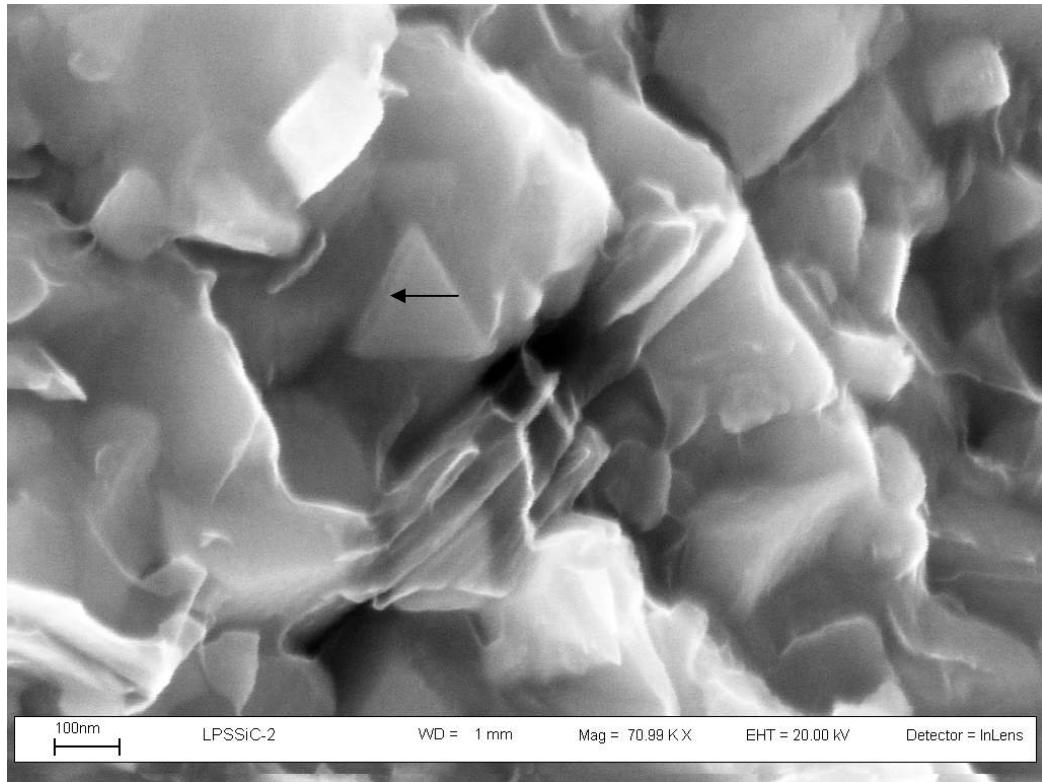


Fig. 4.32: FESEM micrograph of another area of the possible fracture origin on the fracture surface of NYA15-200C-3. Under stains, a step on a WC grain (indicated by an arrow) still is recognizable.

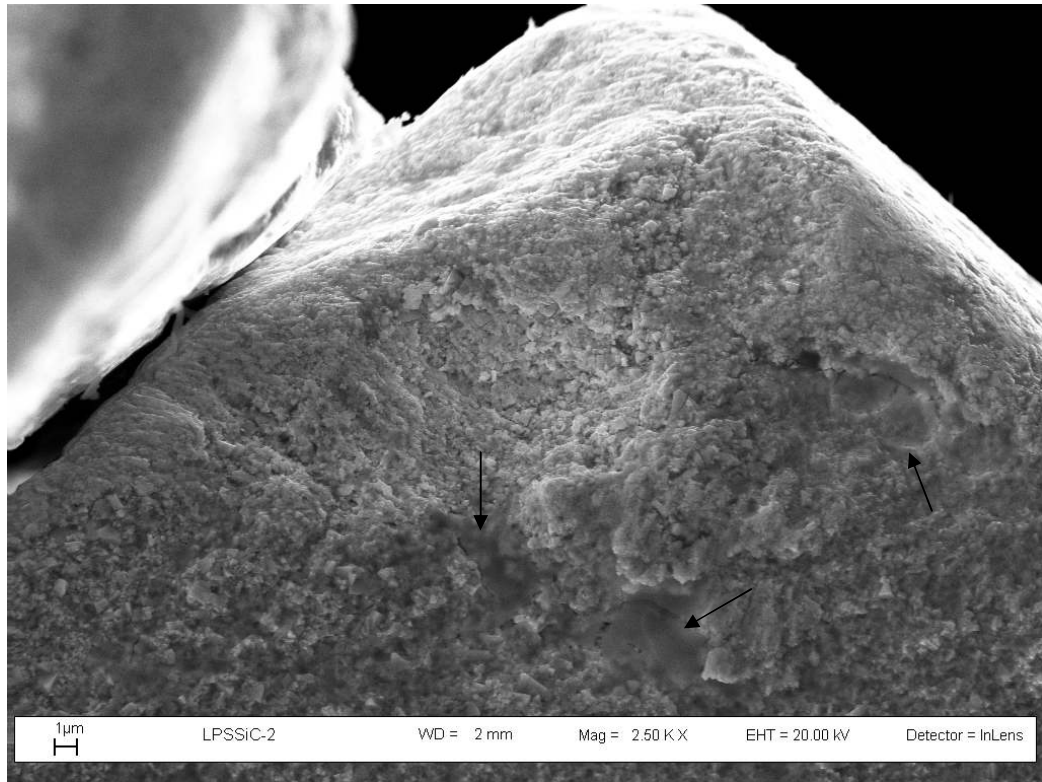


Fig. 4.33: FESEM micrograph: the low magnification appearance of the Corner on the fracture surface of NYA15-200C-3. Arrows point to stained areas.

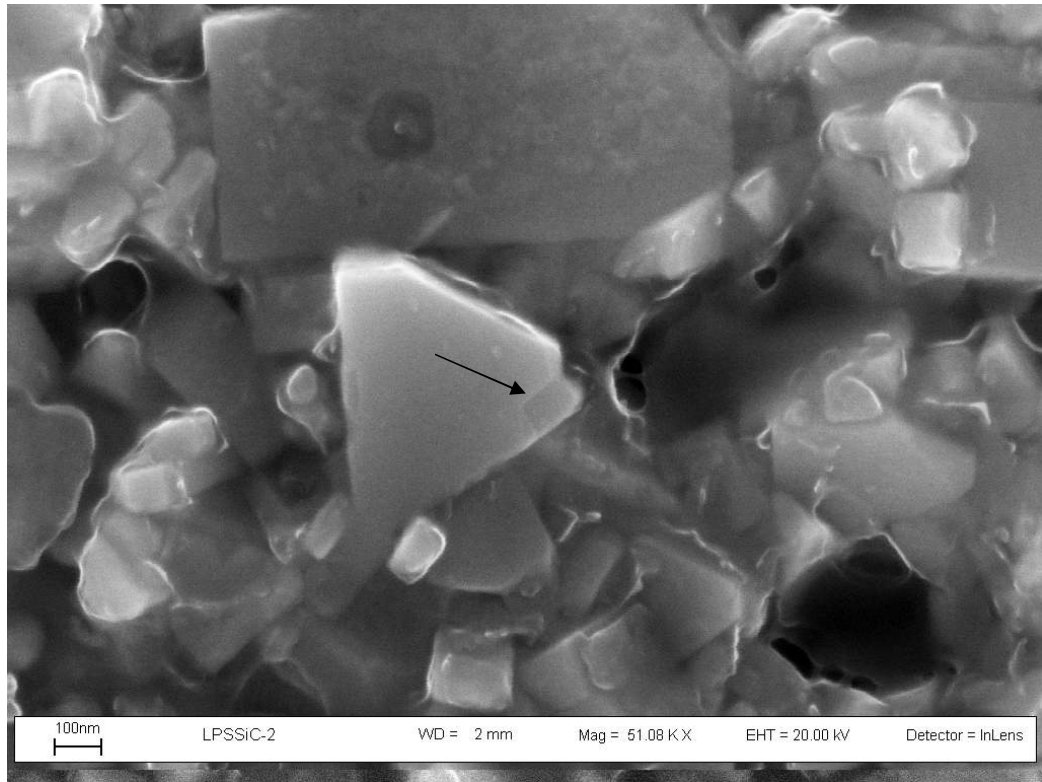


Fig. 4.34: FESEM micrograph of an area of the Corner on the fracture surface of NYA15-200C-3. A step is indicated.

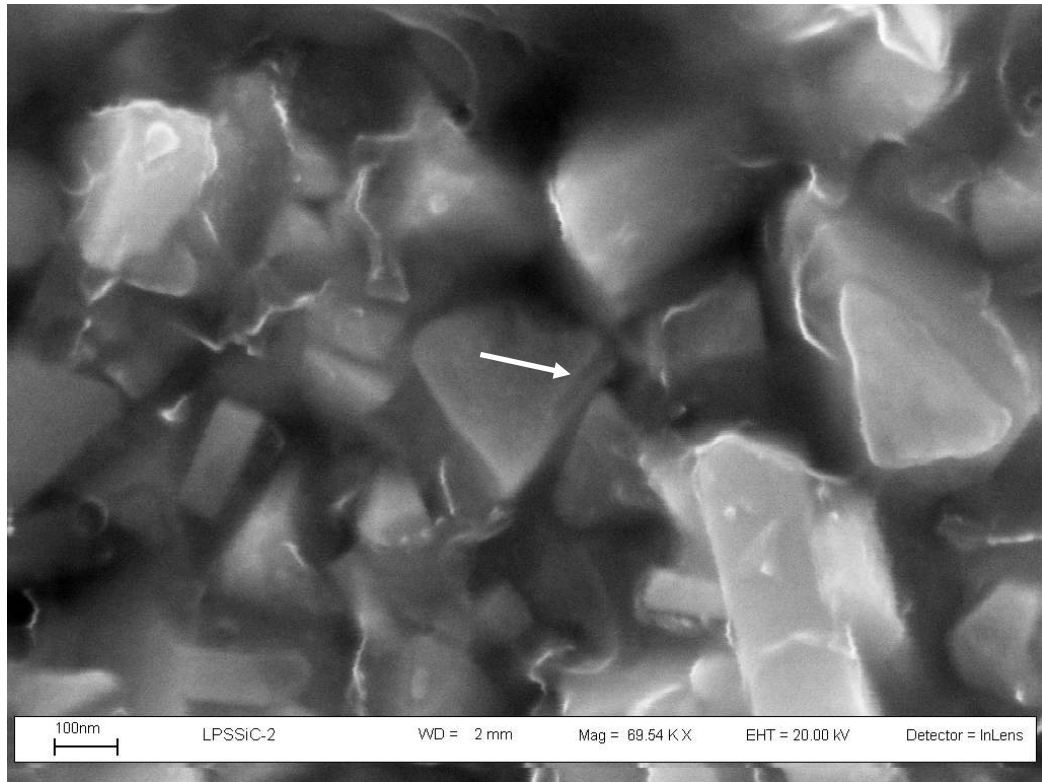


Fig. 4.35: Another FESEM micrograph of the same area as Fig. 4.31. A step is indicated by an arrow.

Both areas in Fig. 4.34 and Fig. 4.35 seem covered by a thin layer.

Fewer steps were found on the fracture surface of NYA15-200C-3 than NYA15-20C-1.

NYA15-400C-2:

The fracture origin of NYA15-400C-2 could be identified at the corner near the tensile side on the fracture surface.

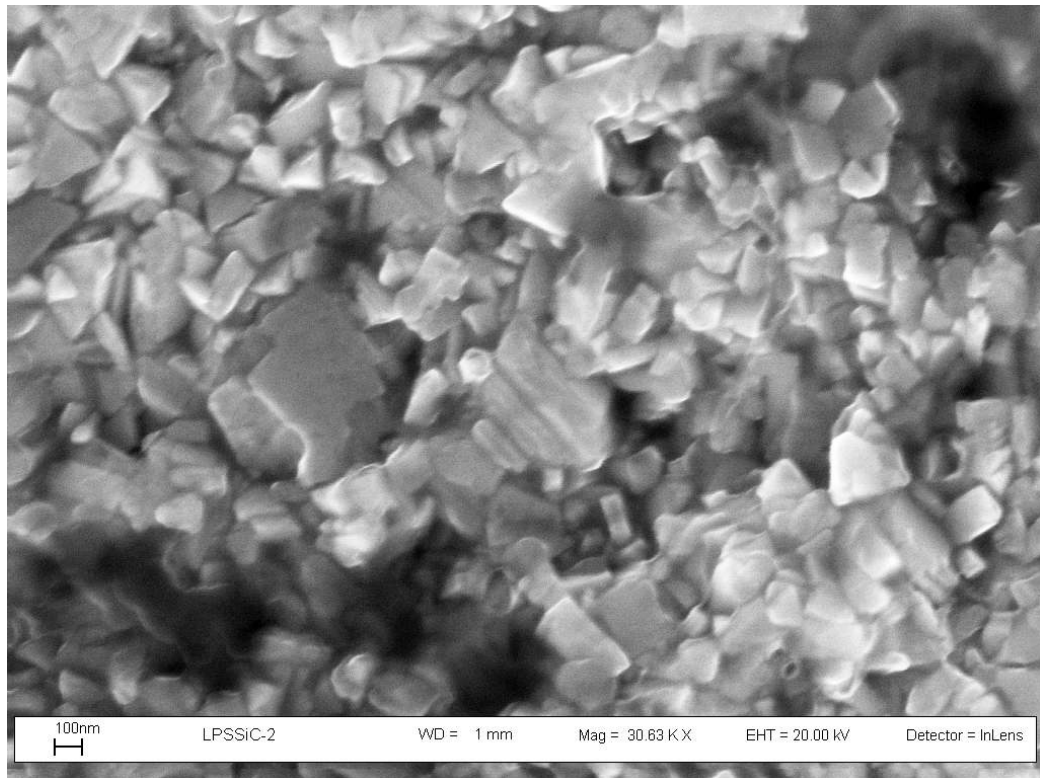


Fig. 4.36: FESEM micrograph of the fracture origin area on the fracture surface of NYA15-400C-2.

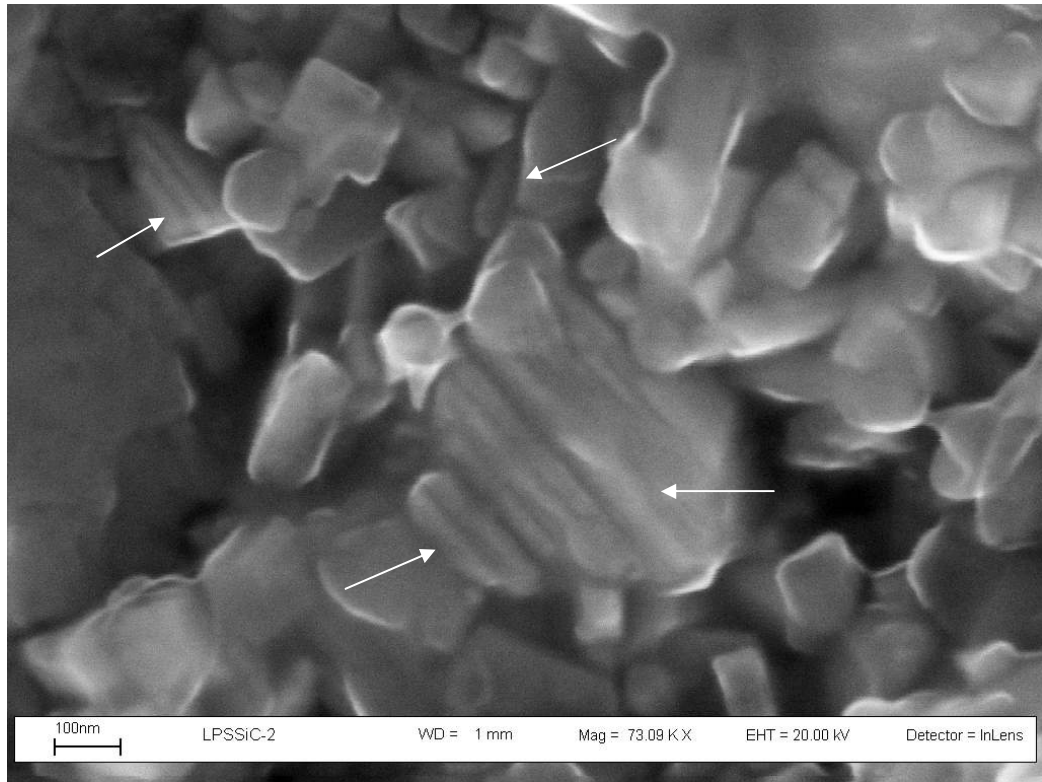


Fig. 4.37: FESEM micrograph of the same area as Fig. 4.36 at higher magnification. More steps on different WC grains can be identified (arrows) at this magnification.

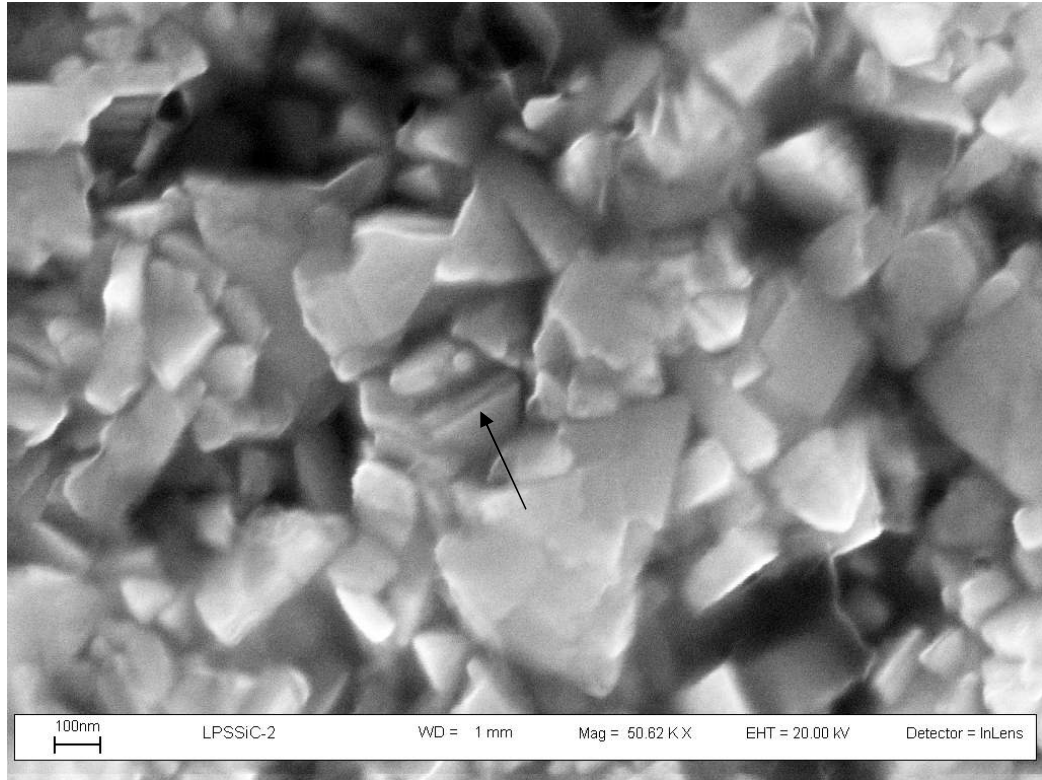


Fig. 4.38: FESEM micrograph of another area in the fracture origin of NYA15-400C-2. A step was found (arrow) despite the stains.

NYA15-600C-3:

The fracture origin of NYA15-600C-3 could be identified on the fracture surface. It was located at a corner near the tensile side.

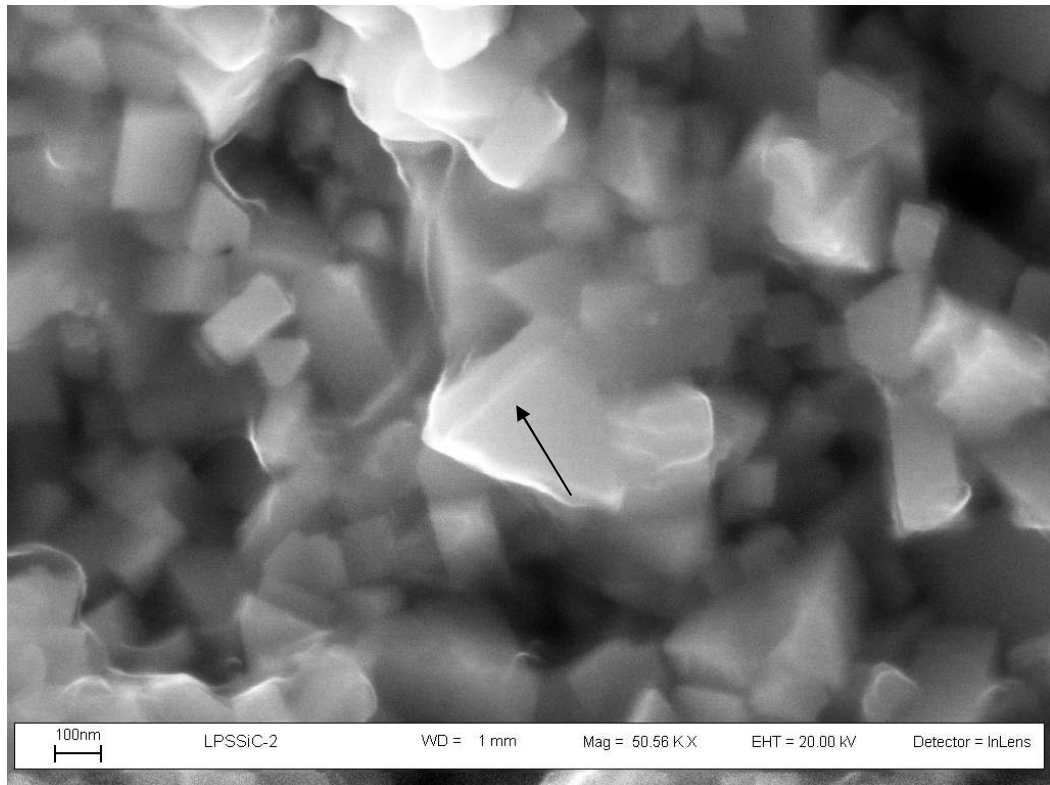


Fig. 4.39: FESEM micrograph of the fracture origin area on the fracture surface of NYA15-600C-3. The arrow points to a step.

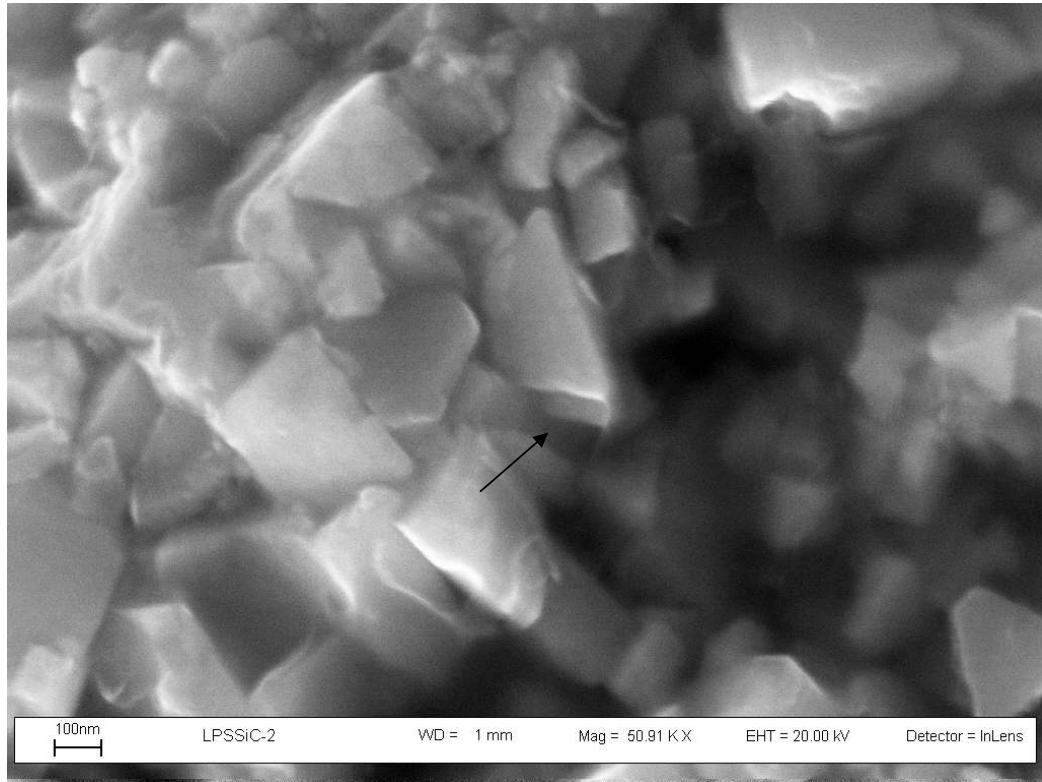


Fig. 4.40: FESEM micrograph: another step (indicated by an arrow) in the fracture origin area on the fracture surface of NYA15-600C-3.

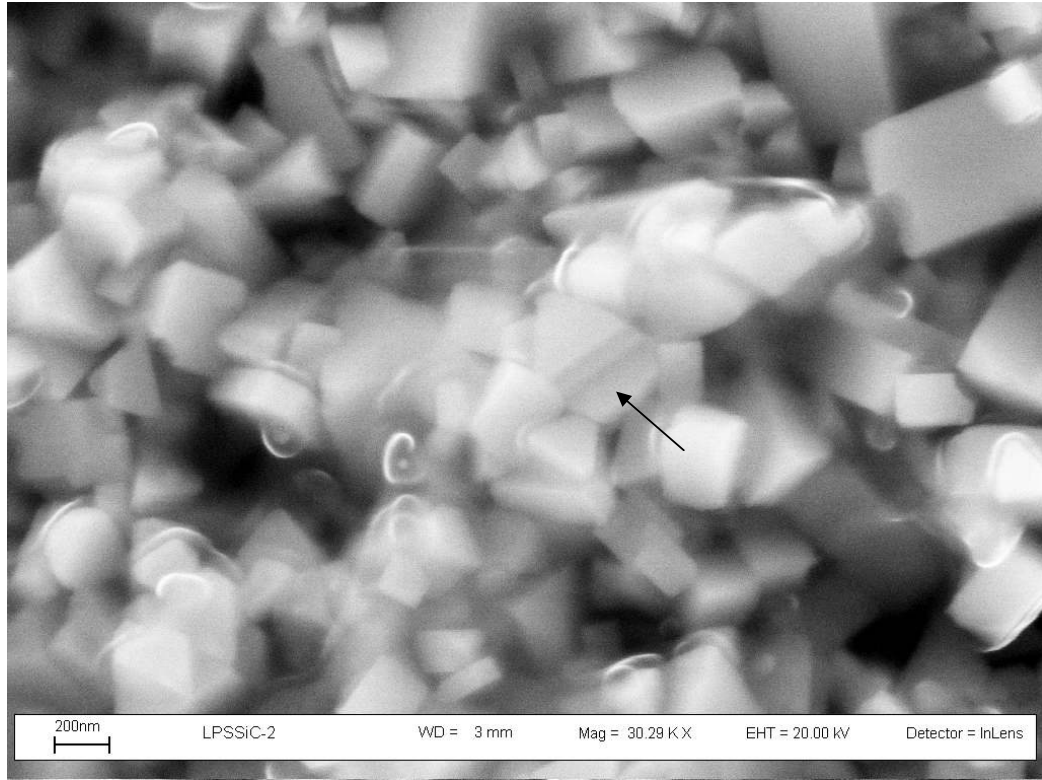


Fig. 4.41: FESEM micrograph: another step (indicated by an arrow) near the fracture origin area on the fracture surface of NYA15-600C-3. All the surfaces in Fig. 4.39, 4.40 and 4.41 are covered by contamination.

NYA15-800C-2:

The fracture origin of NYA15-800C-3 was located at a corner near the tensile side (see Fig. 4.42) on the fracture surface.

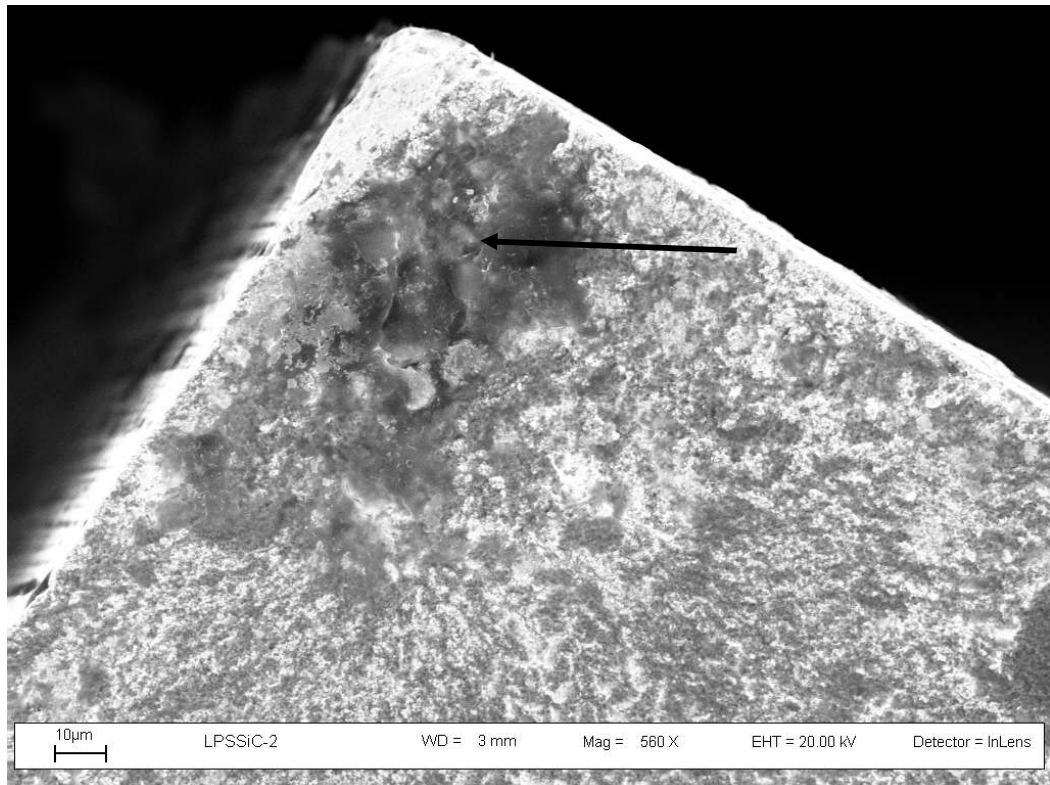


Fig. 4.42: FESEM micrograph: the low magnification appearance of the fracture origin of NYA15-800C-2. The arrow points to the fracture origin. See Fig. 4.43 for more detail. Comparing this image to the stereomicroscope image Fig. 4.16, the surface, especially the fracture origin area, is badly contaminated.

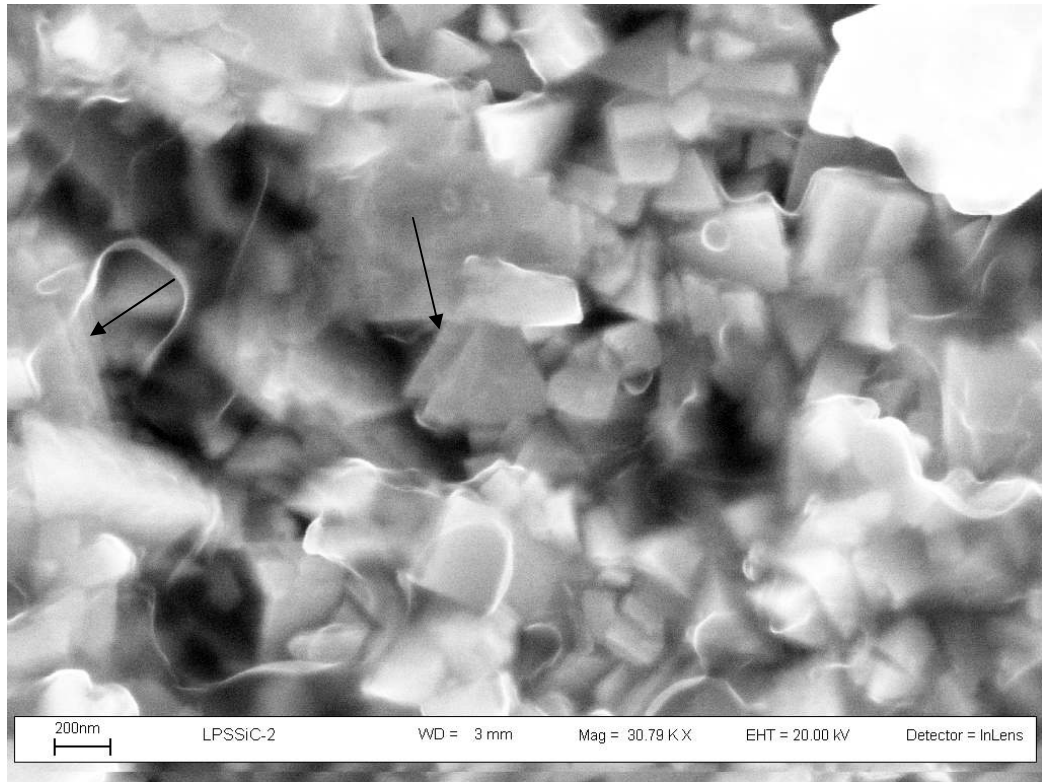


Fig. 4.43: FESEM micrograph of the fracture origin area on the fracture surface of NYA15-800C-2. Arrows point to steps on WC grains. The contamination on the surface of this area interferes the resolution, leaves the steps beneath vague.

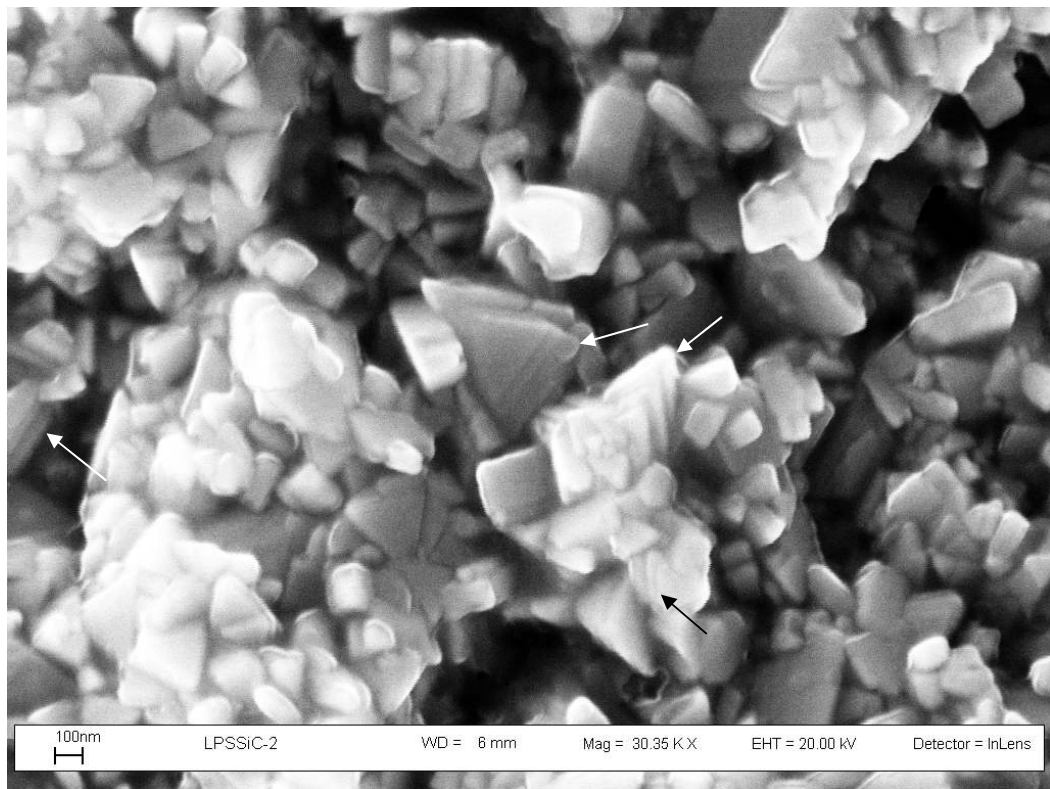


Fig. 4.44: FESEM micrograph of an area near the tensile side on the fracture surface of NYA15-800C-2. This area seems clean and free of stains. Steps can be easily identified.

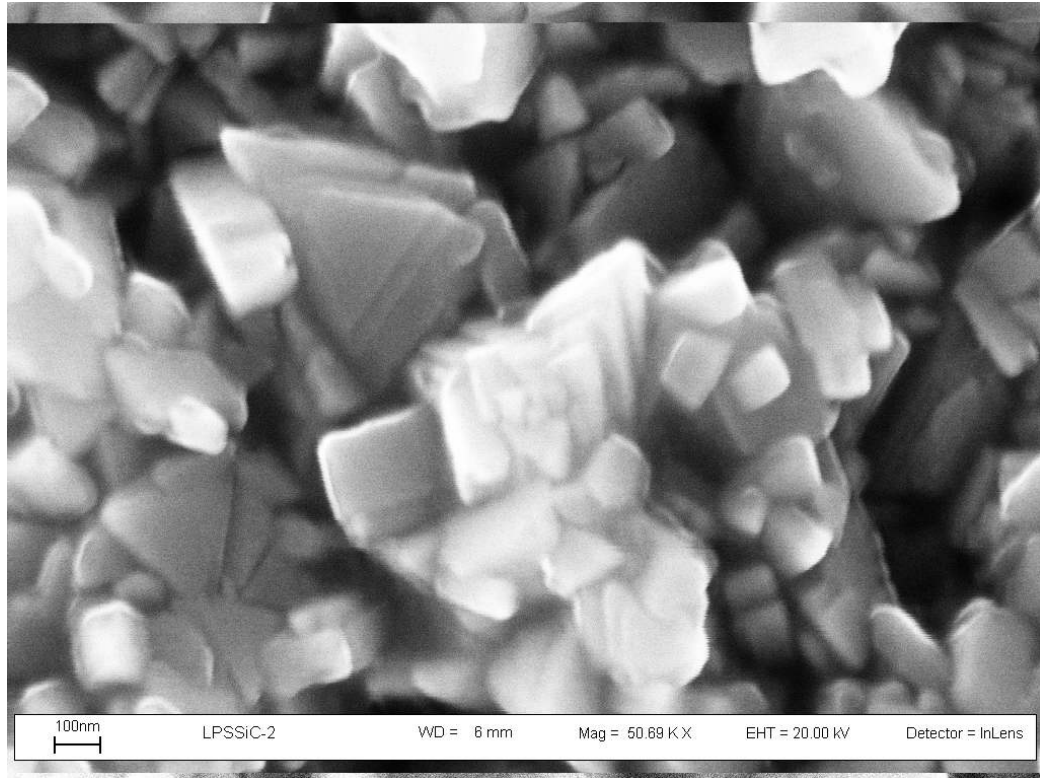


Fig. 4.45: FESEM micrograph: higher magnification of the same area as in Fig. 4.44.

Steps were more frequently observed in 20°C and 800°C specimens than in 200°C, 400°C and 600°C ones. The phenomenon that fewer steps were observed in these middle temperature specimens may be due to the contamination on the fracture surface.

In the NYB grade, different areas on the fracture surfaces of the specimens were studied. Steps were only observed on the fracture surfaces of the samples tested at 400°C, 800°C and 1000°C.

NYB15-400C-3:

Two areas, the fracture origin near the tensile side and a compressive side corner, on the fracture surface of NYB15-400C-3 (see Fig. 4.46) were studied.

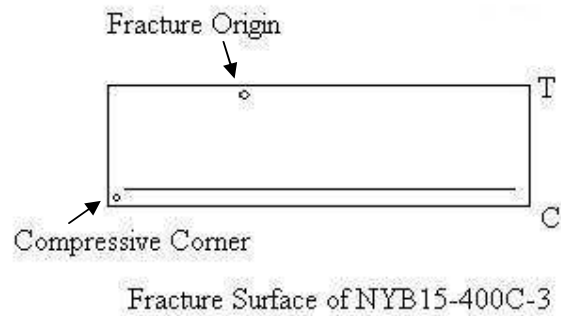


Fig. 4.46: Sketch of NYB15-400C-3 fracture surface showing the areas investigated.

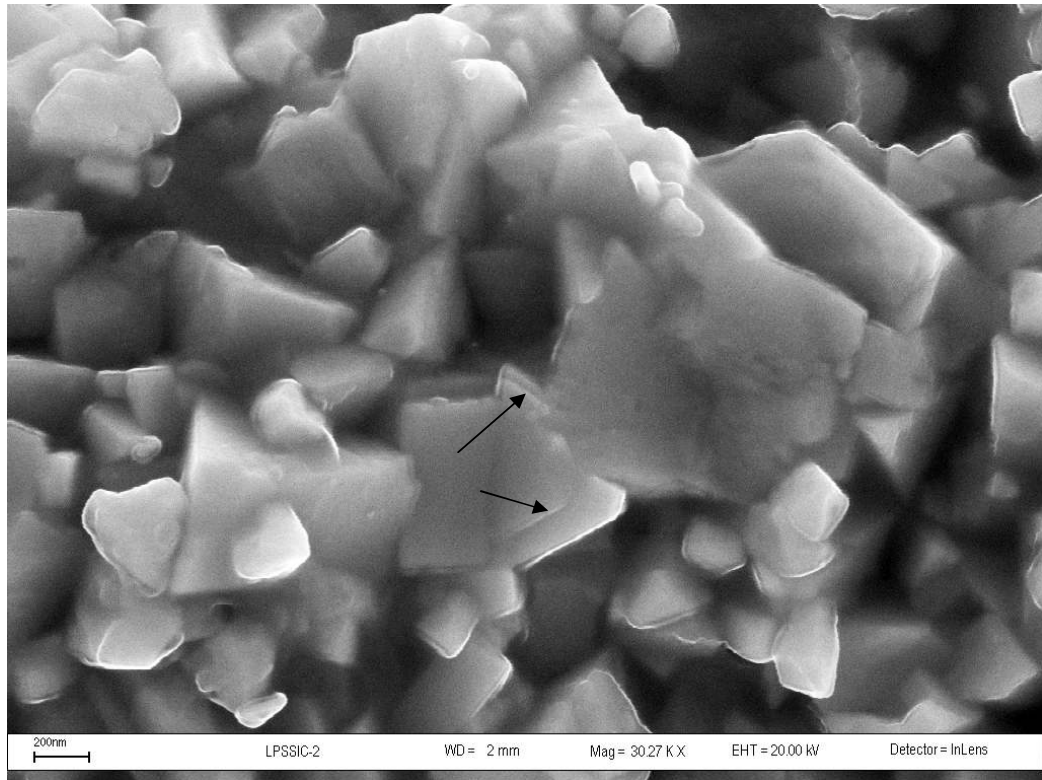


Fig. 4.47: FESEM micrograph of the fracture origin area on the fracture surface of NYB15-400C-3. Two steps were indicated by arrows.

In the area near compressive side, steps were identified as well.

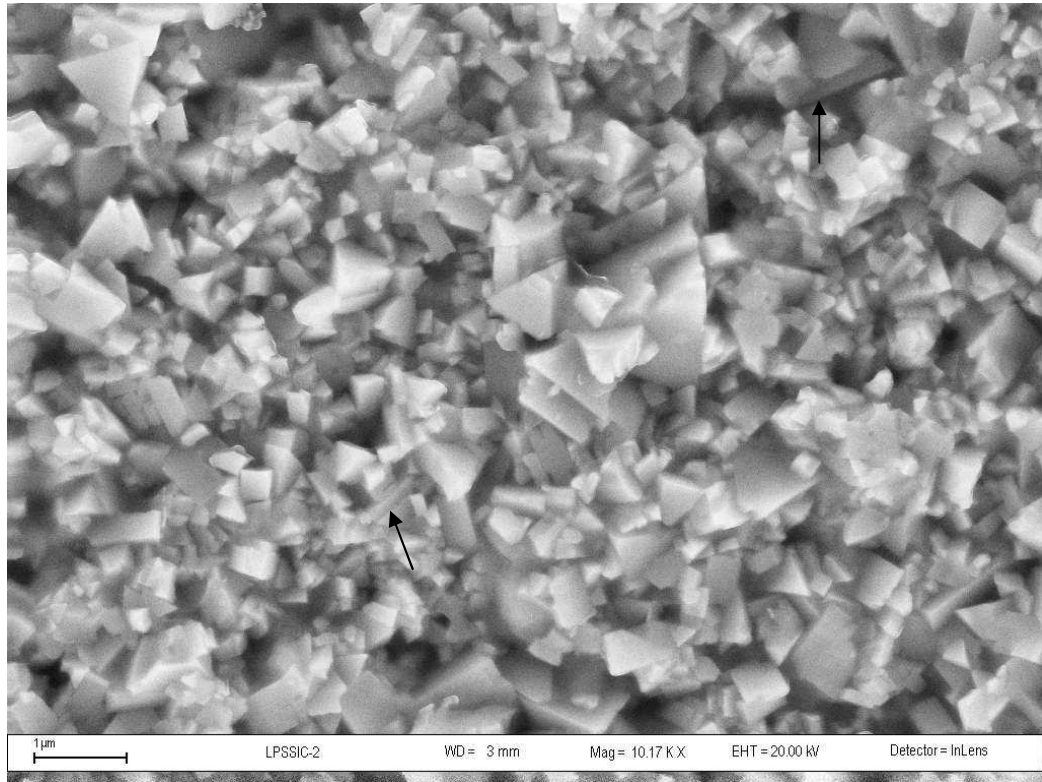


Fig. 4.48: FESEM micrograph of the Compressive Corner on the fracture surface of NYB15-400C-3. Arrows indicate the steps.

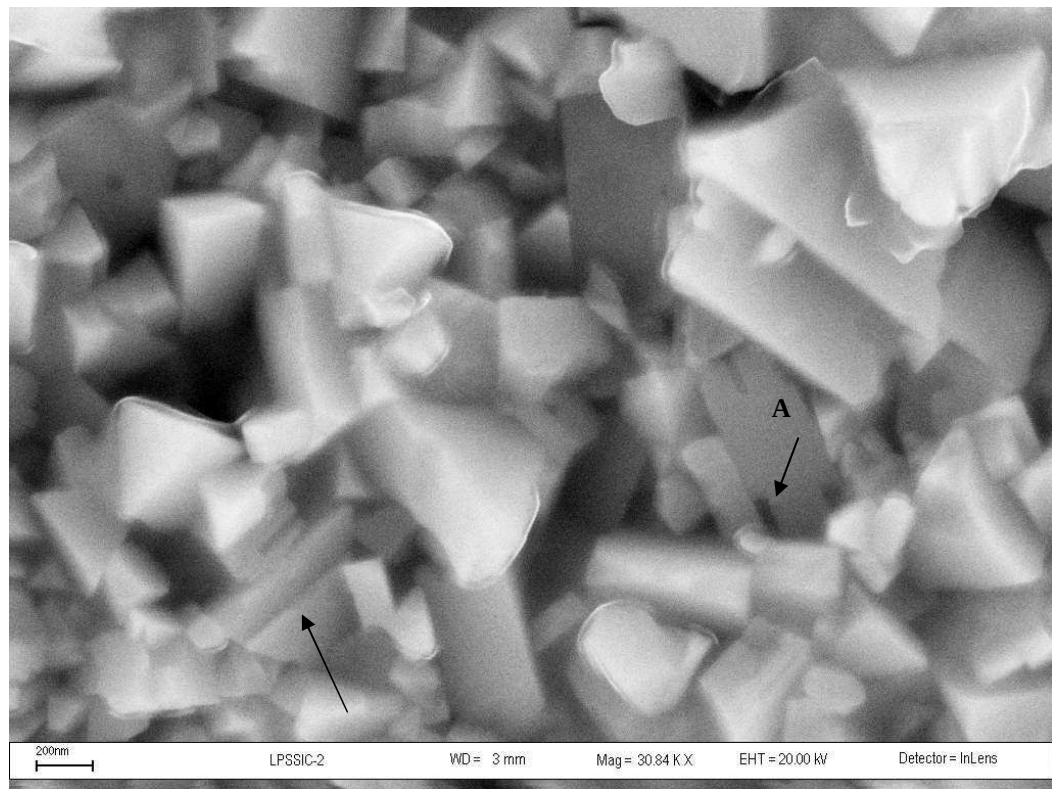


Fig. 4.49: FESEM micrograph: a higher magnification of the same area as Fig. 4.48. Two arrows indicate two grains with steps.

NYB15-800C-3:

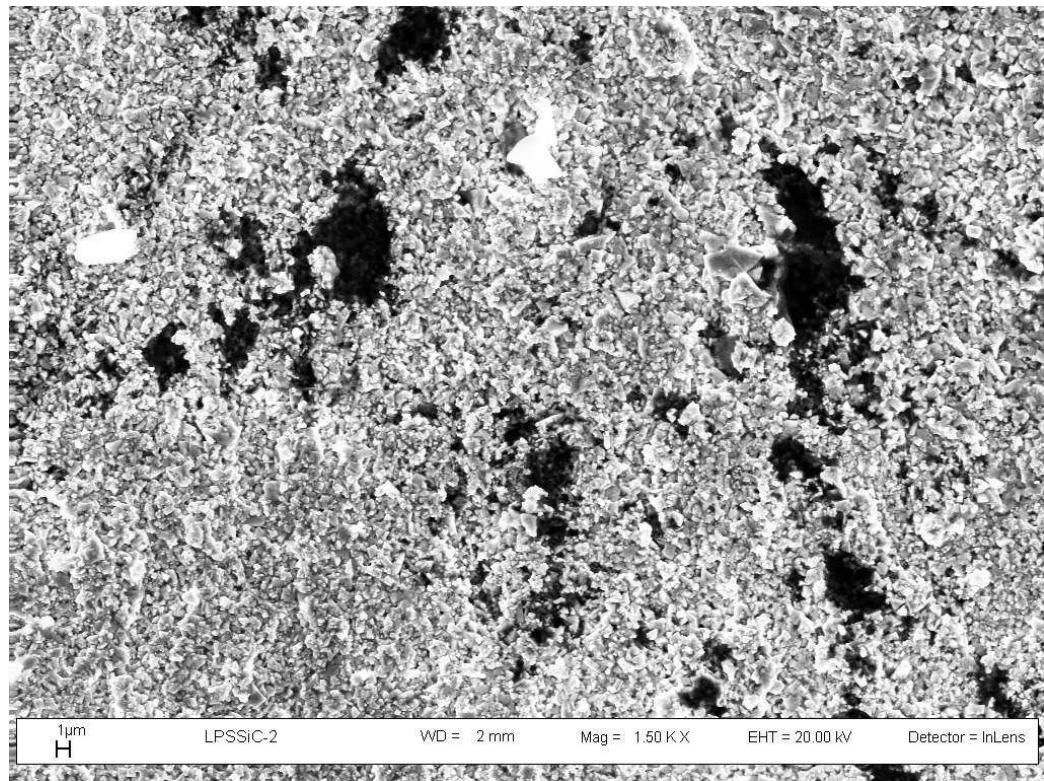


Fig. 4.50: FESEM micrograph: the appearance of the fracture origin at low magnification. Pores were probably the cause of stress concentration, which led to failure.

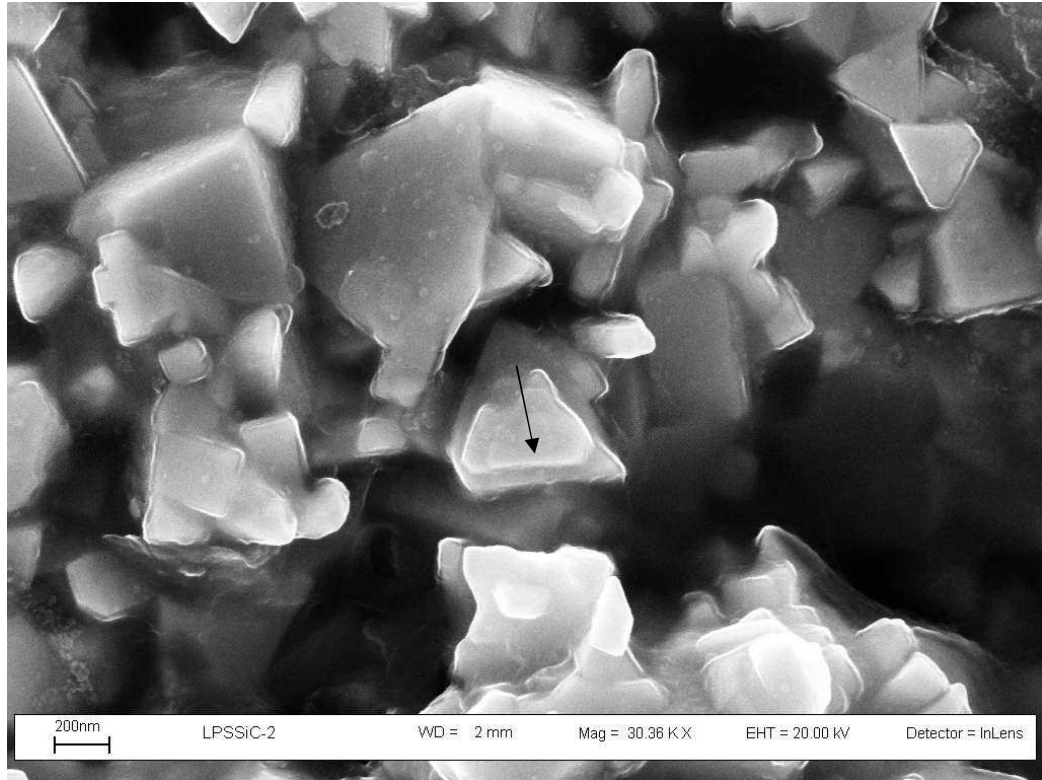


Fig. 4.51: FESEM micrograph of the fracture origin area on the fracture surface of NYB15-800C-3 at higher magnification. A clear step is indicated by an arrow.

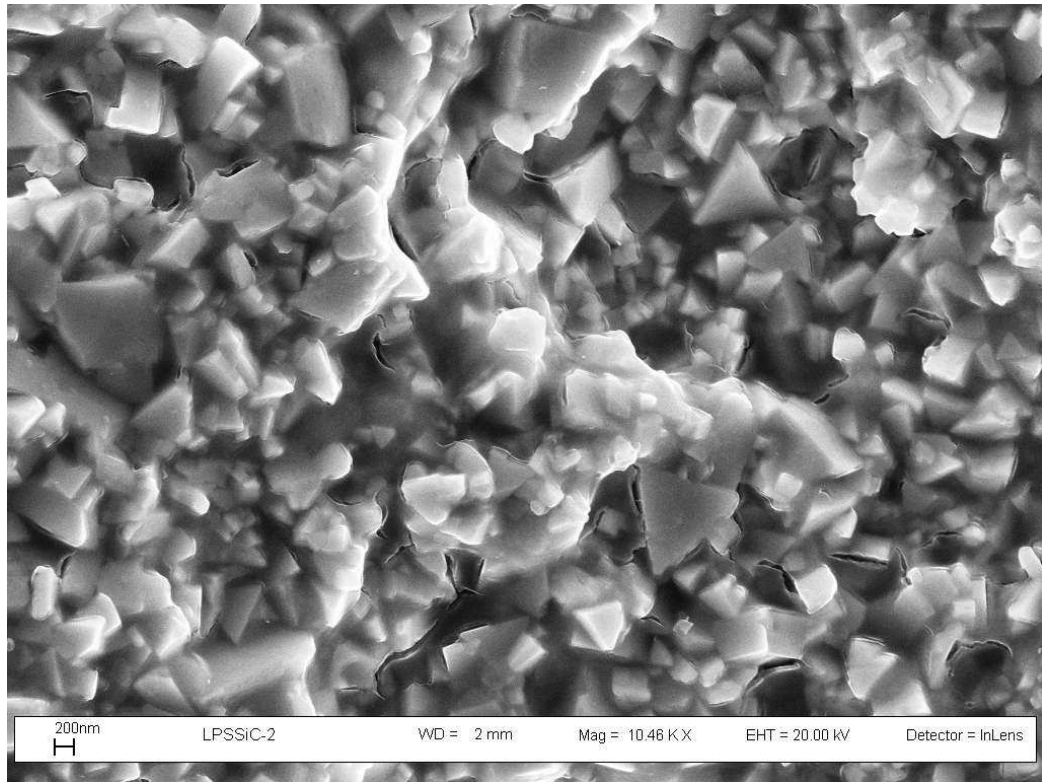


Fig. 4.52: FESEM micrograph of an area near tensile side on the fracture surface of NYB15-800C-3, showing re-solidified cobalt.

NYB15-1000C-3:

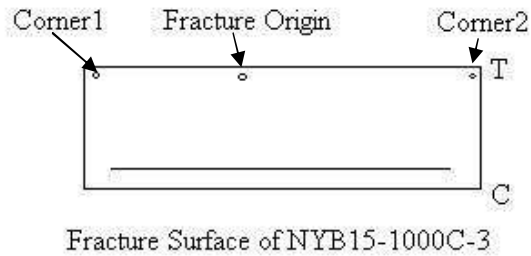


Fig. 4.53: Sketch of NYB15-1000C-3 fracture surface with the areas investigated.

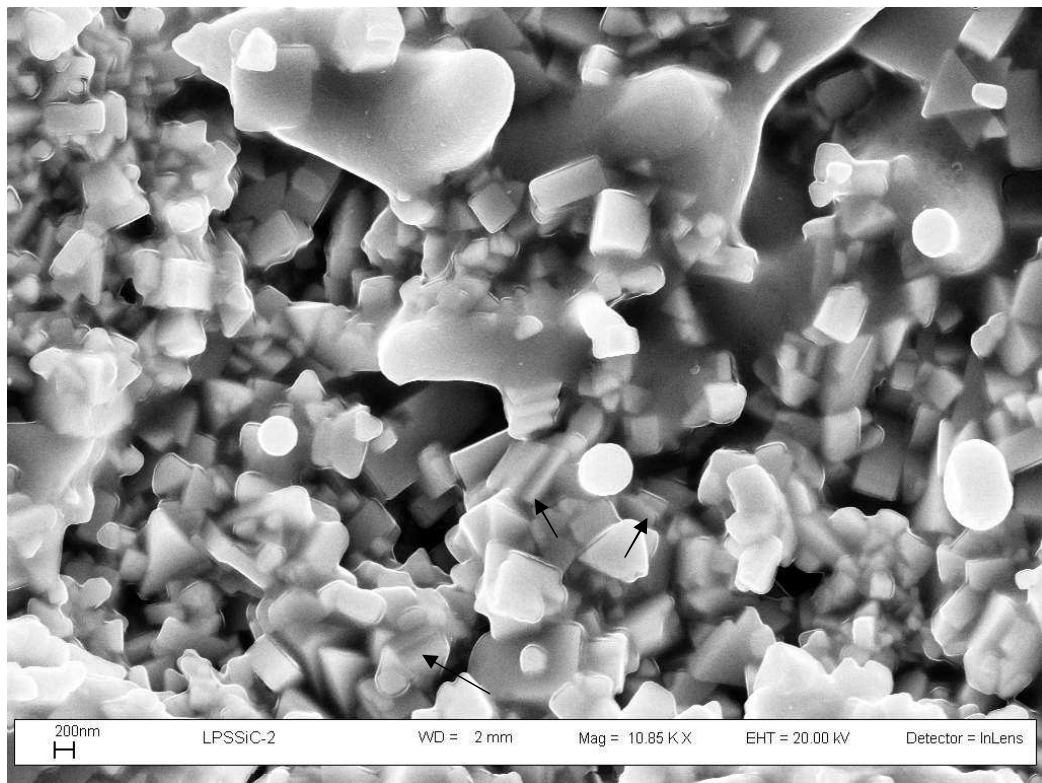


Fig. 4.54: FESEM micrograph of the fracture origin area on the fracture surface of NYB15-1000C-3. Steps are indicated by arrows. It seems that Co droplets, which appear as bright round shapes on the surface, formed during fracture.

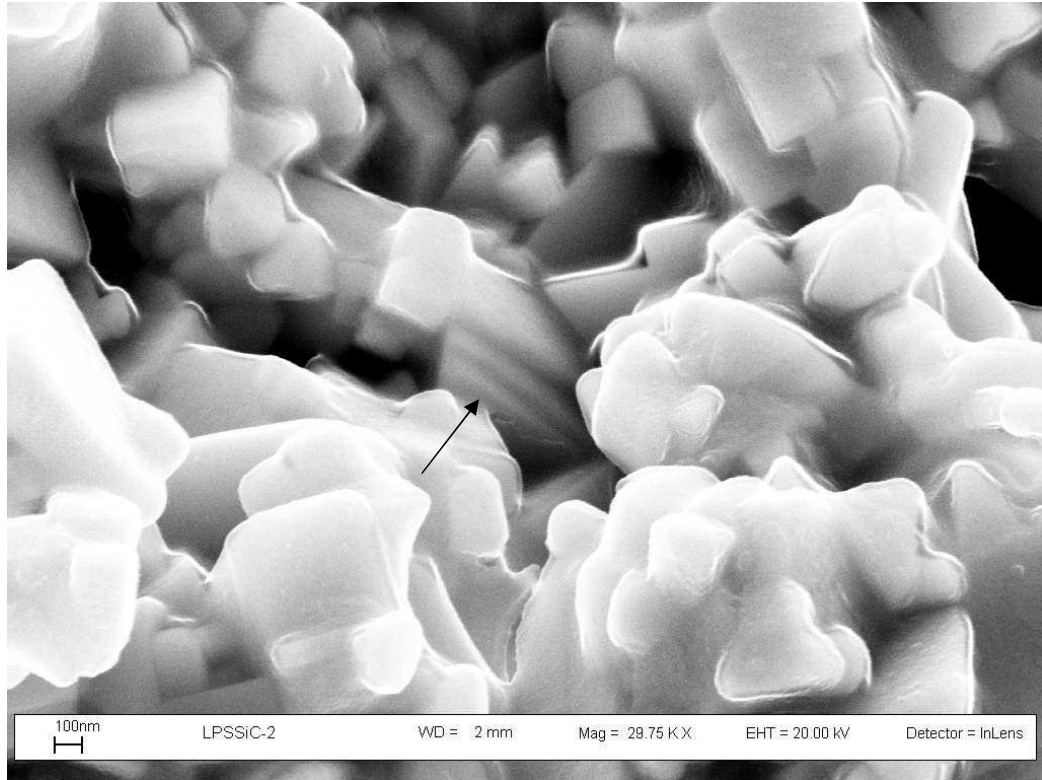


Fig. 4.55: FESEM micrograph of the fracture origin area with steps (indicated by an arrow) on the fracture surface of NYB15-1000C-3. WC grains seem to be covered by contamination and the white lines along the grains are probably related to contaminations.

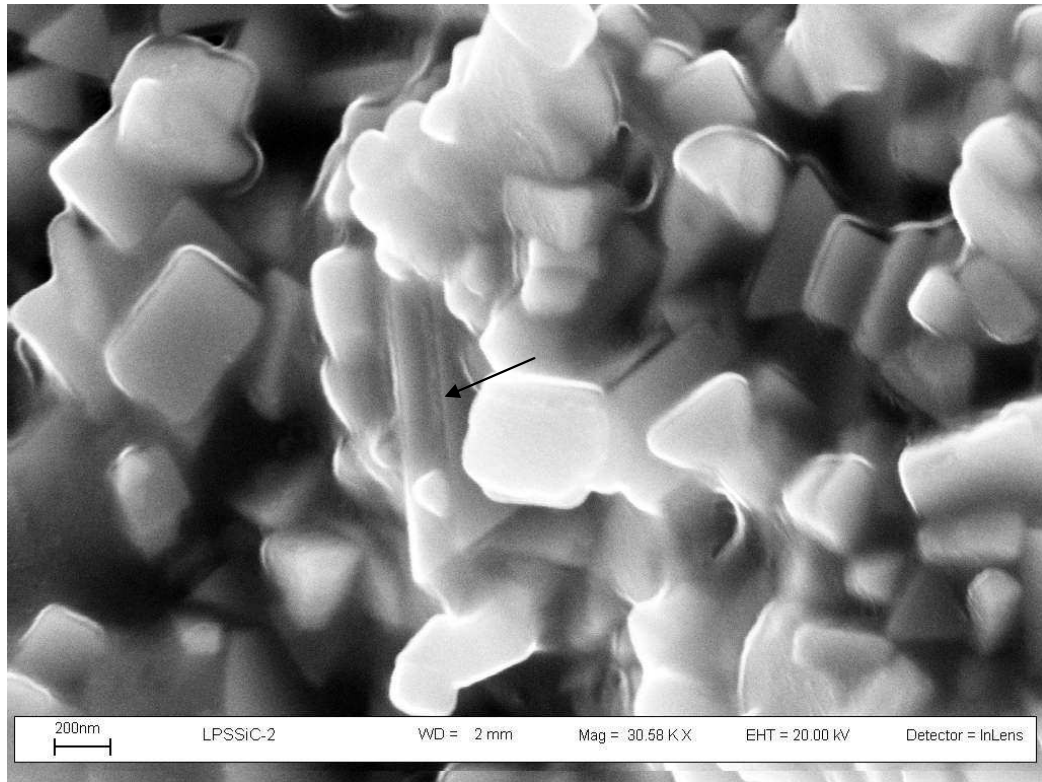


Fig. 4.56: FESEM micrograph of Corner1 near the tensile side on the fracture surface of NYB15-1000C-3. It looks similar to the area of the fracture origin (Fig. 4.54 and Fig. 4.55).

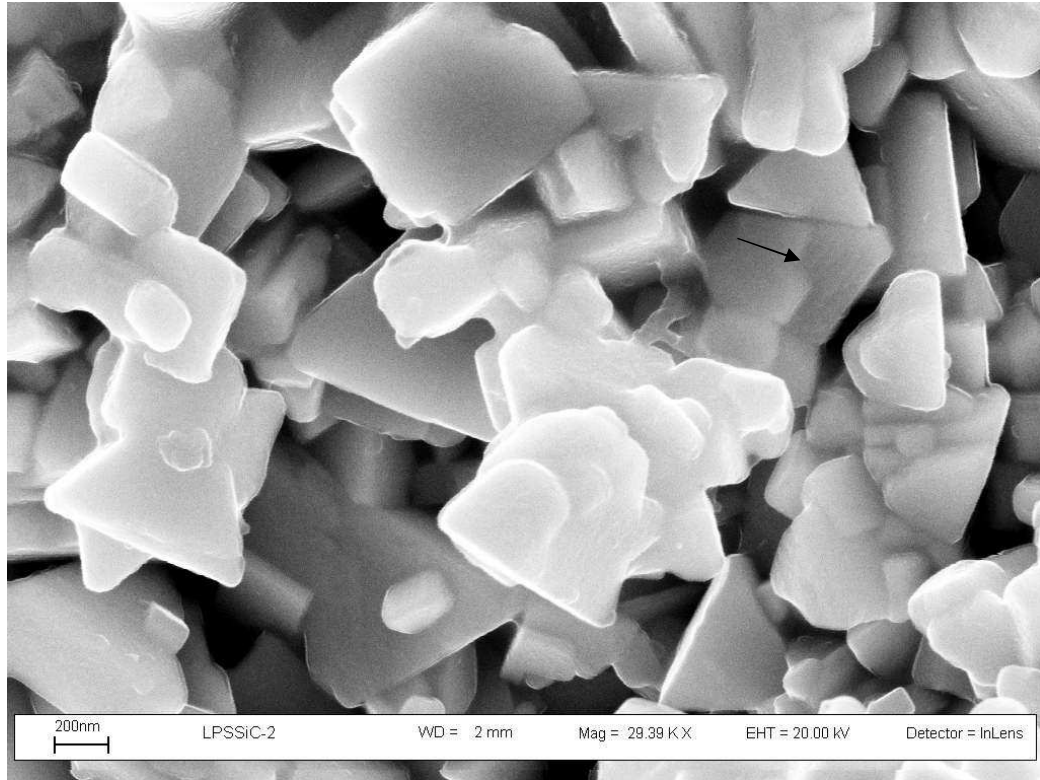


Fig. 4.57: FESEM micrograph of the corner2 near the tensile side on the fracture surface of NYB15-1000C-3. Besides the steps, deformation in a single WC grain (indicated by the arrow) in the form of slip lines can be identified. Contamination in this area seems to be less.

Besides the 400°C, 800°C and 1000°C specimens, no steps were found on the fracture surfaces of the NYB15 grade specimens at other temperatures. Even on the fracture surface of 400°C, 800°C and 1000°C specimens, fewer steps were observed in comparison with those found on the fracture surfaces of NYA15 grade. As shown before, the fracture surfaces of the NYB15 grade are contaminated. Contamination maybe prevents exposure of the step feature.

4.4.2.2 Layers on the Fracture Surfaces

On most of the fracture surfaces of the NYB15 and NYA15 grades, layers of some materials have been observed. Efforts have been made to investigate whether they are contaminations or layers of WC-Co components.

Specimens of the NYB15 grade tested at different temperature were examined.

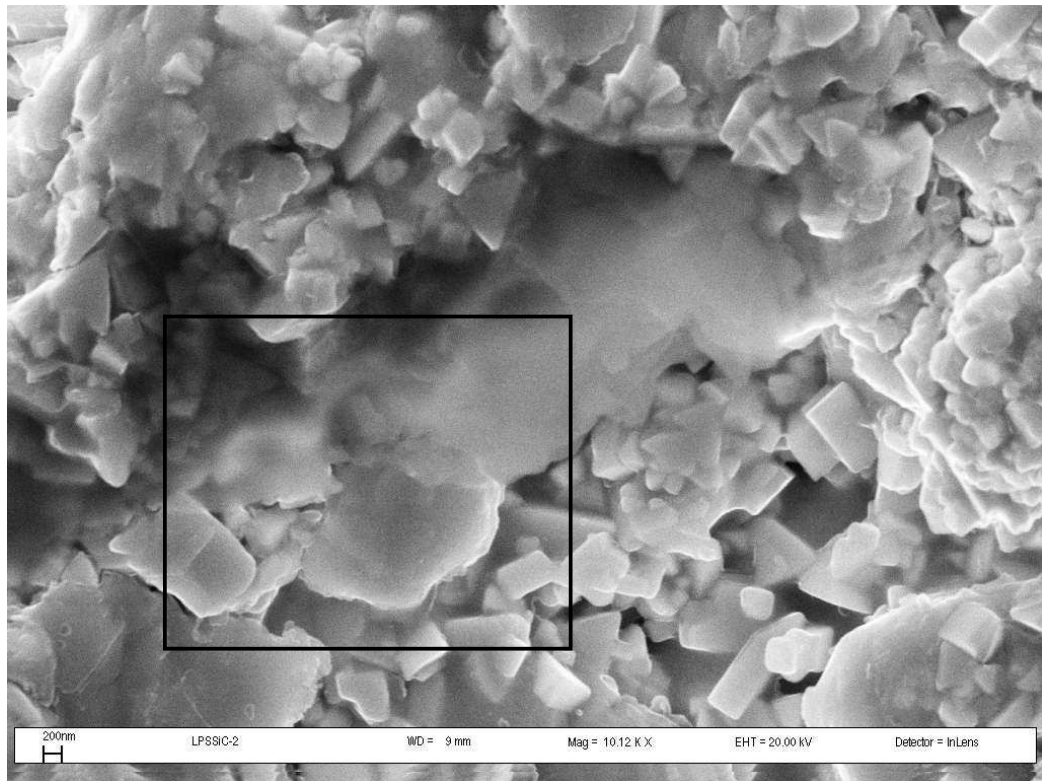


Fig. 4.58: FESEM micrograph of an area covered by a layer at a tensile corner on the fracture surface of NYB15-1000C-3. The rectangular area surrounded by black lines is the area analyzed by EDS. The EDS spectrum and approximate composition are given in Fig. 4.59 and Table 4.2.

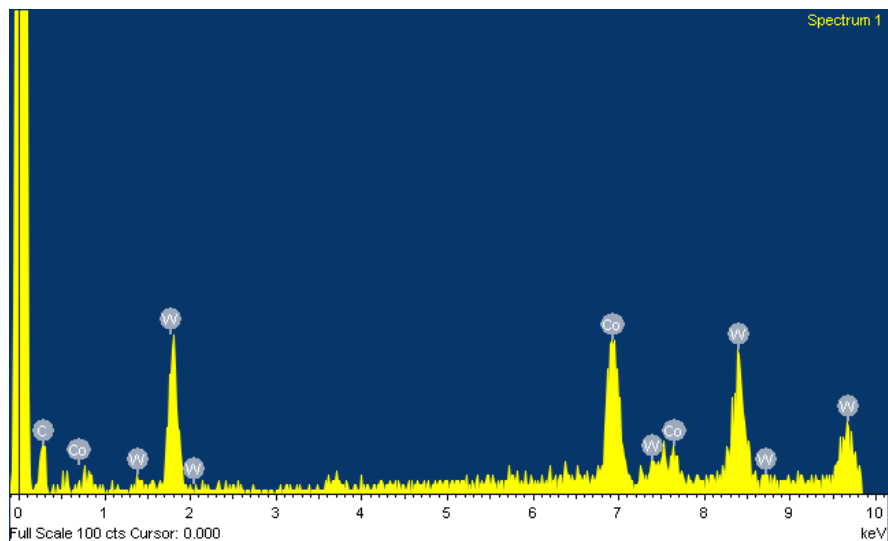


Fig. 4.59: EDS spectrum of the area analyzed in Fig. 4.58. W, Co and C were detected.

Table 4.2: Approximate composition of the area analyzed by EDS in Fig. 4.58.

Element	Weight%	Atomic%
C	14.04	61.78
Co	22.18	19.89
W	63.78	18.33
Totals	100	

The C content is much more than the amount expected in WC, therefore it is partly due to some kind of contamination. The Co content is higher than the 15wt% of the alloy, therefore the layer in Fig. 4.58 is thought to be a thin Co-rich layer. It is thought to be thin because of the large amount of W detected from under it.

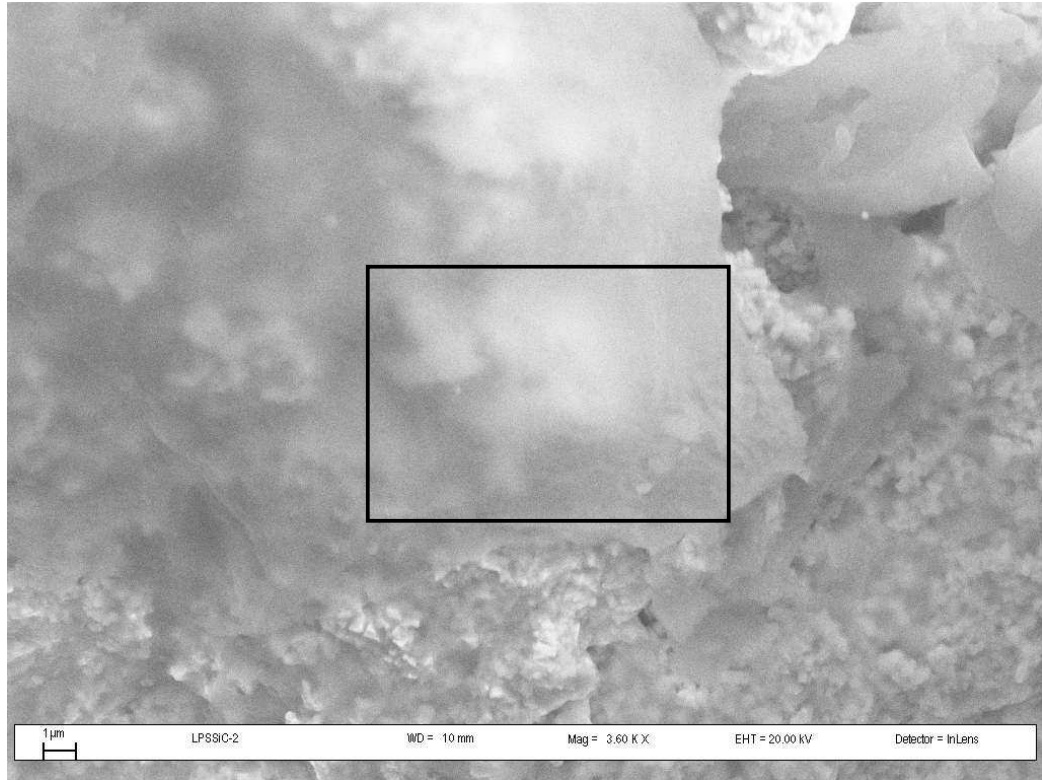


Fig. 4.60: FESEM micrograph of an area covered by a layer at a compressive corner on the fracture surface of NYB15-1000C-3. The area in the center surrounded by the rectangular black line is the area for EDS investigation. The EDS spectrum and results are shown in Fig. 4.61 and Table 4.3.

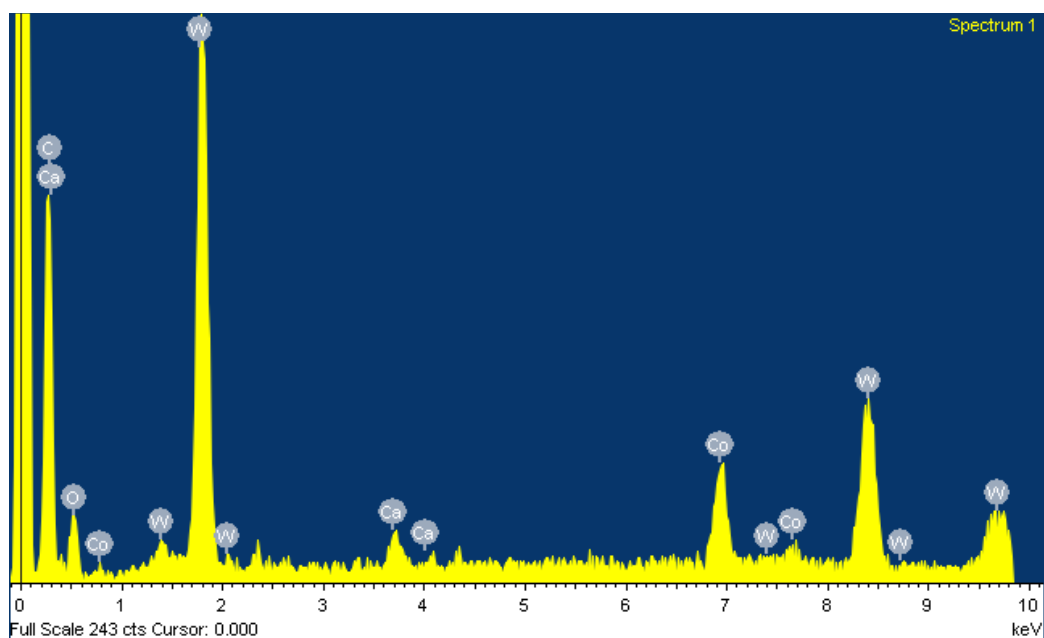


Fig. 4.61: EDS spectrum of the area analyzed in Fig. 4.60. W, Co, C, as well as Ca and O were detected.

Table 4.3: Approximate composition of the area analyzed by EDS in Fig. 4.60.

High carbon content and a small amount of Ca were detected.

Element	Weight%	Atomic%
C	39.29	79.69
O	6.99	10.64
Ca	0.92	0.56
Co	7.56	3.13
W	45.24	5.99
Totals	100	

The high C content, the O and the Ca suggest that the layer consists of contamination. The layer is expected to be thick because of the small amount of Co and WC detected.

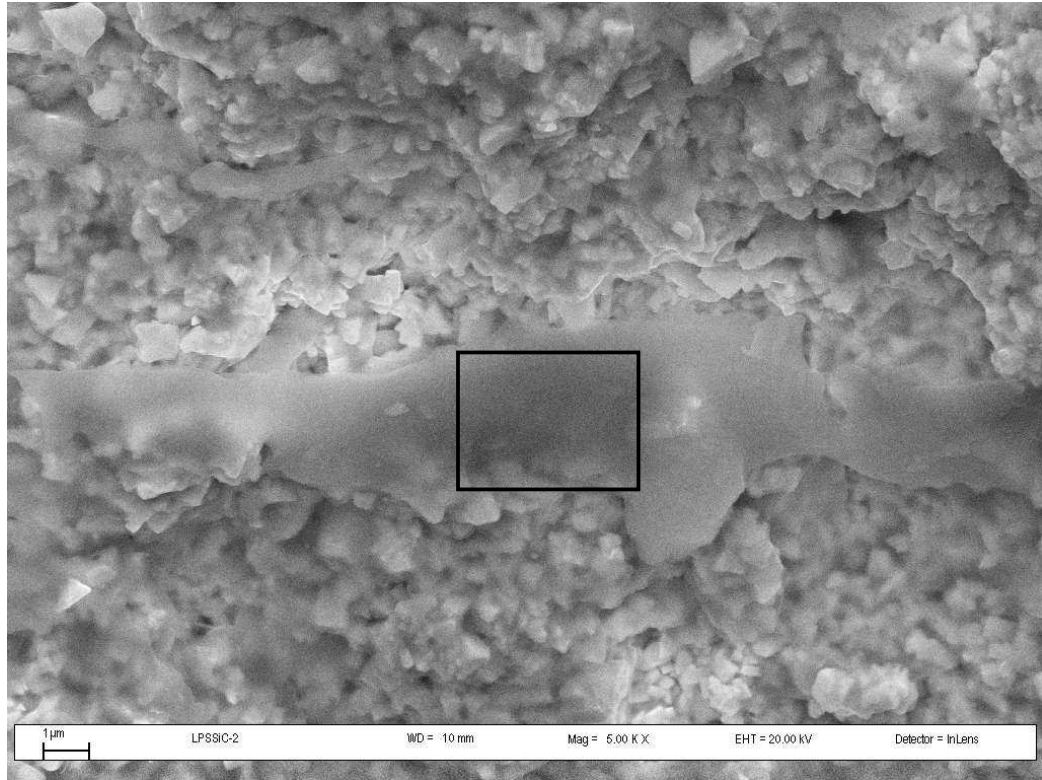


Fig. 4.62: FESEM micrograph of another area covered by a layer at the same compressive corner as in Fig. 4.60 on the fracture surface of NYB15-1000C-3. The EDS investigation was focused on the layer (as indicated by rectangular black line). The EDS spectrum and approximate composition are given in Fig. 4.63 and Table 4.4.

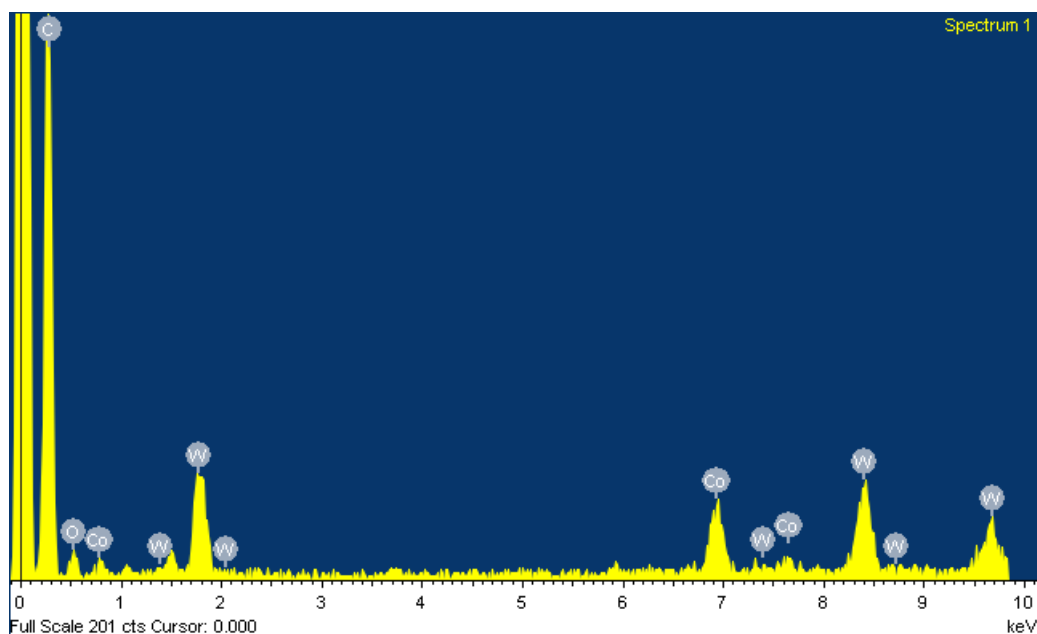


Fig. 4.63: EDS spectrum of the area analyzed in Fig. 4.62. W, Co, C, and O were detected. The carbon peak is very high.

Table 4.4: Approximate composition of the area investigated by EDS in Fig. 4.62.

Carbon content is very high and some oxygen is present.

Element	Weight%	Atomic%
C	58.39	90.61
O	3.55	4.14
Co	6.48	2.05
W	31.58	3.2
Totals	100	

This layer is expected by to an organic, thick layer for the same reasons as given above.

On the fracture surfaces of the other NYB15 specimens, layer were also found and investigated. Results are reported below:

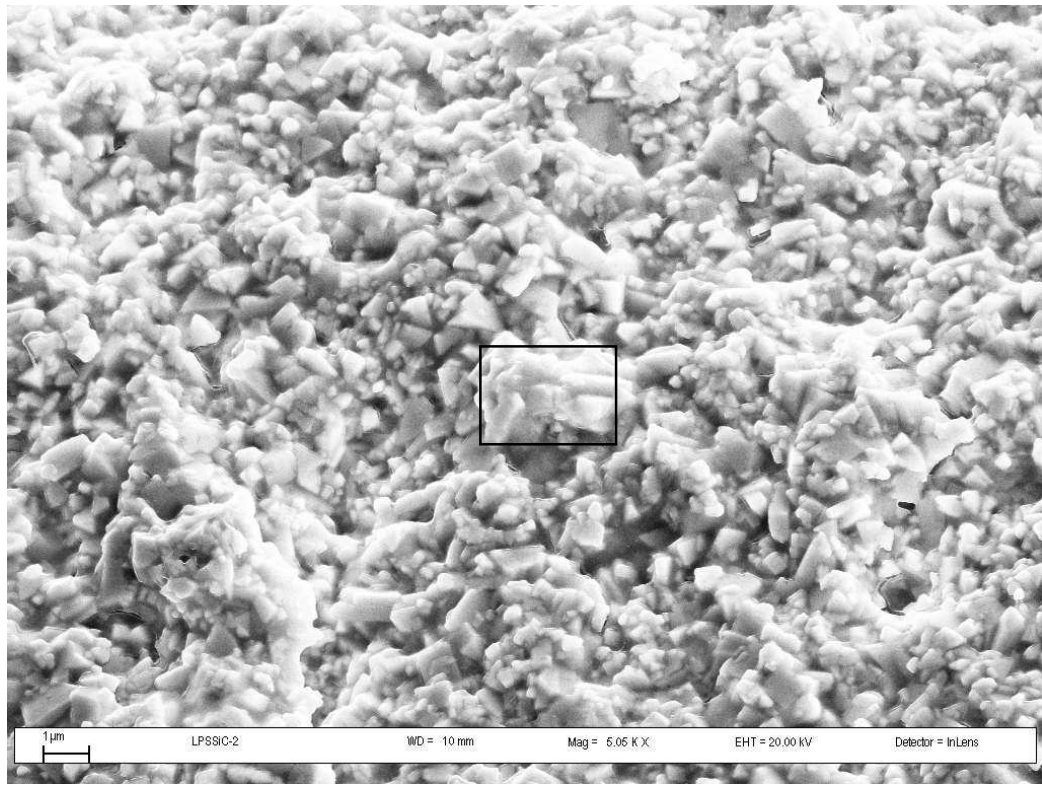


Fig. 4.64: FESEM micrograph of an area covered by a layer near the compressive side on the fracture surface of NYB15-800C-3. The rectangle indicates the EDS investigation area. The EDS spectrum and composition are given in Fig. 4.65 and Table 4.5.

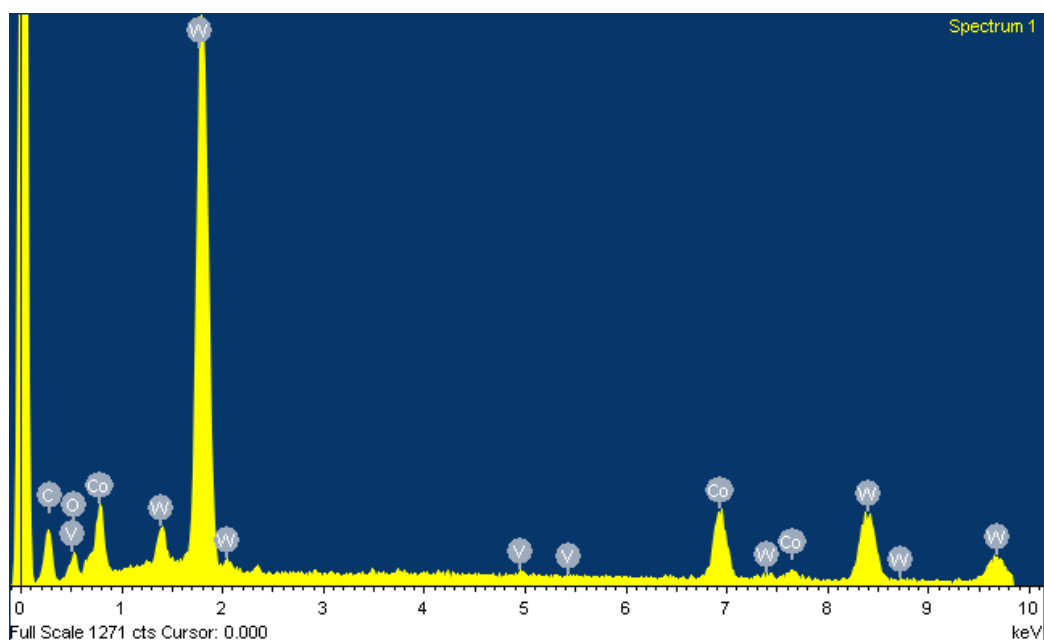


Fig. 4.65: EDS spectrum of the area analyzed in Fig. 4.64. Apart from W, Co, C, and O, V was also detected.

Table 4.5: Approximate composition of the area investigated by EDS in Fig. 4.64. Vanadium was detected as 0.41wt%, which agrees with the vanadium addition of 0.4wt% in NYB15 grade.

Element	Weight%	Atomic%
C	19.1	63.08
O	5.28	13.1
V	0.41	0.32
Co	15.91	10.71
W	59.3	12.8
Totals	100	

The C and O content suggest the presence of a thin layer of contamination. The layer is thin because the W, Co and V content detected is the content expected in the NYB15 grade.

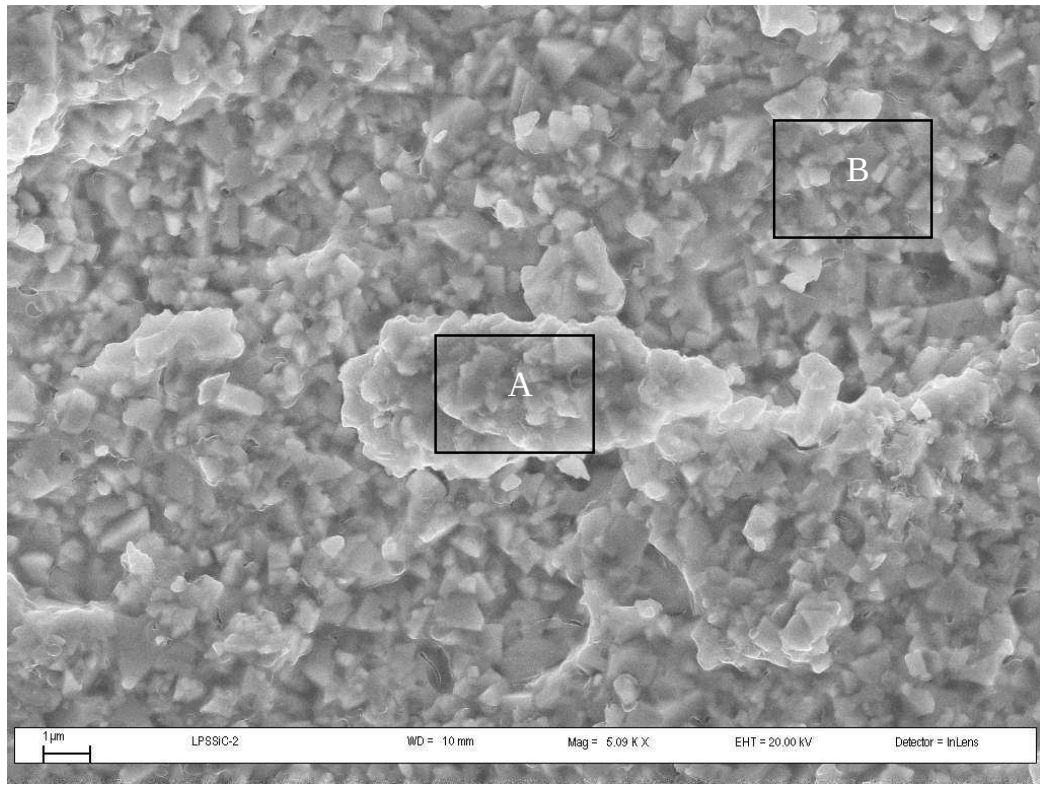


Fig. 4.66: FESEM micrograph of an area covered by a layer near the tensile side on the fracture surface of NYB15-600C-2. Two areas (A and B) were investigated. Comparisons of EDS spectra and approximate compositions are given in Fig. 4.67 and Table 4.6.

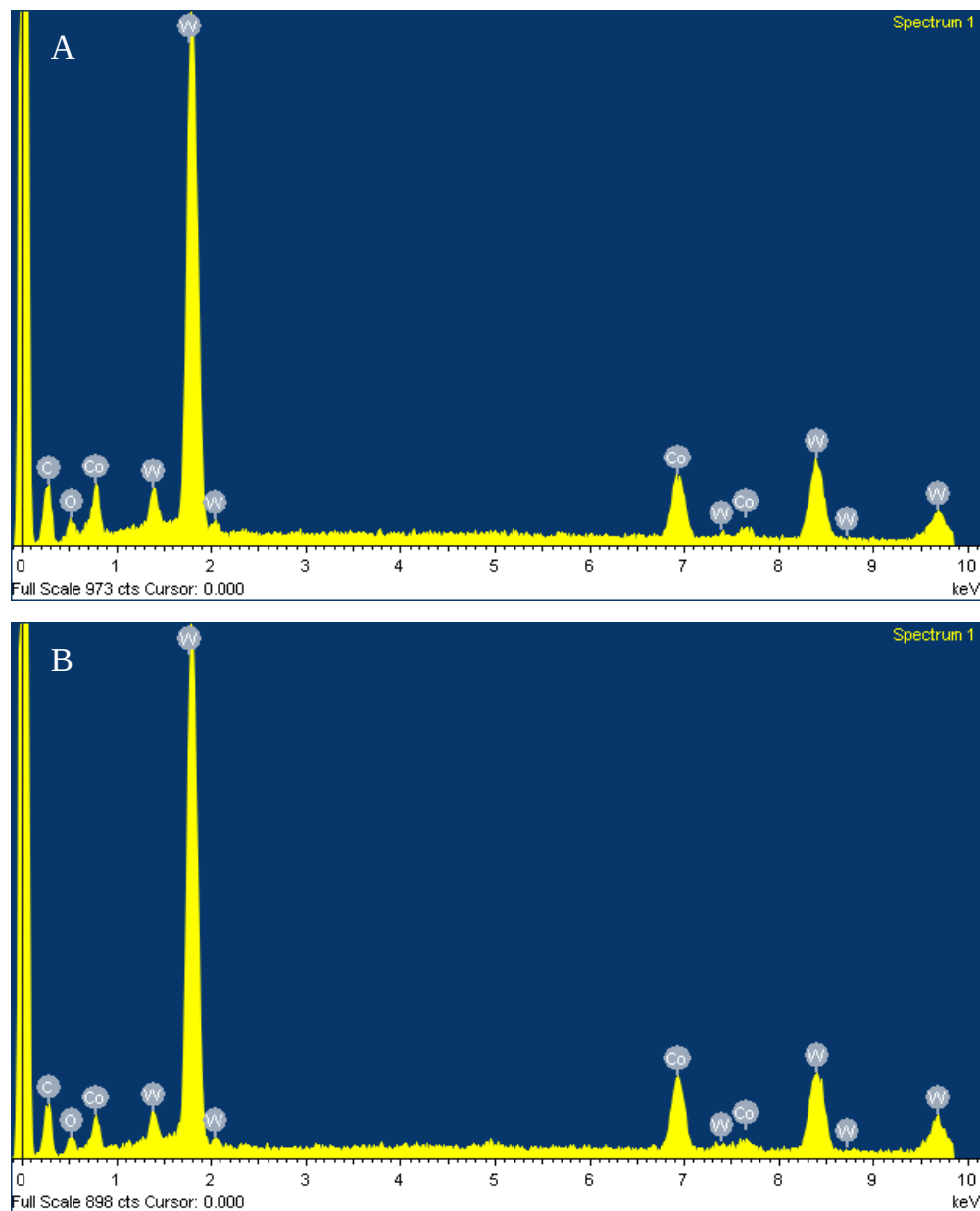


Fig. 4.67: EDS spectra of the areas (A) and (B) analyzed in Fig. 4.66. The spectra look similar.

Table 4.6: Approximate composition of the areas (A) and (B) analyzed by EDS in Fig. 4.66. The content of each element is close.

Element	Weight%(A)	Weight%(B)	Atomic%(A)	Atomic%(B)
C	21.08	17.44	67.43	62.94
O	4.47	4.03	10.74	10.93
Co	14.15	15.25	9.22	11.21
W	60.3	63.28	12.6	14.92
Totals	100	100		

The two areas have the composition expected in NYB15. Vanadium is also visible as a very small peak at about 5 keV. The excess C and the O may come from the atmosphere in the microscope or in the high-temperature testing equipment.

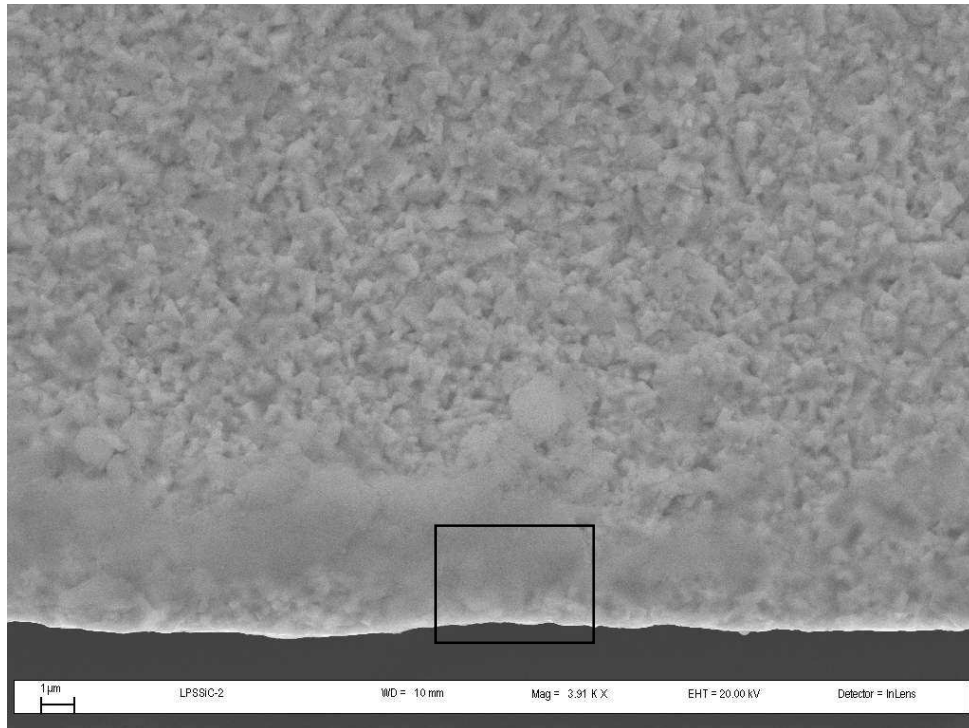


Fig. 4.68: FESEM micrograph of an area near the compressive side on the fracture surface of NYB15-530C-1. The surface is obviously covered by a layer. The rectangular area was analyzed by EDS.

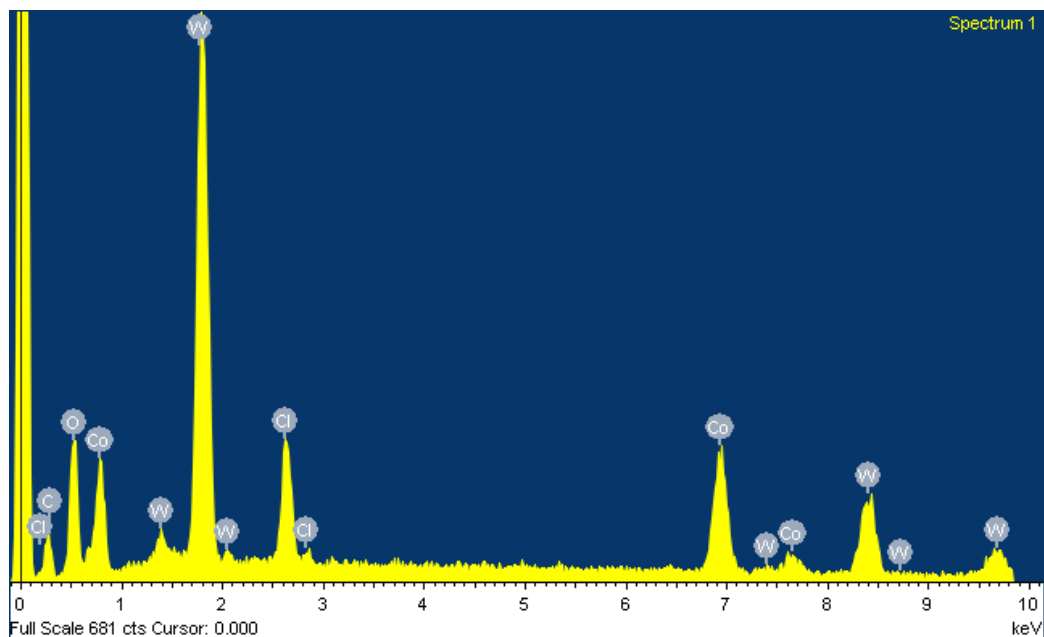


Fig. 4.69: EDS spectrum of the area analyzed in Fig. 4.68. Apart from the high peak of O, Cl was also detected.

Table 4.7: Approximate composition of the area analyzed by EDS in Fig. 4.68. High content of oxygen and the existence of chlorine are the characteristic in this area of NYB15-530C-1.

Element	Weight%	Atomic%
C	12.28	33.78
O	20.52	42.37
Cl	6.64	6.19
Co	17.78	9.97
W	42.78	7.69
Totals	100	

The high O and Cl and the low W suggest that this is a layer consisting of contamination.

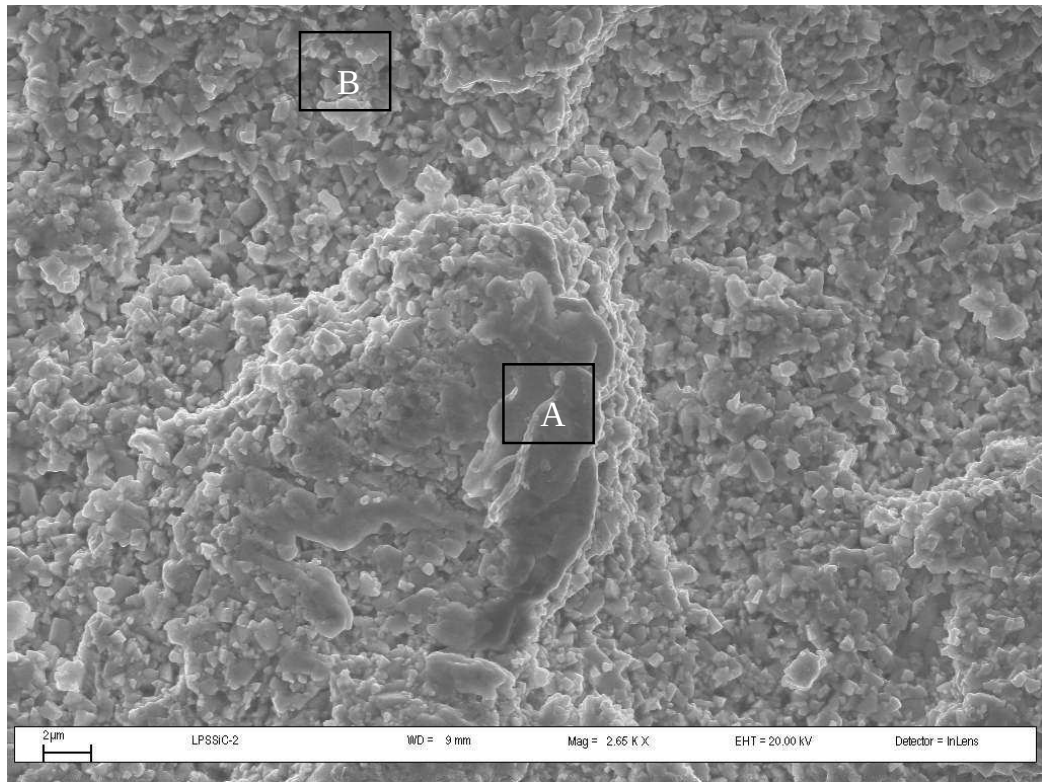


Fig. 4.70: FESEM micrograph of an area near the tensile side on the fracture surface of NYB15-400C-1. Two areas (A and B) are analyzed and compared in Fig. 4.71 and Table 4.8.

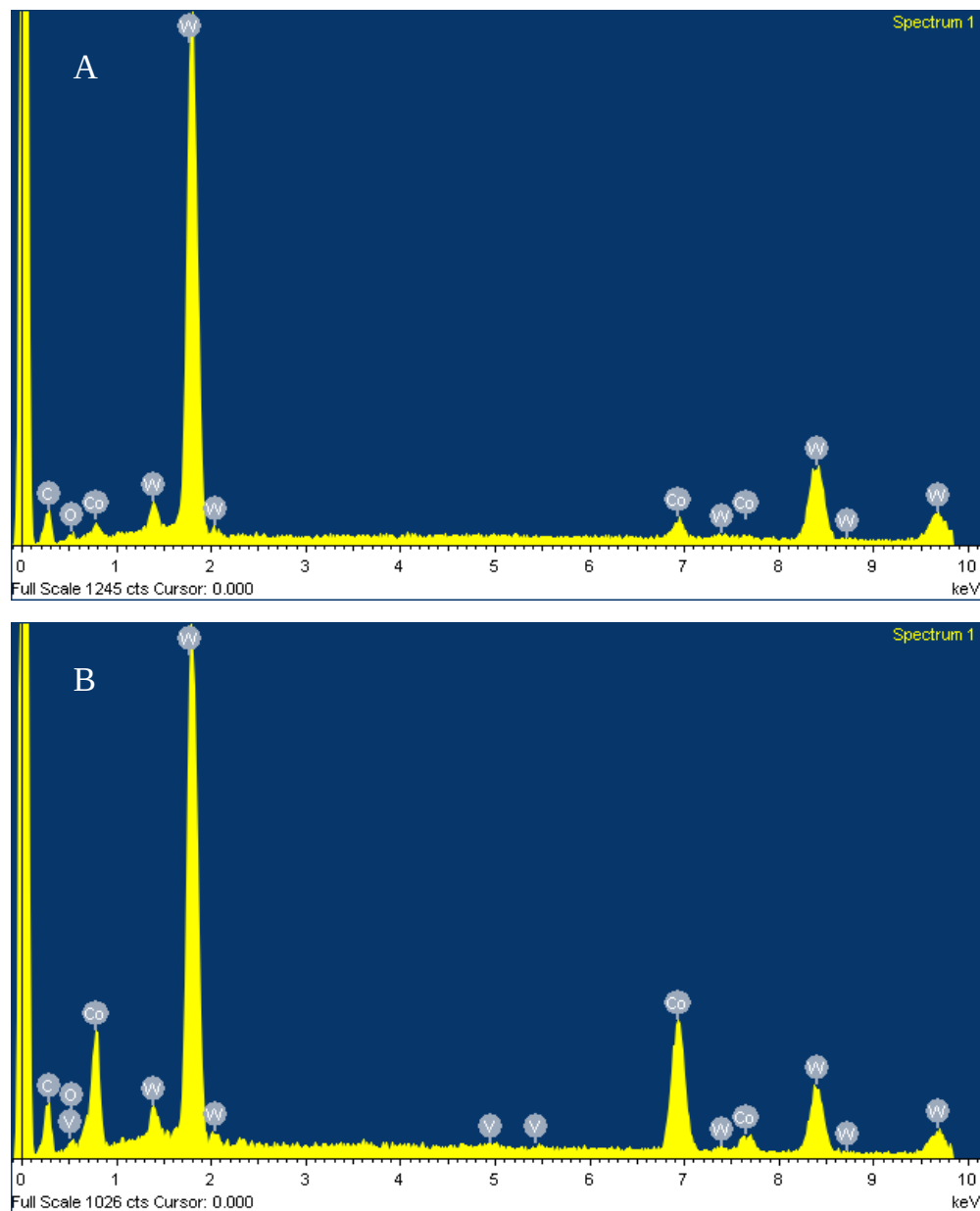


Fig. 4.71: EDS spectra of the areas (A) and (B) analyzed in Fig. 4.70. Vanadium was found in (B) but not in (A). The peaks of each element in (A) and (B) look different.

Table 4.8: Approximate composition of the areas (A) and (B) analyzed by EDS in Fig. 4.70. The (A) area seems to be covered by a layer of W-rich material and the Co content in (B) area is much higher than that of (A) area.

Element	Weight%(A)	Weight%(B)	Atomic%(A)	Atomic%(B)
C	15.92	18.71	68.17	64.42
O	1.82	1.57	5.84	4.07
V	0	0.44	0	0.36
Co	5	27.93	4.37	19.6
W	77.26	51.35	21.62	11.55
Totals	100	100		

The results of this comparison are surprising since area A was expected to be richer in Co than area B.

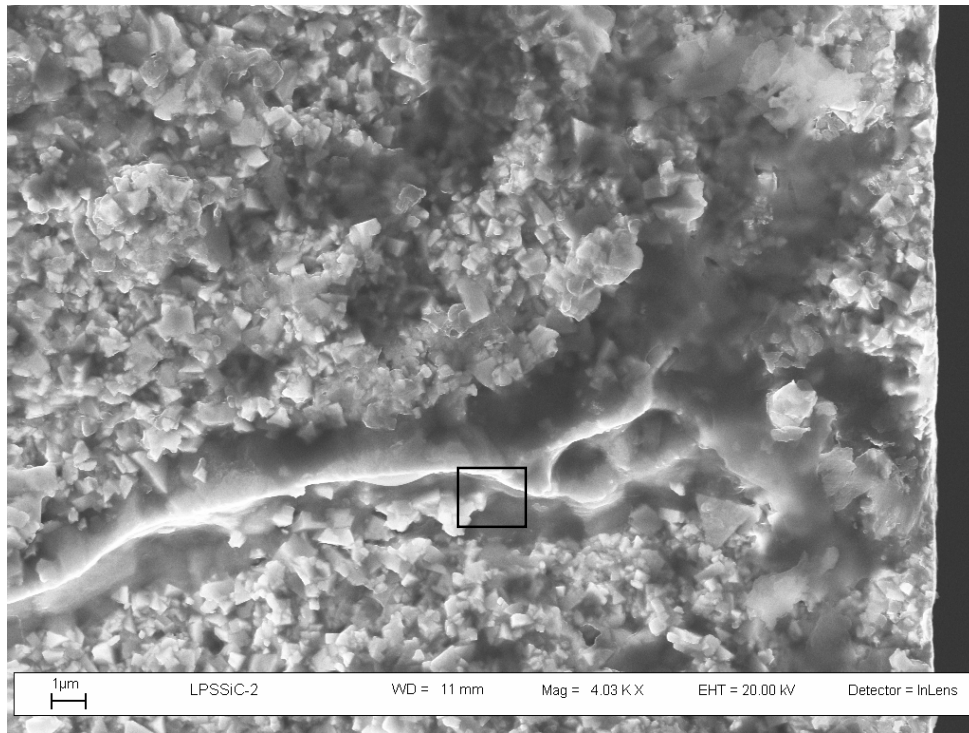


Fig. 4.72: FESEM micrograph of an area covered by a layer at the fracture origin on the fracture surface of NYB15-400C-3. The bright ridge was investigated.

Table 4.9: Approximate composition of the area analyzed by EDS in Fig. 4.72. It can be concluded that the ridge is Co-rich and is a Co ridge formed during plastic deformation and fracture.

Element	Weight%	Atomic%
C	20.04	58.23
O	1.45	3.16
V	0.66	0.45
Co	58.12	34.41
W	19.73	3.75
Totals	100	

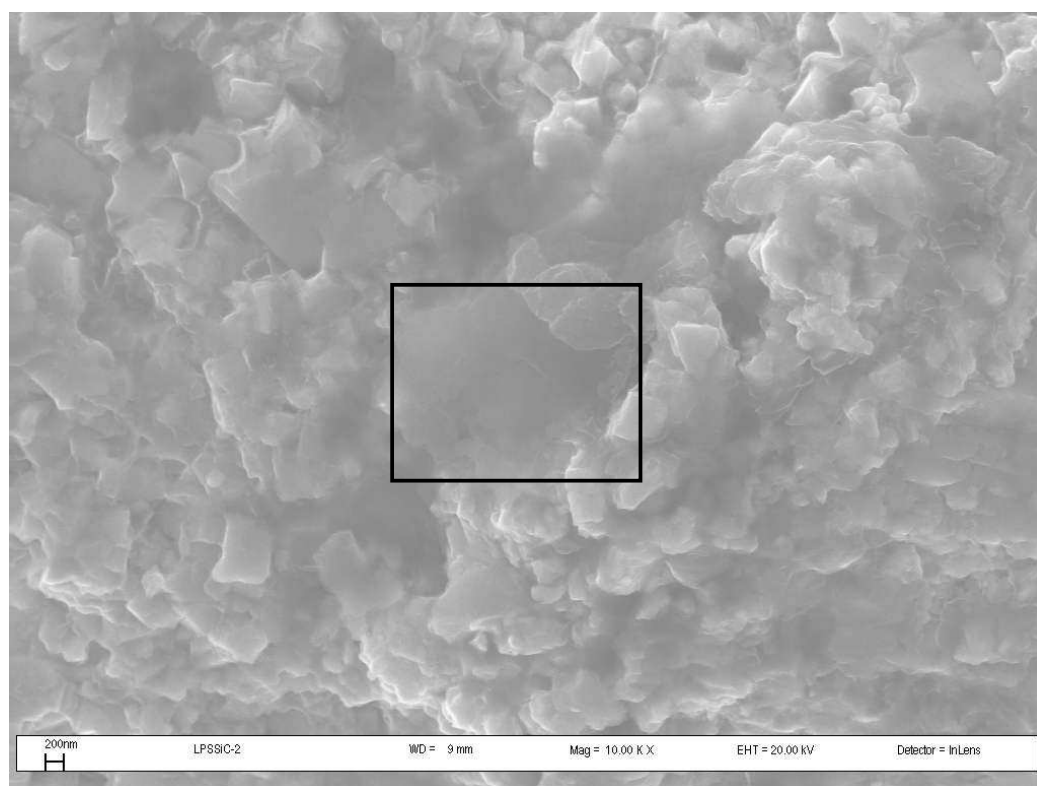


Fig. 4.73: FESEM micrograph of an area near the compressive side on the fracture surface of NYB15-200C-4. The central area was analyzed.

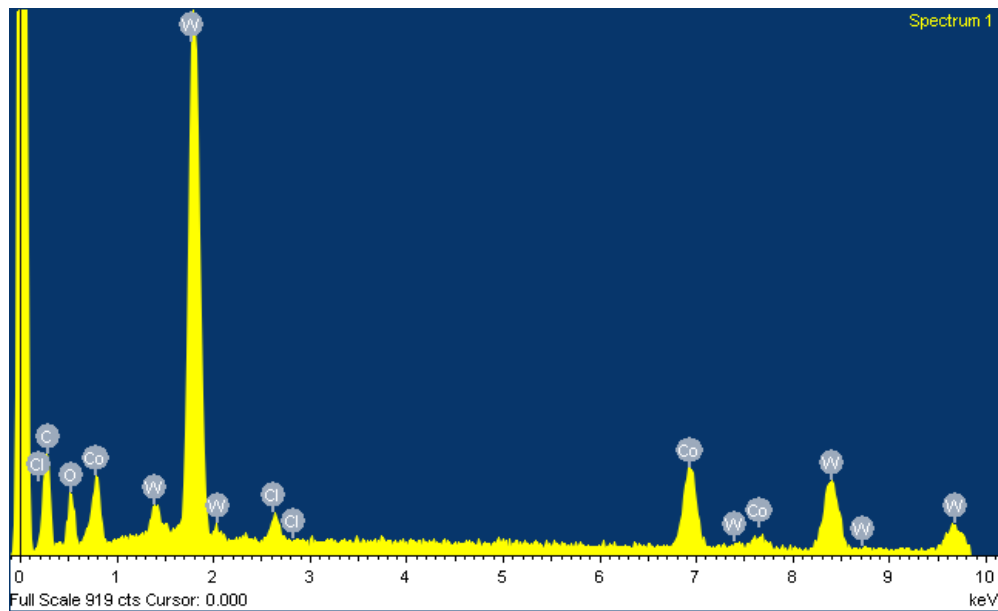


Fig. 4.74: EDS spectrum of the area analyzed in Fig. 4.73. Cl was again detected.

Table 4.10: Approximate composition of the area analyzed by EDS in Fig. 4.73.

Element	Weight%	Atomic%
C	26.13	64.4
O	10.39	19.22
Cl	1.58	1.32
Co	14.9	7.49
W	47	7.57
Totals	100	

The area investigated appears to be covered by a layer of contamination.

As can be see at low magnification in a stereomicroscope (Fig. 4.13-Fig. 4.18), the fracture surfaces of the NYA grade are contaminated. Fig. 4.75 shows the fracture origin of NYA15-600-3. EDS investigation on the fracture surface of NYA15-800C-2 was carried out to find what elements are present in the contamination (Fig. 4.76).

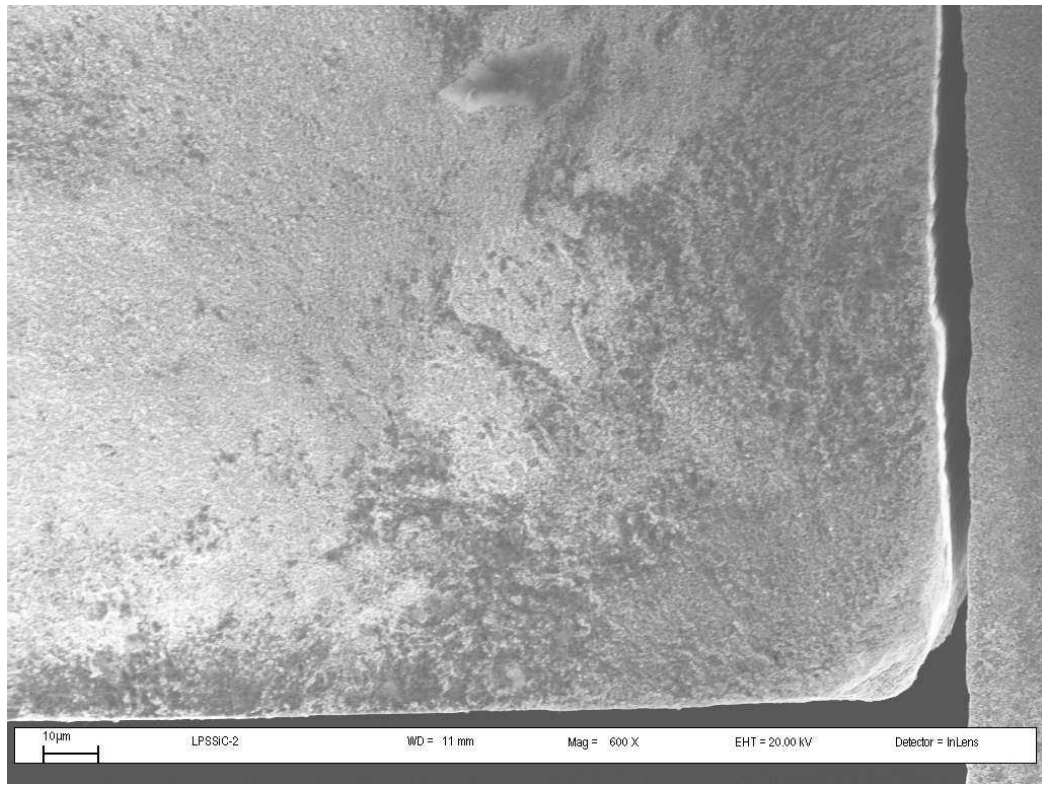


Fig. 4.75: FESEM micrograph of the fracture origin area on the fracture surface of NYA15-600-3. This area is covered by some material which looks darker than the WC-Co.

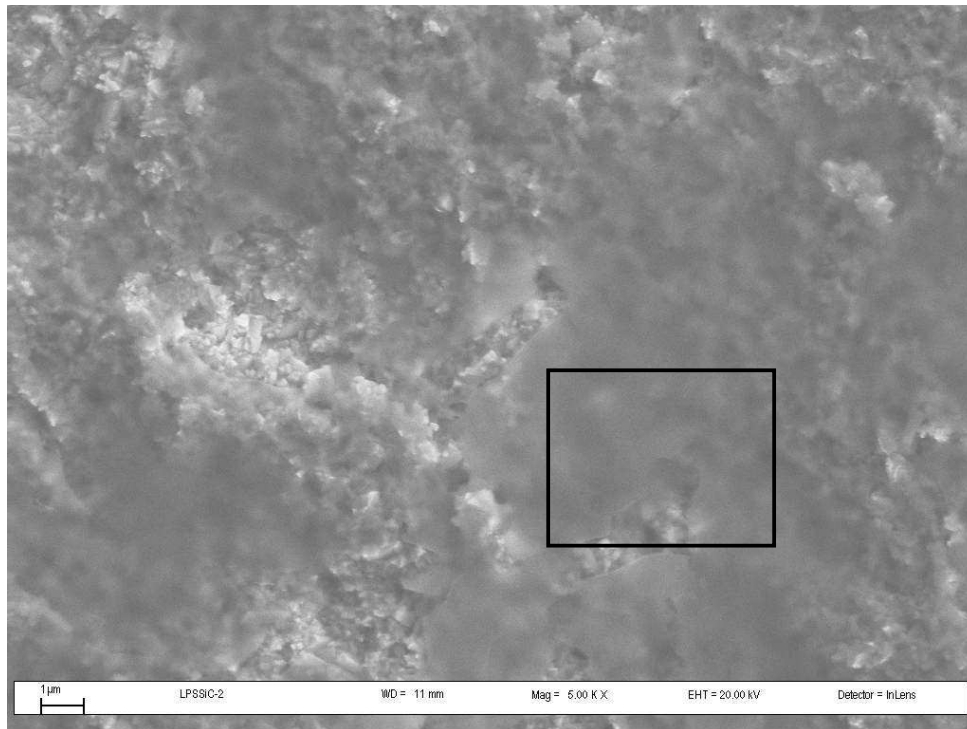


Fig. 4.76: FESEM micrograph of a layer covered on the fracture origin area of NYA15-800C-2. EDS analysis was carried out in the rectangular area.

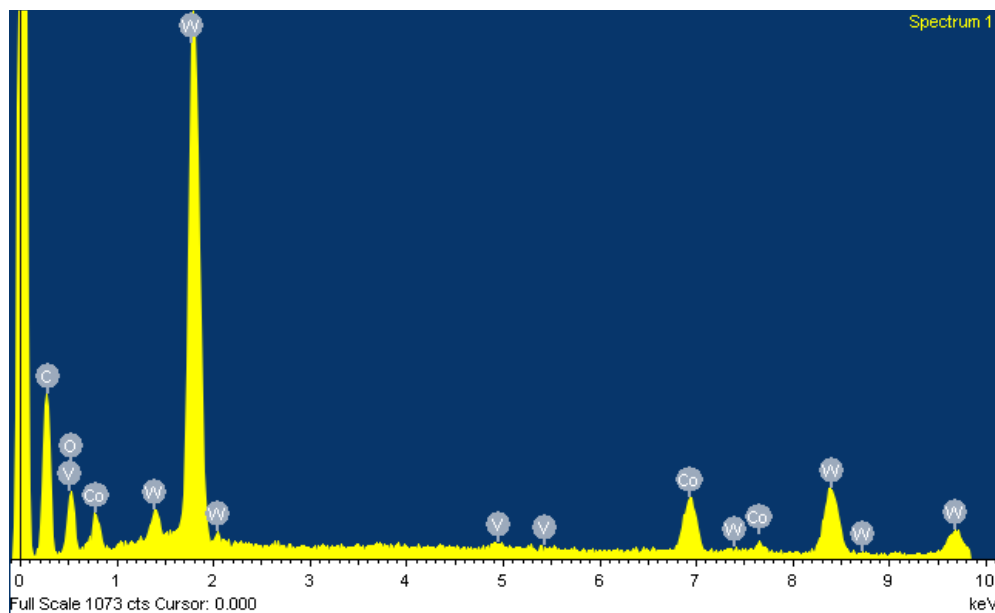


Fig. 4.77: EDS spectrum of the area analyzed in Fig. 4.76. Vanadium was detected in NYA15 grade.

Table 4.11: Approximate composition of the area analyzed by EDS in Fig. 4.76.

High oxygen content was detected.

Element	Weight%	Atomic%
C	36.19	72.2
O	12.27	18.37
V	0.37	0.17
Co	9.34	3.8
W	41.84	5.45
Totals	100	

On the fracture surfaces of the NYB15 grade tested at different temperature, oxygen was always found, accompanied by calcium in NYB15-1000C-3 (Fig. 4.61), chlorine in NYB15-530C-1 (Fig. 4.69) and NYB15-200C-4 (Fig. 4.74). These elements, as well as some high carbon content in some cases (e.g. Fig. 4.61 and Fig. 4.63) seem to be components of some contamination. EDS confirmed the existence of a cobalt ridge (Fig. 4.72) and a cobalt layer at least in two cases. These cobalt features form during fracture.

Contamination can be observed in a stereomicroscope on the fracture surfaces of the NYA15 grade. EDS investigation provides information on the high carbon and oxygen content in the layers at high temperature.

The visible contamination in the NYA15 grade and the EDS confirmed contamination in the NYB15 grade could not be removed by cleaning in an ultrasonic bath with chemicals such as acetone and methanol.

The general present of oxygen and high carbon on the fracture surfaces is expected to be due to the atmosphere in which the bending tests were carried out.

4.4.2.3 S15 Fracture Surfaces and Co Drift

The fracture surfaces of the S15 grades look very different from those of the NYA and NYB grades. No steps were found on the WC grains. Clear evidence of cobalt movement could be observed on the fracture surface of S15-1000C. Dimples and ridges around WC grains appear on the fracture surface of S15-200C.

S15-200C-1:

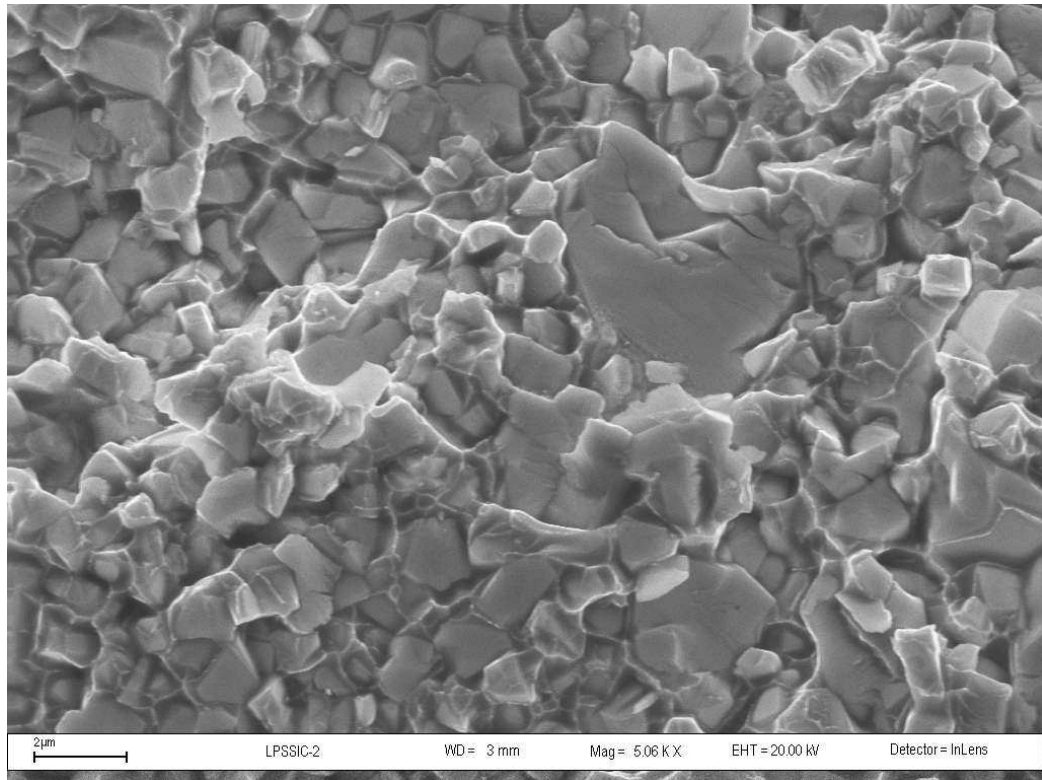


Fig. 4.78: FESEM micrograph of the fracture origin area on the fracture surface of S15-200C-1. Fractured WC grains exhibiting river patterns as well as cobalt dimples and ridges are clearly visible.

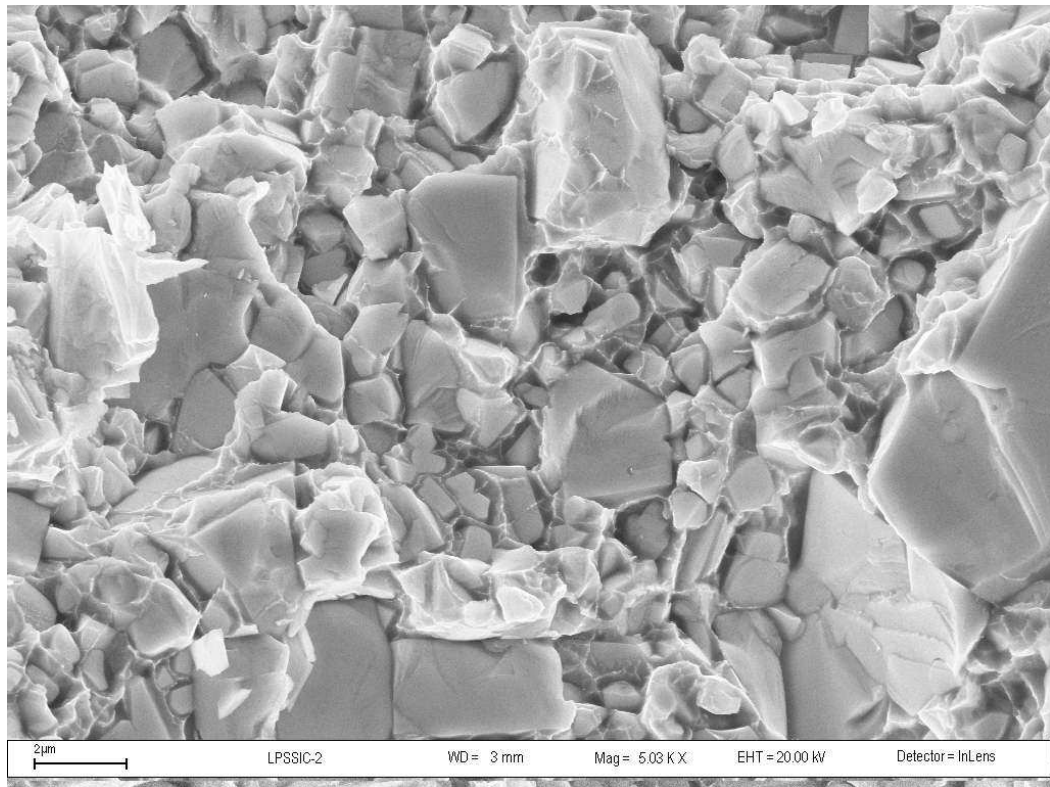


Fig. 4.79: FESEM micrograph of an area near compressive side on the fracture surface of S15-200C-1. Similar typical features, such as fractured WC grains, cobalt dimples and ridges, as those near the tensile side have been observed.

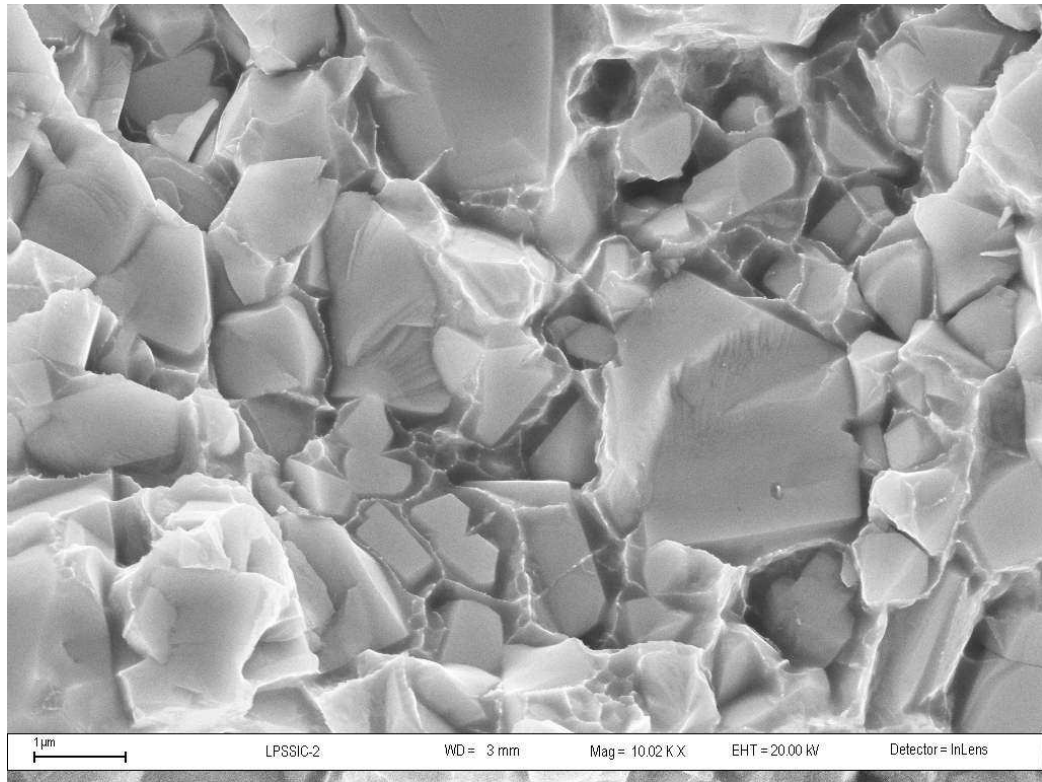


Fig. 4.80: A higher magnification FESEM micrograph of the same area as in Fig. 4.79. Fractured WC grains can be observed.

S15-1000C-1:

Areas investigated on the fracture surface of S15-1000C-1 are shown in Fig. 4.81.

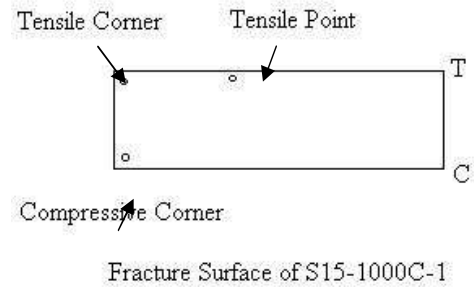


Fig. 4.81: Sketch of S15-1000C-1 fracture surface with the areas investigated.

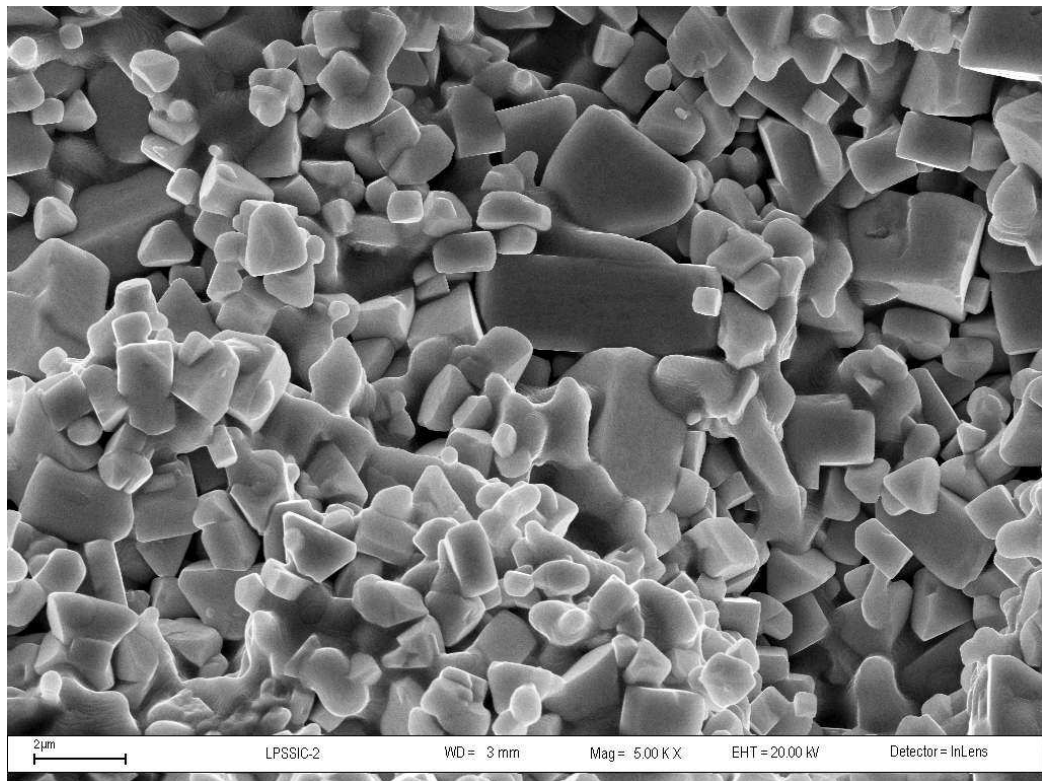


Fig. 4.82: FESEM micrograph of the Tensile Point (see Fig. 4.81) on the fracture surface of S15-1000C-1 at relatively low magnification (5000 $\times$). At this magnification, the surface seems to be denuded of cobalt, which is proved not to be true by the following micrographs.

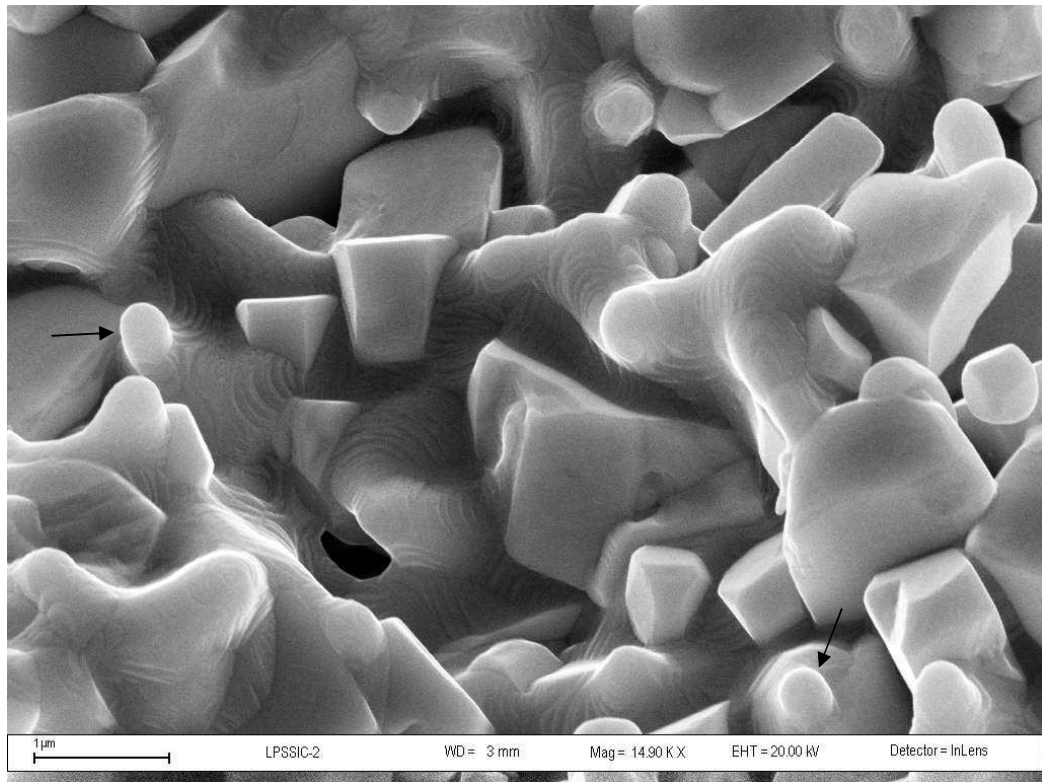


Fig. 4.83: FESEM micrograph of the Tensile Point on the fracture surface of S15-1000C-1 at high magnification (15000×). Lava-like Co (see Fig. 4.84) around WC grains indicates Co movement during fracture. Co tips (indicated by arrows) seem to form during fracture then be rounded afterwards.



Fig. 4.84: Example of frozen lava around a Hawaii volcano [terrageria.com].

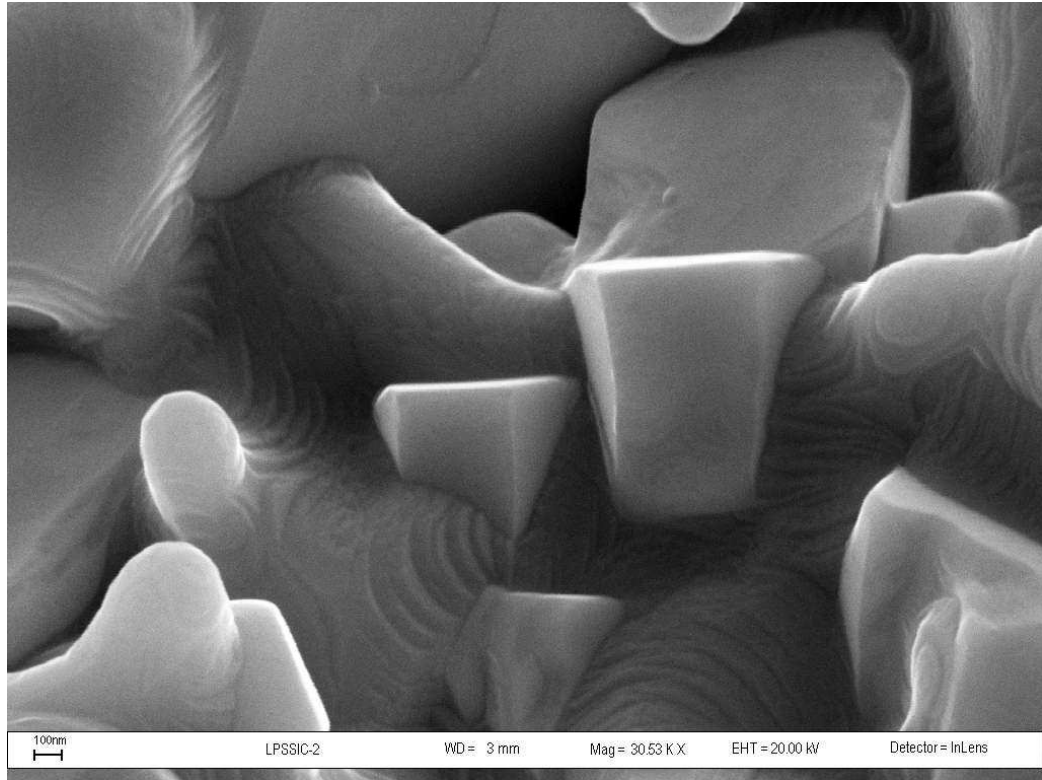


Fig. 4.85: FESEM micrograph of cobalt around WC grains on the fracture surface (in the area near tensile surface) of S15-1000C-1 in the same area as Fig. 4.83 at higher magnification (30000 $\times$). Lava-like Co movement and a Co ligaments tips can be more easily observed.

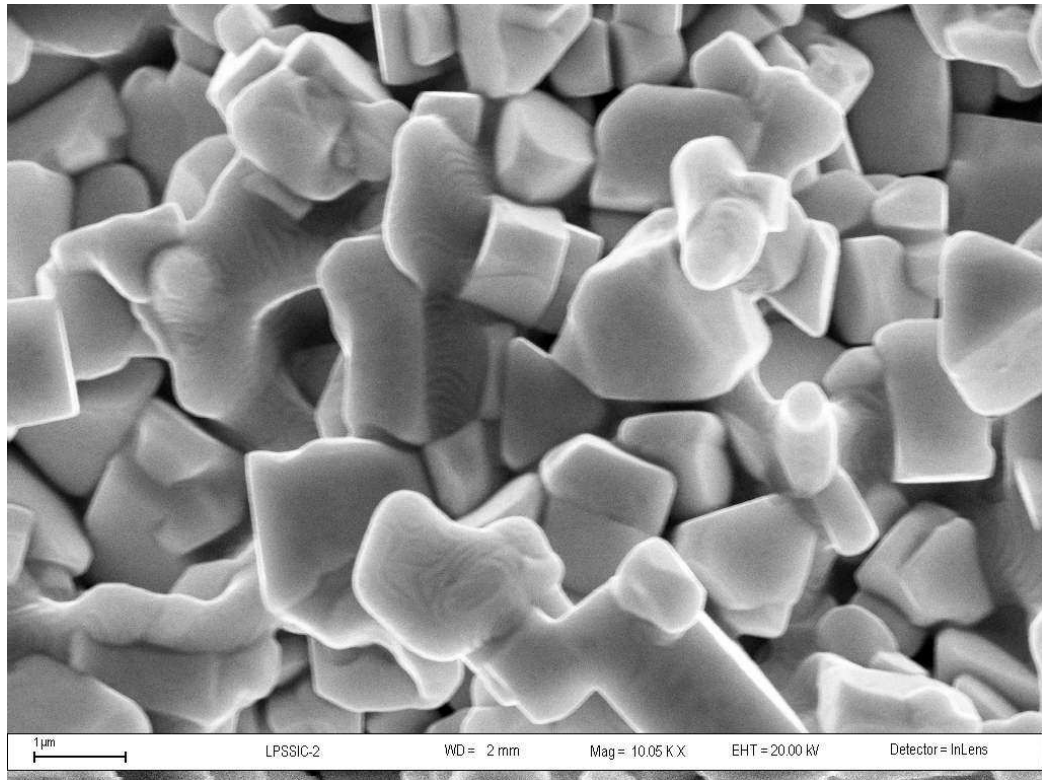


Fig. 4.86: FESEM micrograph of the Tensile Corner (see Fig. 4.81) on the fracture surface of S15-1000C-1. Similar appearance as that of the Tensile Point can be observed.

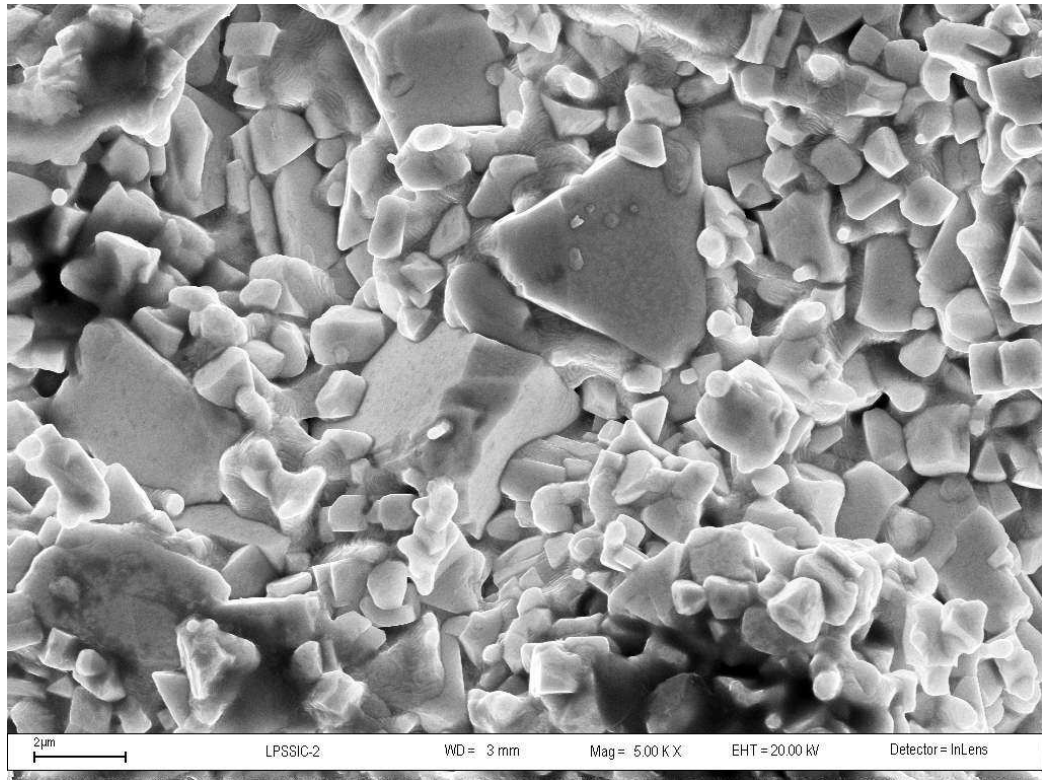


Fig. 4.87: FESEM micrograph of the Compressive Corner on the fracture surface of S15-1000C-1 at relative low magnification (5000×).

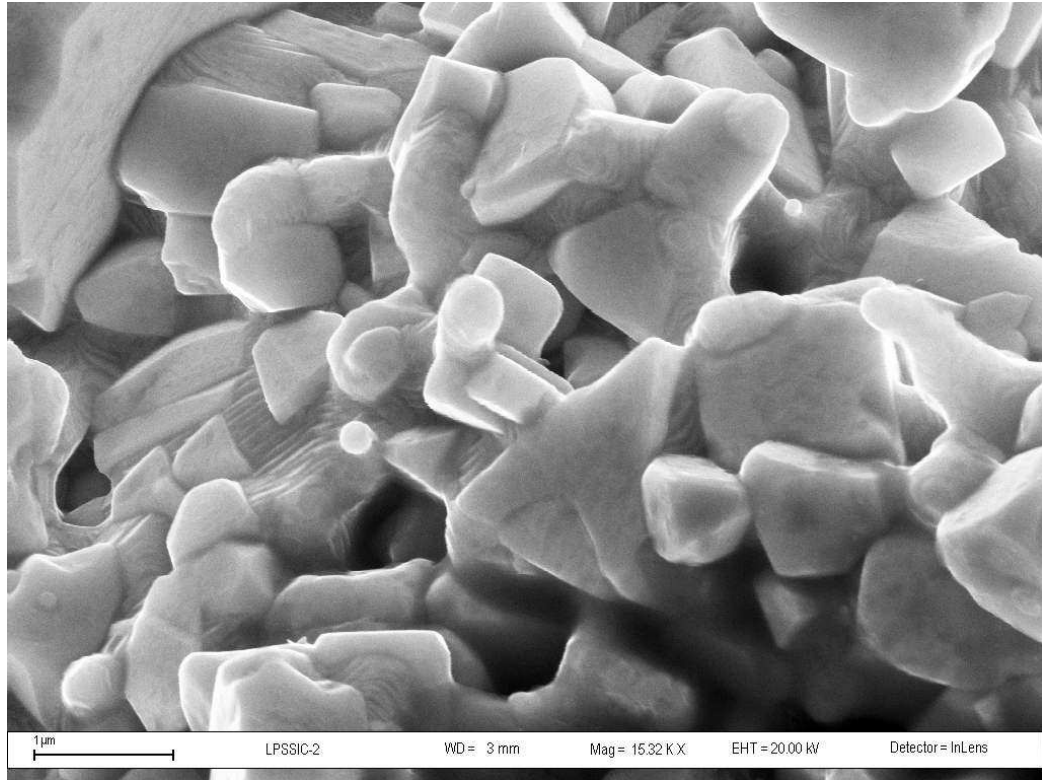


Fig. 4.88: FESEM micrograph of the Compressive Corner on the fracture surface of S15-1000C-1. Co movement and Co ligaments tips are visible.

The fracture surfaces of S15 grade look different from those of NYA15 and NYB15 grades. Besides the difference between different grades, the fracture surfaces of S15-1000C and S15-200C specimen are dissimilar. The lava-like cobalt features on S15-1000C strongly suggests cobalt drift during fracture at 1000°C. The features on S15-200C are typical and common in WC-Co [Erling et al., 2000].

4.5 Co/W Ratios on the Fracture Surfaces of NYB Grade

The cobalt layers found on the fracture surfaces of NYB15 (see Fig. 4.52) grade imply possible cobalt movement during bending. EDS analysis of NYB15 grade was carried out to compare the amount of cobalt present near the compressive side to that near the tensile side on the fracture surfaces. Heights of the Co K α peaks and W L β peaks were measured then Co/W ratios were calculated. At least three measurements were made in different areas on the fracture surface of each specimen tested at different temperatures. The results are summarized in Table 4.12 and illustrated in Fig. 4.89.

Table 4.12: Summary of the Co/W ratios on areas at the tensile and compressive sides of the fracture surfaces of the NYB15 grade. The temperatures are those at which the NYB15 samples were tested.

Areas on fracture surfaces	Temperature (°C)	Average Co/W ratios	Standard deviation
Near tensile edge	1000	1.55	±0.17
	800	2.17	±0.22
	600	2.08	±0.24
	530	2.18	±0.19
	400	1.94	±0.22
	200	2.13	±0.13
Near compressive edge	1000	1.94	±0.13
	800	2.28	±0.14
	600	2.23	±0.35
	530	2.5	±0.30
	400	2.28	±0.41
	200	2.4	±0.46

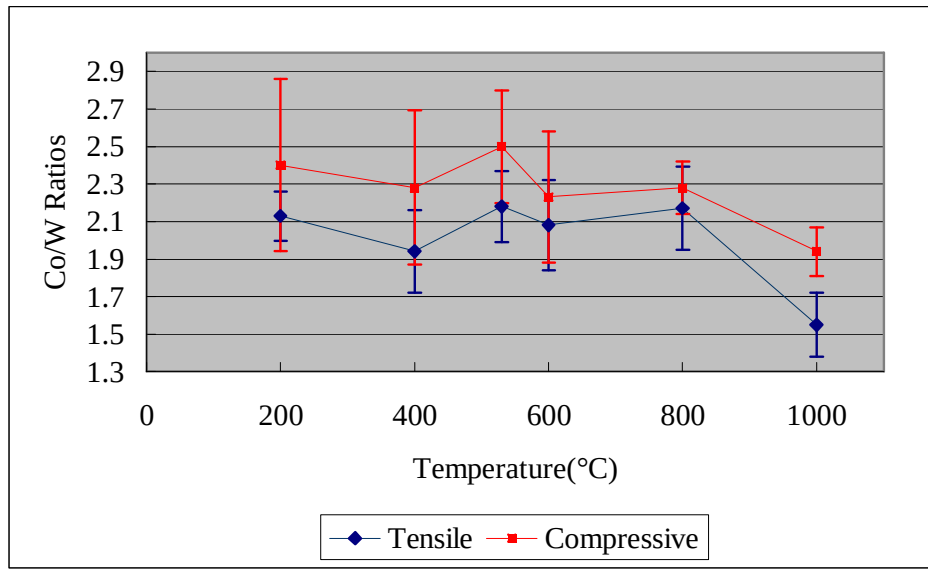


Fig. 4.89: Co/W ratios on the fracture surfaces of the NYB15 grade, as reported in Table 4.12.

Despite the large standard deviation, Fig. 4.89 indicates that the Co/W ratios on the compressive side of the fracture surfaces of NYB15 are consistently higher than those at the tensile side.

The Co/W ratios on the side surfaces of NYB15-1000C-4 and NYB15-200C-2 were also calculated. Three different areas on the side surfaces were investigated:

- areas far from the fracture surface which represent the bulk material;
- an area very near the tensile side and the fracture outcrop on the side surface, i.e. the tensile corner on the side surface;
- an area very near the compressive side and the fracture outcrop on the side surface, i.e. the compressive corner on the side surface.

The results are listed in Table 4.13 and illustrated in Fig. 4.90:

Table 4.13: Co/W ratios on the side surfaces of NYB15-1000C-4 and NYB15-200C-2.

Areas on side surfaces	Temperature (°C)	Average Co/W ratios	Standard deviation
Bulk material	1000	2.31	± 0.14
	200	2.25	± 0.13
Tensile corner	1000	2.25	± 0.17
	200	2.37	± 0.15
Compressive corner	1000	2.14	± 0.07
	200	2.17	± 0.11

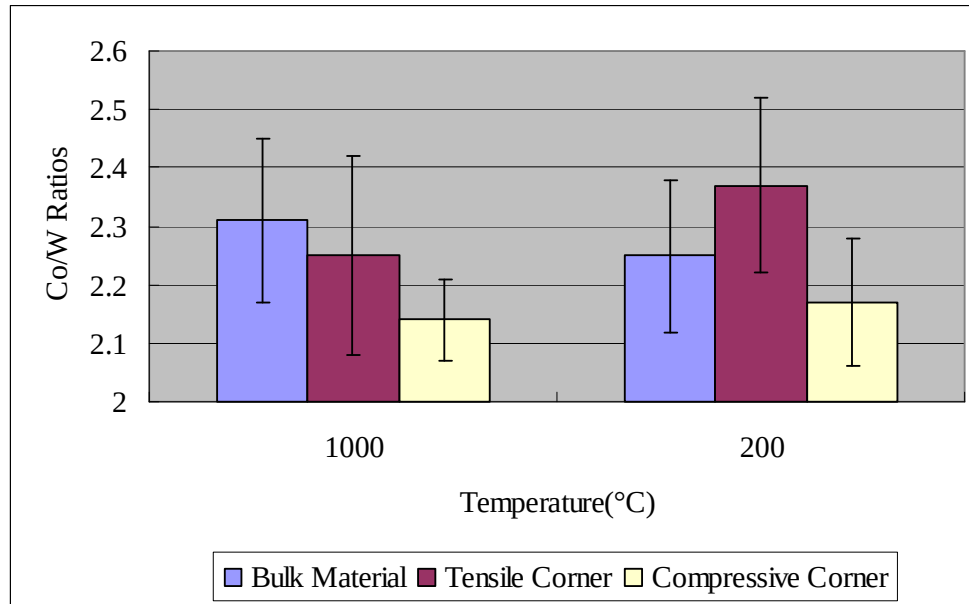


Fig. 4.90: Co/W ratios of the three areas on the side surfaces of NYB15-1000C-4 and NYB15-200C-2, from the data in Table 4.13.

On the side surfaces of both NYB15-1000C-4 and NYB15-200C-2, the Co/W ratios at the tensile corners seem to be higher than those at the compressive corners, which would be consistent with the measurements on the fracture

surfaces because it would indicate that more cobalt drifted towards the fracture surface on the compressive side of the sample (leaving the region below the surface poorer of cobalt) than on the tensile side. Keeping in mind the large standard deviation, the measurements from the bulk suggest that the Co/W ratio was originally ± 2.3 .

4.6 Microstructure Observation

4.6.1 Side Surfaces

The side surfaces of NYA15-1000C-2, and NYA15-20C-2 were examined in a FESEM and S15-1000C-2 in both a FESEM and SEM in order to look for features similar to those observed by Östberg [Östberg, 2005] in deformed cutting tools, i.e. widening of gaps between grains (or microcracks?) and WC grain dissolution. The results are reported below.

4.6.1.1 NYA15 Grade

The results from the examination of NYA15-1000C-2 are shown in Fig. 4.91 to Fig. 4.95.

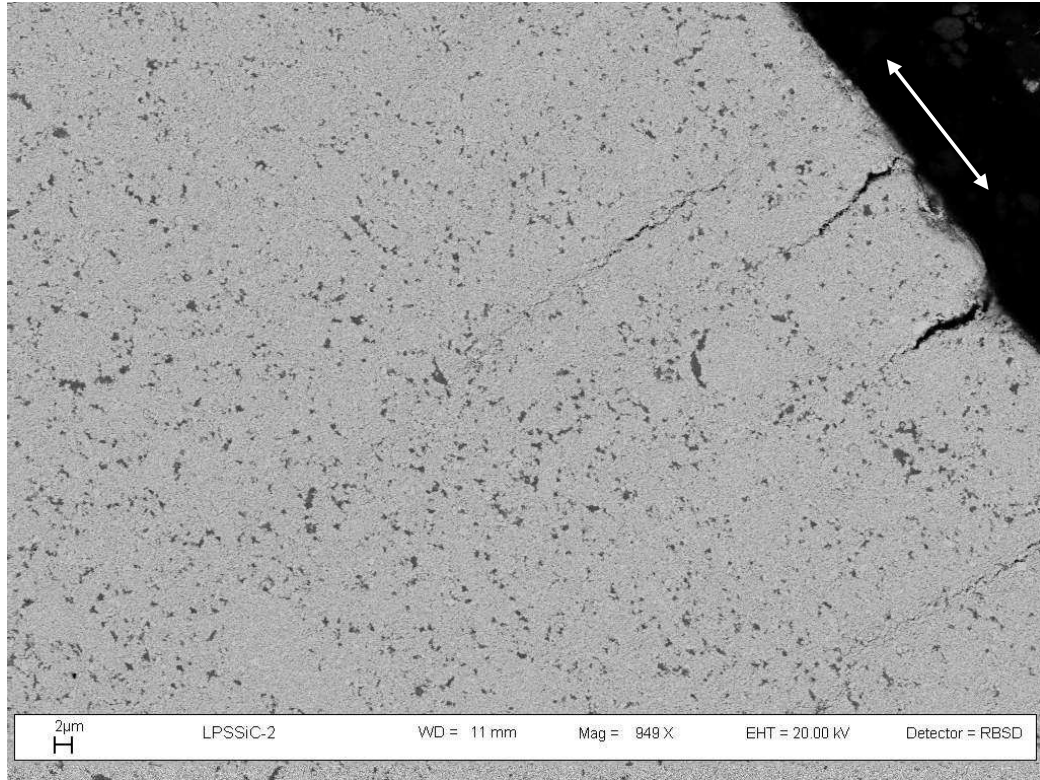


Fig. 4.91: FESEM micrograph of an area near the tensile surface of NYA15-1000C-2 at low magnification. The edge between the side surface and the tensile surface can be seen at the north-east corner. The applied stress direction is shown in the micrograph. The two arrows indicate tensile stress. Microcracks can be seen perpendicular to the tensile surface. Some microcracks were found to originate within the material but did not propagate to the edge. These cracks suggest that at 1000°C the material had almost the consistency of clay.

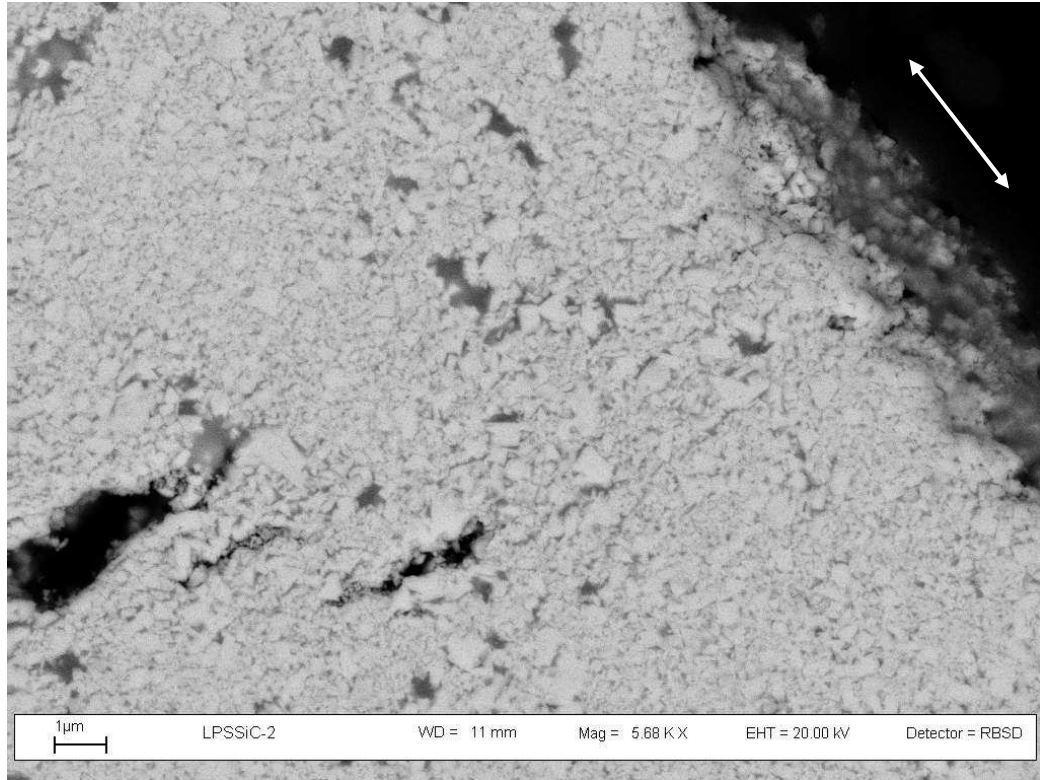


Fig. 4.92: FESEM micrograph of an area near the tensile surface of NYA15-1000C-2 at high magnification. The applied stress direction is shown. At higher magnification, more microcracks or widened gaps between grains are clearly seen. These features are consistent with those observed by Östberg, who interpreted them as being widened gaps. The microcracks and widened gaps lie perpendicular to the stress direction.

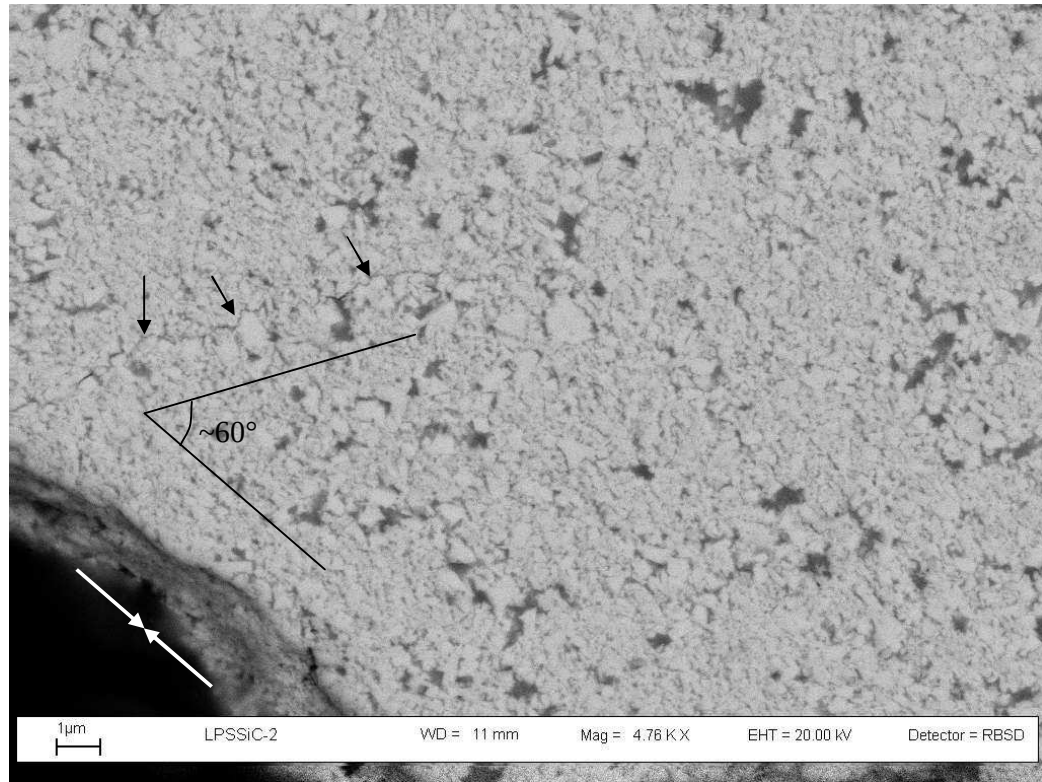


Fig. 4.93: FESEM micrograph of an area near the compressive surface of NYA15-1000C-2. The edge between the side surface and the compressive surface can be seen at the southwest corner. The applied stress direction is shown in the micrograph by white arrows. A long microcrack at about 60° to the compressive surface is indicated by three black arrows. This appears to be a shear crack.

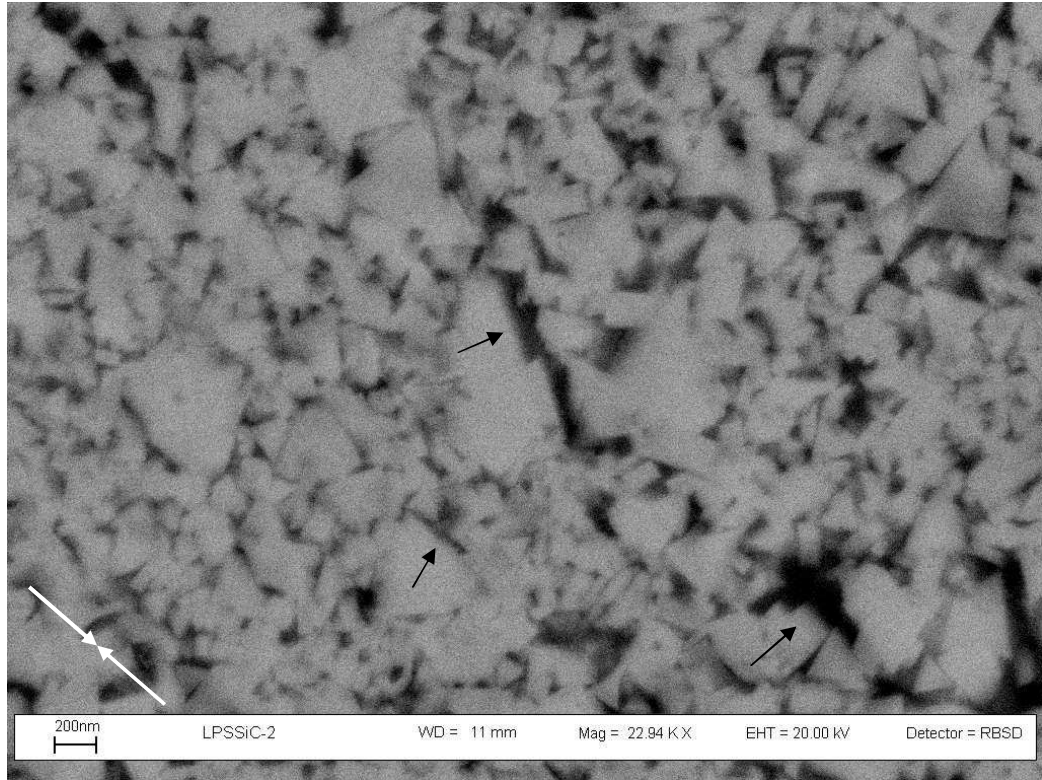


Fig. 4.94: FESEM micrograph of another area near the compressive surface of NYA15-1000C-2. White arrows indicate the compressive stress direction. The dark areas in this micrograph (as indicated by black arrows) seem to be debonding of WC grains or thickened cobalt layers formed under compressive stress. They lie at about 30° or less to the stress direction.

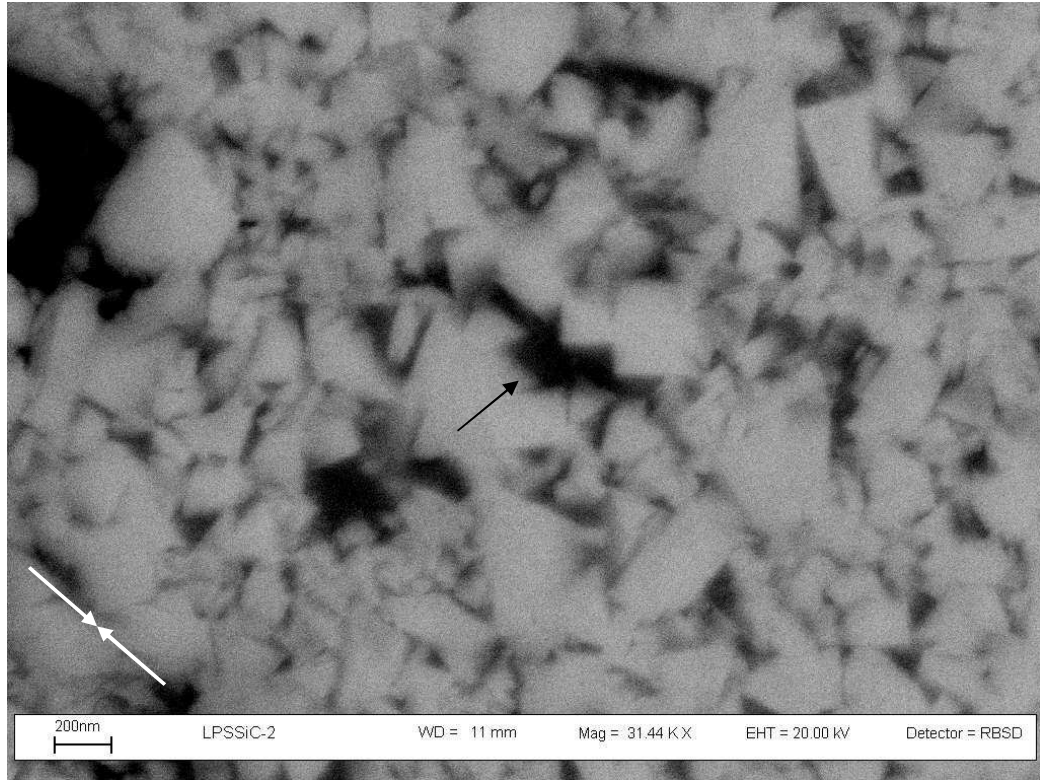


Fig. 4.95: FESEM micrograph of an area near the compressive surface of NYA15-1000C-2 at higher magnification. White arrows indicate the compressive stress direction. A black arrow points to another example of debonding of WC grains or thickening of the cobalt layer.

The results from the examination of NYA15-20C-2 are shown in Fig. 4.96 and Fig. 4.97.

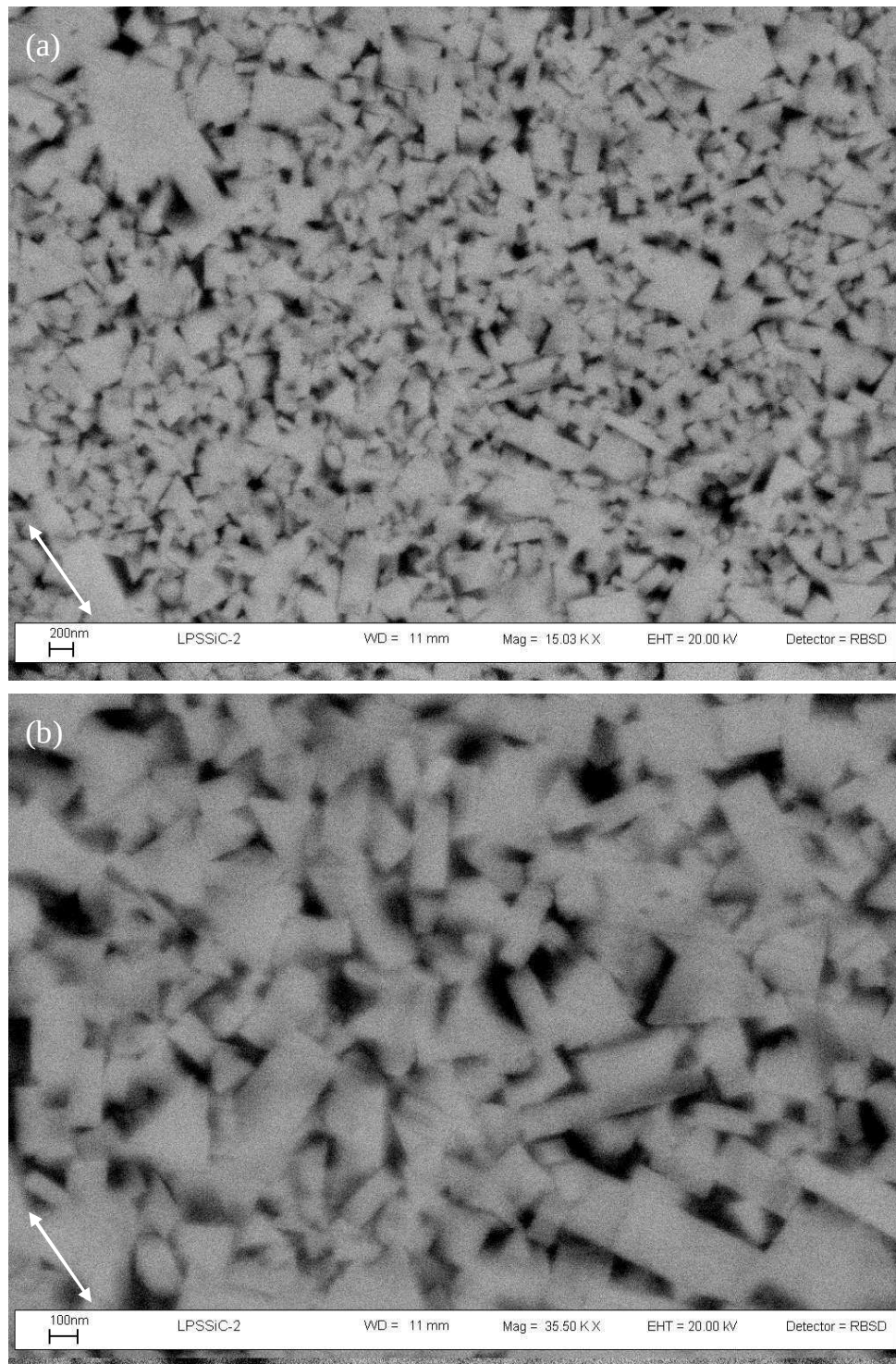


Fig. 4.96: FESEM micrograph of an area near the tensile side of NYA15-20C-2 at low magnification (a) and at high magnification (b). White arrows indicate the tensile stress direction.

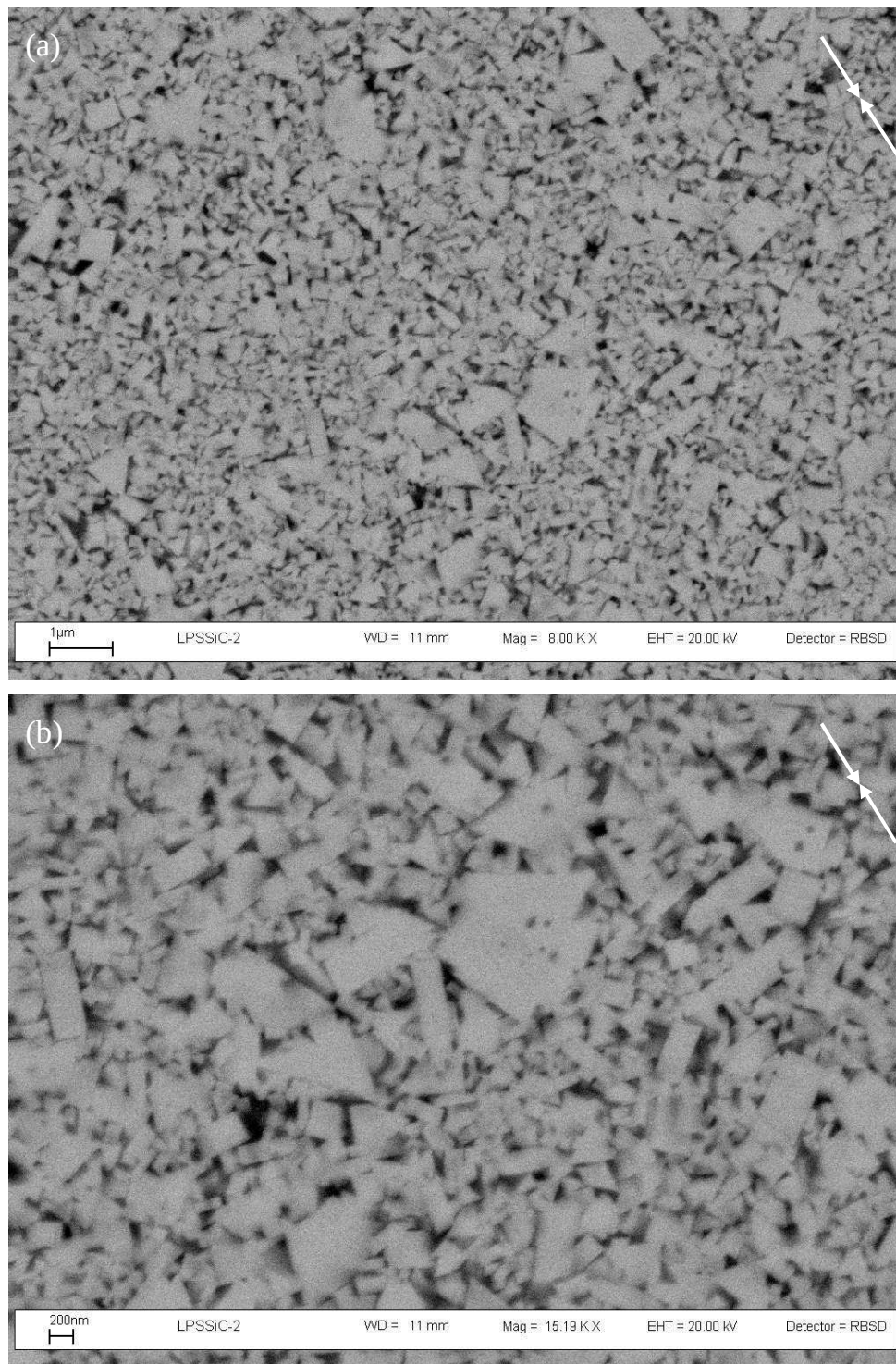


Fig. 4.97: FESEM micrograph of an area near the compressive side of NYA15-20C-2 at low magnification (a) and at high magnification (b). White arrows indicate the tensile stress direction.

By comparing the microstructure of NYA15-1000C-2 near the tensile side with those near the compressive side, differences in the direction of microcracks or thickened cobalt layers can be observed. On the tensile side, the cracks or thickened cobalt layers were perpendicular to the tensile stress direction, while on the compressive side the same features were parallel to the compressive stress direction or at angles $< 90^\circ$. The side surface micrographs of NYA15-20C-2 show no obvious differences between the tensile and compressive sides. Besides, by comparing Fig. 4.91 and Fig. 4.97(a), one notices that at 20°C there were no cobalt “pockets” observed at 1000°C, therefore the cobalt “pockets” must be due to cobalt drift (or infiltration) at the high temperature.

Note: the microstructure investigation reported above was done on NYA15-1000C and not on NYB15-1000C because NYA15-1000C did not fracture; therefore the effects of cobalt drift were expected to be most visible. On the contrary the investigation described in section 4.5 was done only on NYB15-1000C because no NYA15-1000C fracture surfaces were available.

4.6.2.2 S15 Grade

Since the WC grain size of S15 grade is larger, SEM micrographs were suitable for cobalt mean free path measurement (the results of cobalt mean free path measurement are listed in section 4.6.4). Microstructure observation results from FESEM and SEM are reported from Fig. 4.98 to Fig. 4.104.

4.6.2.2.1 *Rounded WC Grains*

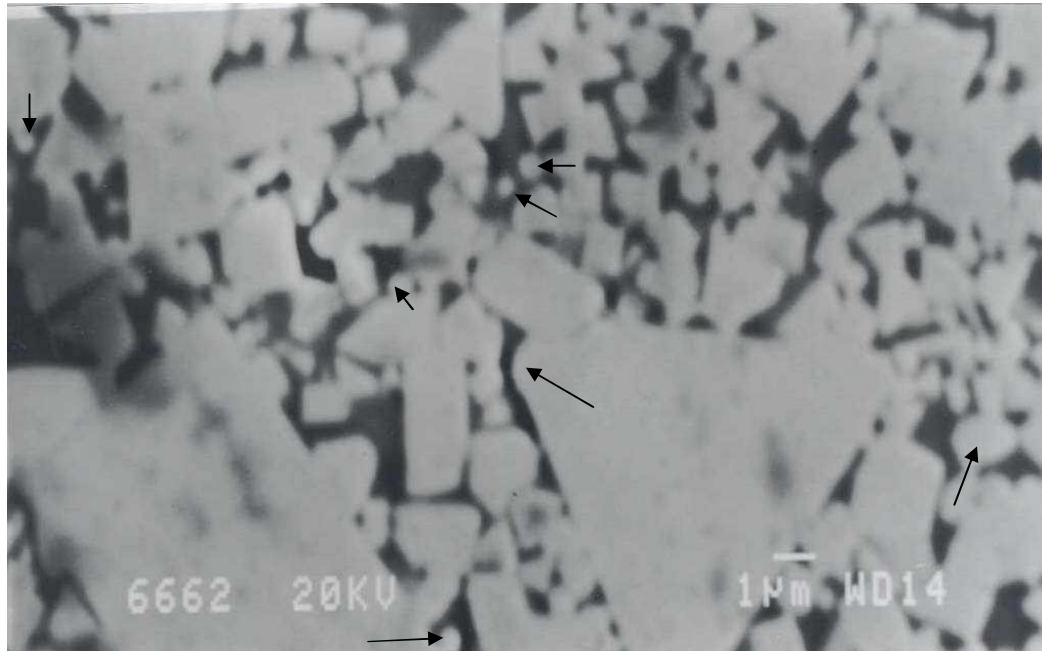


Fig. 4.98: SEM micrograph of an area very near the tensile side and about 25µm away from the fracture outcrop on the side surface of S15-1000C-2. This area was under tensile stress during testing. Arrows point to rounded grains.

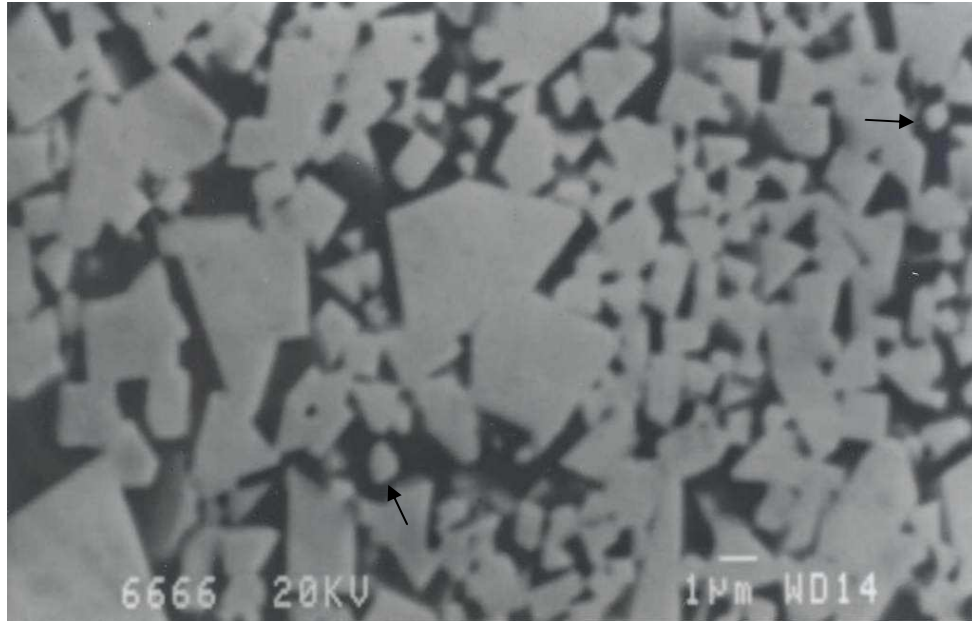


Fig. 4.99: SEM micrograph of another area near the tensile side on the side surface of S15-1000C-2, approximately 120 μ m away from the fracture outcrop. Arrows indicate rounded WC grains.

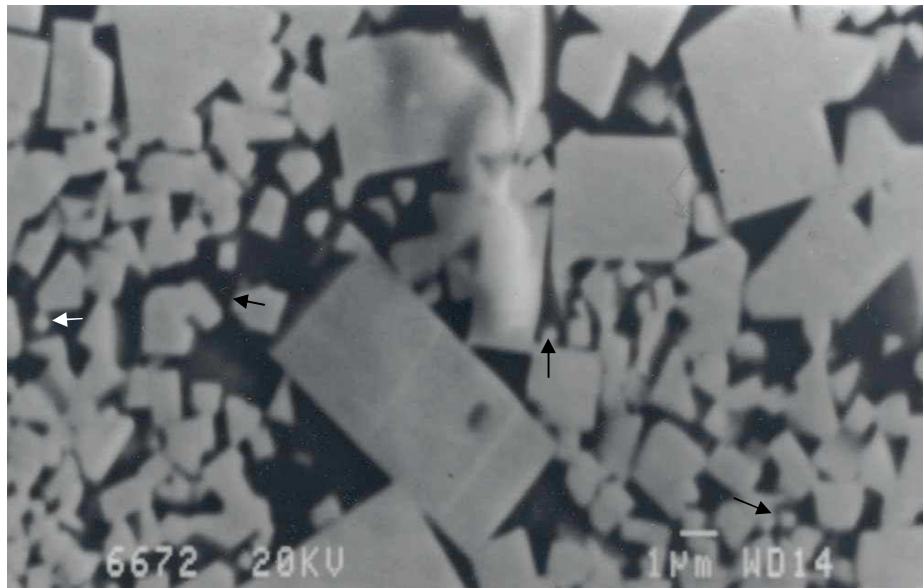


Fig. 4.100: SEM micrograph of an area very near the fracture outcrop and the compressive side on the side surface of S15-1000C-2. This area was under compressive stress during testing. Arrows point to examples of rounded WC grains.

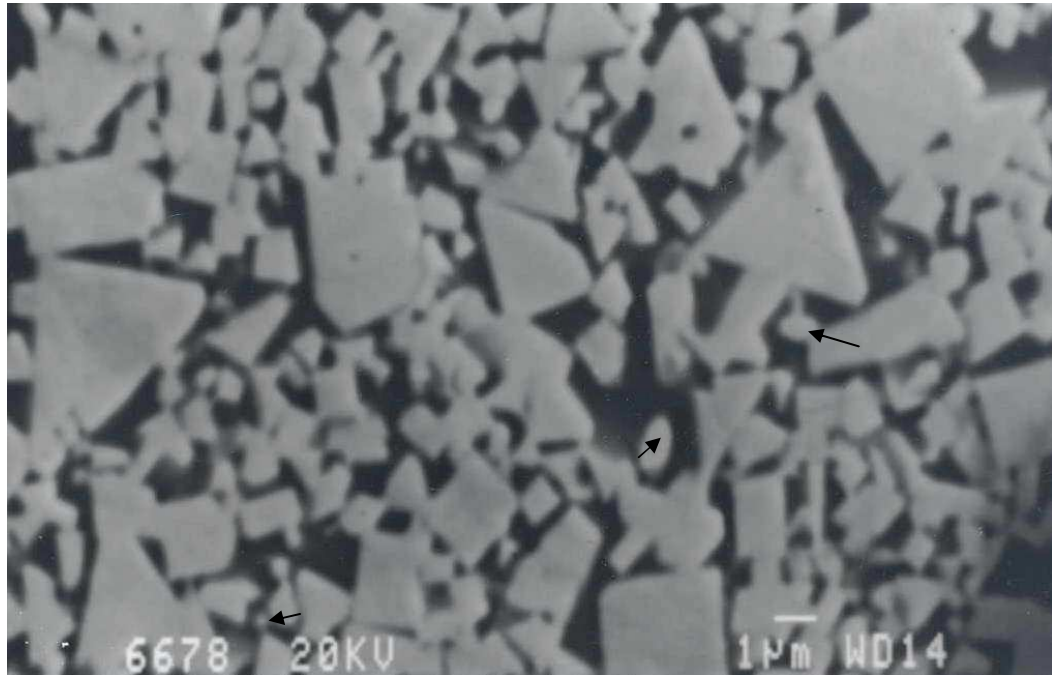


Fig. 4.101: SEM micrograph of an area very near the fracture outcrop and about 20µm away from the compressive side on the side surface of S15-1000C-2. This area was under compressive stress during testing. Arrows point to rounded WC grains.

It can be concluded from the SEM micrographs that both the areas subjected to tensile and compressive stresses show rounded WC grains. Majority of the rounded WC grains were found near the fracture outcrop. The number of rounded WC grains decrease as one moves away from the fracture outcrop. It was also observed that the majority of the rounded grains were small and practically isolated, i.e. completely surrounded by Co binder.

4.6.2.2.2 Microcracks

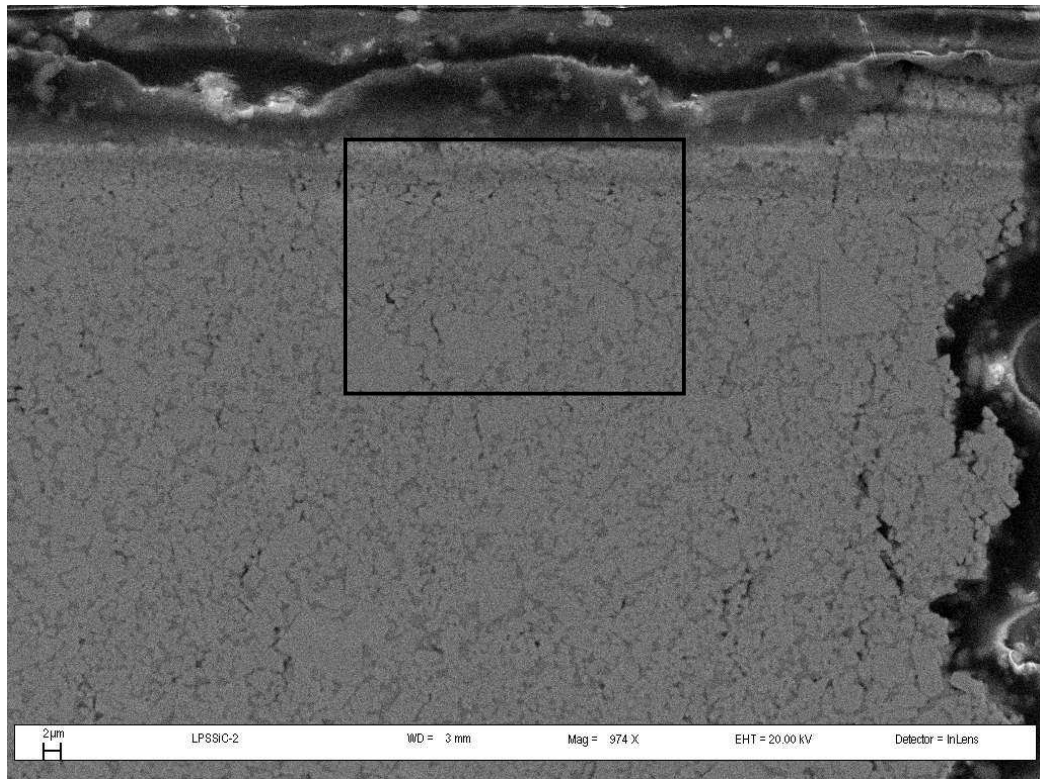


Fig. 4.102: FESEM micrograph of the tensile corner on the side surface of S15-1000C-2. The fracture outcrop can be seen on the right side and the tensile edge can be seen on the upper part of the micrograph. There are many black lines observed near the fracture outcrop and inside the material which are interpreted as being cracks. Their general direction is perpendicular to the tensile edge. The details of the rectangular area are shown in Fig. 4.103.

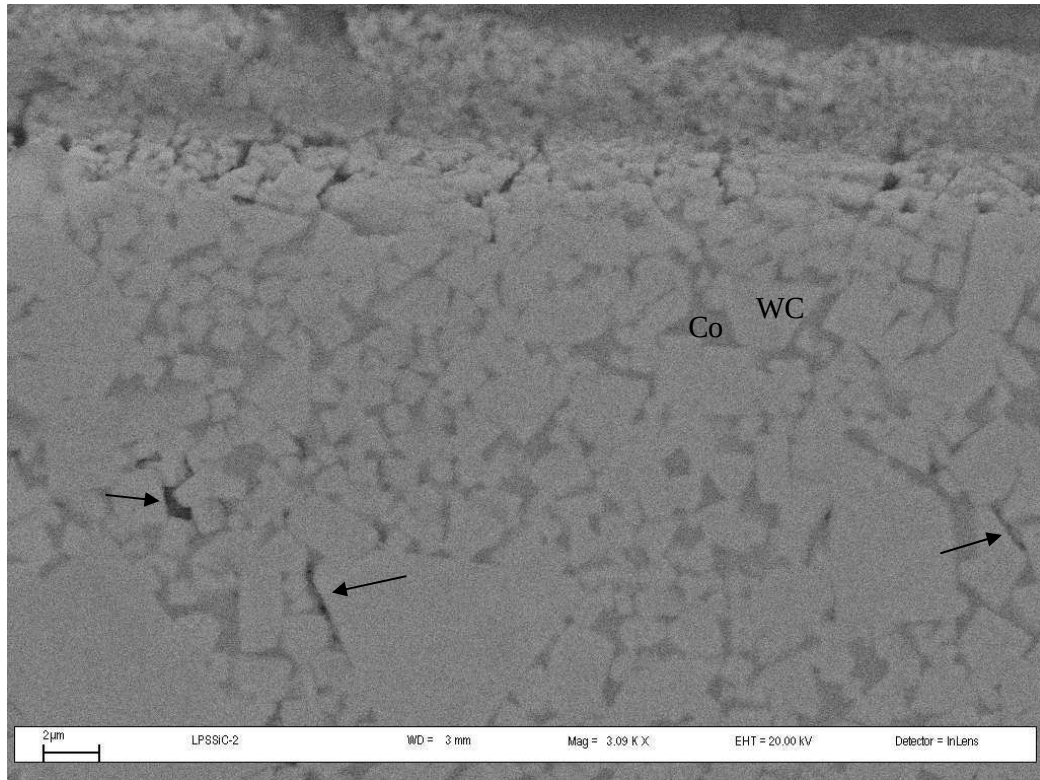


Fig. 4.103: FESEM micrograph of the rectangular area in Fig. 4.102. The tensile edge can be seen on the upper part of the micrograph. The white angular grains are WC grains and the grey material between WC grains is Co binder (as indicated). The black areas (pointed out by arrows) between WC grains are microcracks.

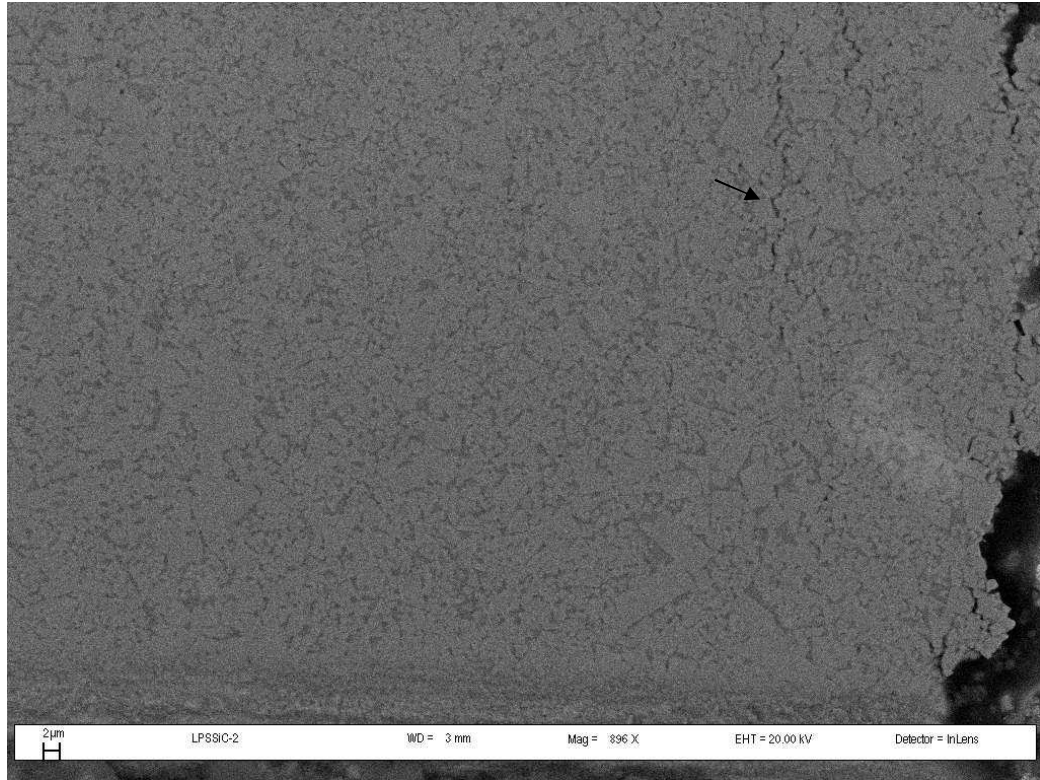


Fig. 4.104: FESEM micrograph of the compressive corner on the side surface of S15-1000C-2. The fracture outcrop can be seen on the right side and the compressive edge on the bottom part of the micrograph. Microcracks can also be observed near and parallel to the fracture outcrop (as indicated by an arrow), but no microcracks were observed when moving away from the fracture outcrop.

The microstructural observation on the side surface of S15-1000 grade reveals that microcracks formed parallel to the fracture outcrop near the tensile side and along the fracture outcrop. The contrast on the micrographs suggest that the black areas between WC grains are microcracks and not Co layer widening.

4.6.3 Mean Free Path and Contiguity Calculation

The contiguity and cobalt mean free path of the as-received NYA15, NYB15 and S15 grades, i.e. prior to 3-point bending, were calculated by using the equations given in section 2.1.6.3. The results of these microstructure parameter calculations, listed in Table 4.14, will be compared to the results from the cobalt mean free path measurements (section 4.6.4) and will also be discussed in chapter 5.

Table 4.14: Contiguity and cobalt mean free path data for each grade.

Grade	Volume Percentage of Co (V_{Co} , %)	Grain Size (μm)	Mean Free Path (μm)	Contiguity
S15	23.74	1.30	0.50	0.20
NYA15	23.44	0.30	0.12	0.20
NYB15	23.59	0.35	0.13	0.19

According to Luyckx and Love [Luyckx and Love, 2006], the carbide skeleton in WC-Co is continuous only when the contiguity is higher than 0.25-0.3. Therefore in these grades the carbide skeleton is not continuous and the applied stress is carried by the cobalt as well as the carbide.

4.6.4 Mean Free Path Measurements

The cobalt Mean Free Path measurements were carried out by using linear analysis on the side surface of S15-1000C-2 in order to verify claims by Östberg that under stress at 1000°C cobalt infiltrates the WC/WC boundaries. Areas close to the fracture outcrop, both near the tensile side and near the compressive side were investigated (see Fig. 4.105). Both the cobalt mean free paths in the direction perpendicular and parallel to the tensile and compressive faces of the specimen were measured. Table 4.10 summarizes the results:

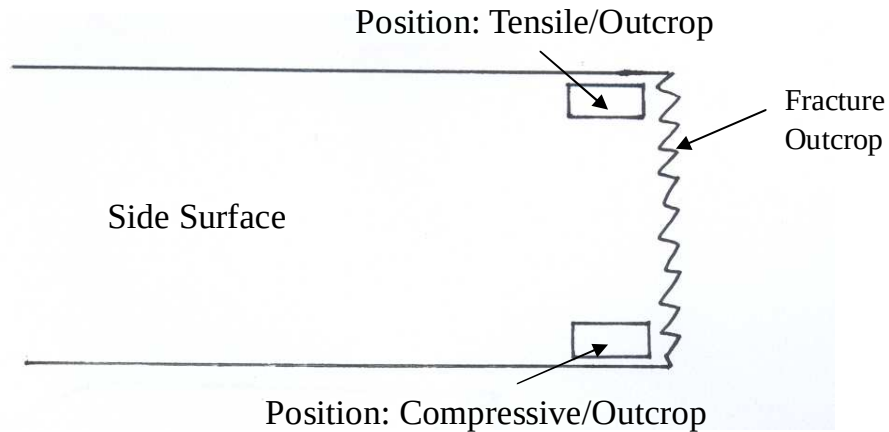


Fig. 4.105: Sketch of the areas investigated in the cobalt mean free path measurement on the side surface of S15-1000C-2.

Table 4.15: Summary of the cobalt mean free path measurement results. “Position” is shown in Fig. 4.105. “Parallel” and “perpendicular” mean parallel and perpendicular to the tensile and compressive faces.

Position	Co MFP (parallel)	Co MFP (perpendicular)	WC grain size
Tensile/Outcrop	0.56±0.45	0.68±0.56	1.31±0.91
Compressive/Outcrop	0.73±0.67	0.85±0.59	1.30±0.94

On the tensile side the cobalt layers perpendicular to the applied stress direction (“perpendicular”) appears to be larger than those parallel to the stress, which would be consistent with cobalt infiltration when grains are pulled apart. On the compressive side one would expect the cobalt layers perpendicular to the applied stress direction (“perpendicular” MFP) to be narrower than those parallel to the stress. However when pushing the grains close together, the cobalt may be squeezed into all layers available, as discussed by Clausen et al. [Clausen et al., 2006]. However the standard deviations are so large that these results cannot lead to definite conclusions.

5 DISCUSSIONS AND CONCLUSIONS

In this chapter the results are discussed. From these results and from relating the findings of this investigation to the results of other investigators, the main high temperature deformation mechanisms have emerged.

As given in section 3.1, the plastic strain at fracture at 1000°C reported by Milman et al. [Milman et al., 2002] was 4.7% for the NYA grade, 4.3% for the NYB grade and 3% for the S grade. This investigation has shown that the strain at 1000°C is due to cracks, cobalt flow with consequent sliding of the WC grains (although WC grain sliding has not been proved in this investigation) and deformation of WC grains (i.e. slip, which was seldom observed in this investigation, because it would not generally be detectable on fracture surfaces or outcrops polished after deformation). It was found that the contribution of the cracks to the total strains was at most 10%. Therefore most of the strain appeared to be due to deformation and particularly to cobalt drift. The evidence of cobalt drift is the following:

- a) cobalt layers on fracture surfaces (e.g. Fig. 4.52);
- b) cobalt features indicating that cobalt drifted similarly to volcanic lava (e.g. Fig. 4.82-Fig. 4.88);
- c) Co/W ratio on fracture surfaces being consistently higher on the compressive than on the tensile side, with the value in the bulk being intermediate (section 4.5);
- d) Co/W ratio on fracture outcrops appearing to be higher on the tensile side than on the compressive side (section 4.5);
- e) evidence of Co pockets and widening of Co layers occurring at 1000°C (e.g. Fig. 4.91-Fig. 4.95).

The evidence of Co drift not only confirms the results of Östberg [Östberg, 2005], but strengthens them because the evidence provided here is more direct, particularly in the case of the “lava-like” features in Fig. 4.82. In the case of the S grade, cracks contributed to the strain less than in the NY grades, but in the S grade the plasticity of cobalt during fracture was more obvious as seen on the fracture surfaces. The higher plasticity of cobalt during fracture in the S grade is expected to be due to the larger mean free path, allowing Co more freedom of movement. In the NY grades, Co movement was more constrained but it is expected that grains could slide over each other more easily on account of their smaller size, which must have contributed to the higher total strain than in the S grade. The contiguity of the WC in the three grades is 0.20 (section 4.6.3), which is not high enough to have a continuous WC skeleton [Luyckx and Love, 2006]. Therefore the cobalt carried much of the stress, deformed and grains moved with it, sliding over each other. Grain sliding was not proved here, but evidence that it happens at high temperature was provided by Mari et al [Mari et al., 1992].

Widened gaps between grains (and/or microcracks?) were observed (Fig. 4.91-Fig. 4.95 and Fig. 102-Fig. 103). These features are similar to those observed by Östberg [Östberg, 2005], who reported that 10% of the WC grain boundaries were separated and infiltrated by Co, and are also similar to the cobalt layers or cobalt pockets observed at interfaces between WC grains by Mari et al. (Fig. 2.26). The widened gaps (and/or microcracks?) lie perpendicular to the applied tensile stress direction both in our material and in Östberg’s.

The rounded WC grains observed in the S15 grades (Fig. 4.98-Fig. 4.101) also agree with Östberg’s results (Fig. 2.25). The rounded WC grains result from dissolution of WC into the cobalt phase at high temperature, since the solubility of

WC in cobalt increases with temperature.

The NYA15 grade did not fracture at 1000°C because at that temperature it was the toughest of the three grades. This is expected to be due to the fine grain size which allowed easy grain sliding. Also, as reviewed in section 2.2.4.3, a lower W content in the NYA grade binder, which results from the higher addition of VC, makes the material more ductile at 1000°C. The long cracks that did not propagate up to fracture show the high toughness of NYA at 1000°C.

The deformation of WC grains was seldom observed. Fig. 4.57 is a possible example of a WC grain with slip lines. Few examples of WC grain deformation were reported by Mari et al. and by Östberg. This can be explained by the stress having been partly carried by the soft Co phase and the difficulty in observing slip lines on fracture surface or repolished surfaces.

During the investigation of the fracture surfaces, steps were observed on WC grains, which are not slip steps because they are inconsistent with the slip system of WC. Fractography revealed that steps on WC grains were present at all temperatures in the NYA15 grade and in some specimens in the NYB15 grade (NYB15-1000C-3, NYB15-800C and NYB15-400C-3). No steps were found on the WC grains on the S15 fracture surfaces. On the basis of the TEM evidence provided by Egami et al. [Egami et al., 1993] and by Lay et al. [Lay et al., 2001], the steps are interpreted as due to the precipitation of (V,W)C particles at the WC/Co interfaces. The formation of (V,W)C prevented the reprecipitation of W in solution and the “filling up” of steps formed when WC went into solution. The NYA15 grade contained 0.8wt%VC, the NYB15 grade 0.4wt% VC, while no VC was added to the S15 grade [Luyckx et al., 1998]. The higher VC content in the NYA15 grade produced the higher amount of (V,W)C particles and so led to the

higher density of steps compared to the NYB15 grade. In the S15 grade, without VC addition, no steps were found. The step formation has been reported to be possibly due also to carbon content, as explained in section 2.3, but no evidence of differences in C content between NYA, NYB and S was available.

In conclusion, this investigation has provided direct evidence that WC-Co grades with 15wt%Co and grain sizes ranging from 0.3 to 1.3 μ m, undergo large plastic strains when tested in bending at 1000°C and that the strains can be accounted for mainly by cracking, Co drift and movement of WC grains. This investigation has also provided direct evidence that additions of VC to WC-Co causes the presence of steps on the WC grains and that the incidence of steps increases with increasing VC content. Previously, these steps had been observed only by transmission electron microscopy, but fracture surfaces showed the steps clearly because the (V,W)C particles formed along the WC boundaries, weakened the WC-Co interfaces and made them an easy path for fracture propagation.

APPENDIX: Macrocracks Opening Measurement

All macrocracks whose opening displacement was wider than about $3\mu\text{m}$ on the side surface of NY15A-1000C-1 (named from No.1 to No.8) were measured and are presented in Appendix A.

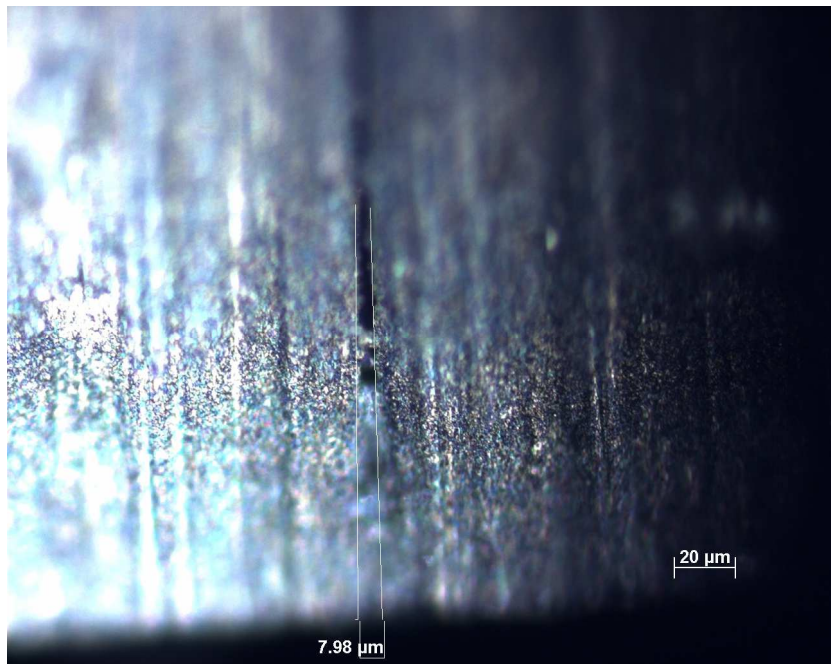


Fig. A1: Macrocrack No.1 which is $7.98\mu\text{m}$ wide on the side surface of NY15A-1000C-1

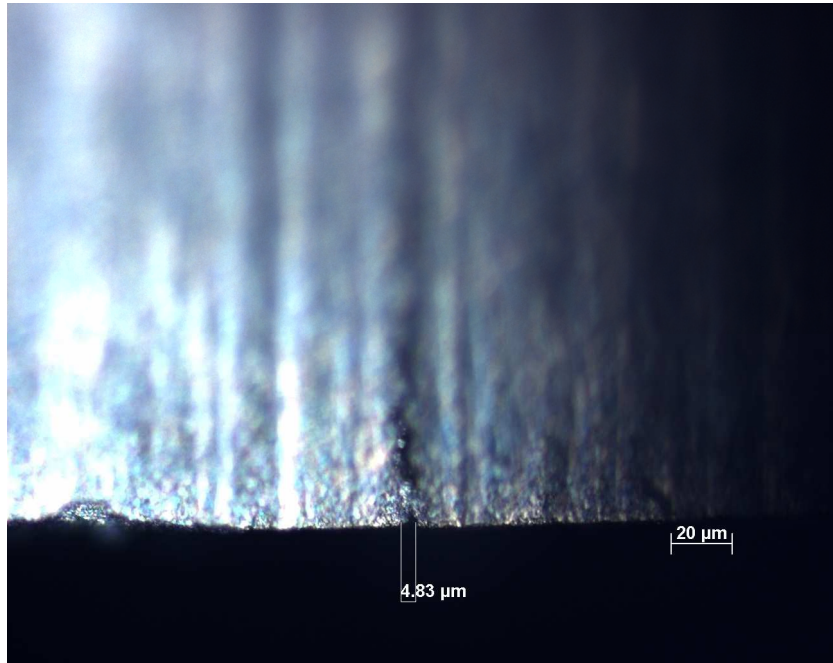


Fig. A2: Macrocrack No. 2 which is 4.83μm wide on the side surface of NY15A-1000C-1

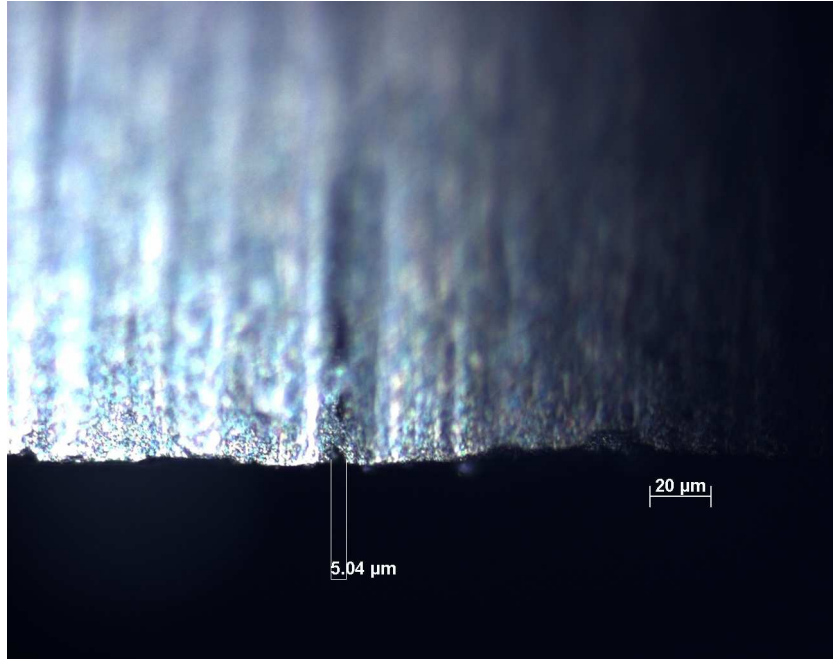


Fig. A3: Macrocrack No.3 which is 5.04μm wide on the side surface of NY15A-1000C-1

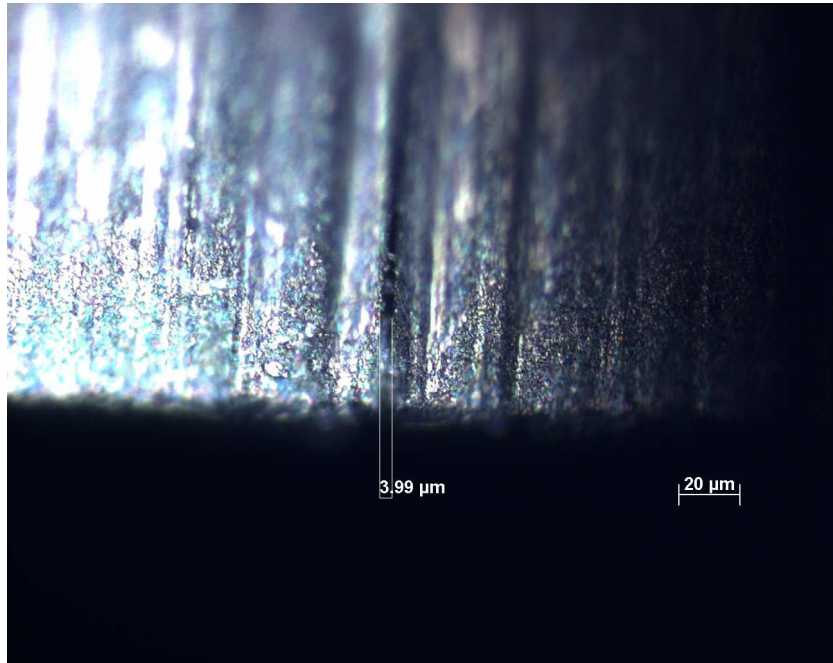


Fig. A4: Macrocrack No.4 which is 3.99μm wide on the side surface of NY15A-1000C-1

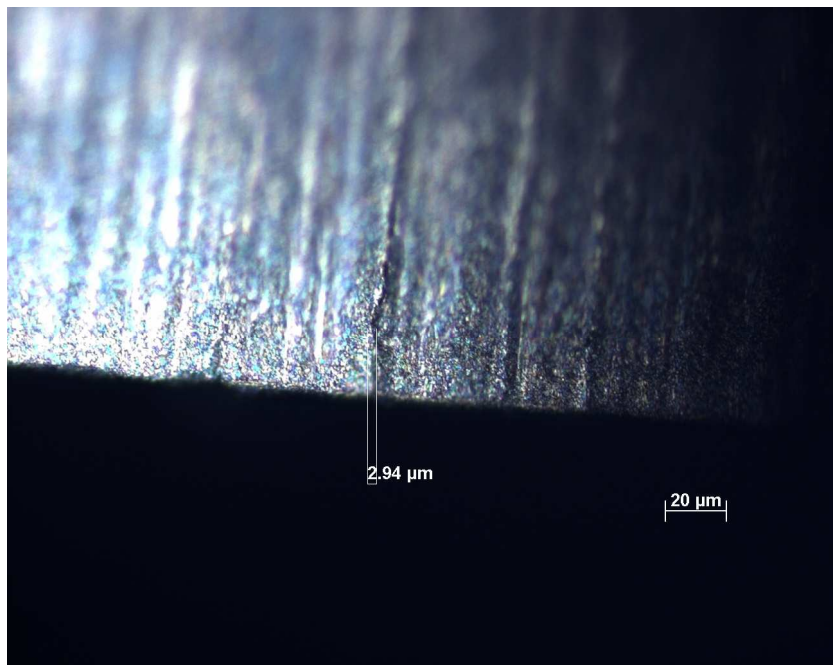


Fig. A5: Macrocrack No.5 which is 2.94μm wide on the side surface of NY15A-1000C-1

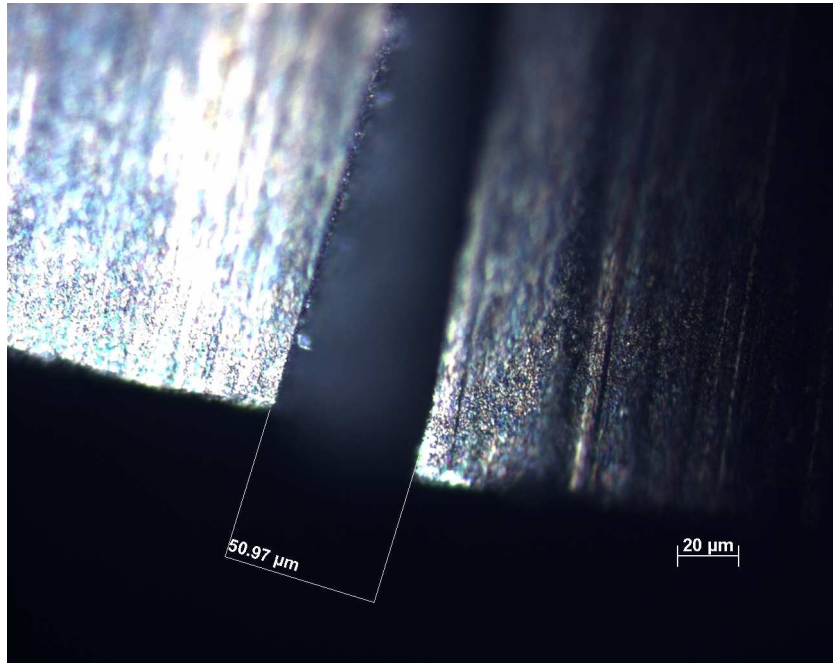


Fig. A6: Macrocrack No.6 which is 50.97μm wide on the side surface of NY15A-1000C-1

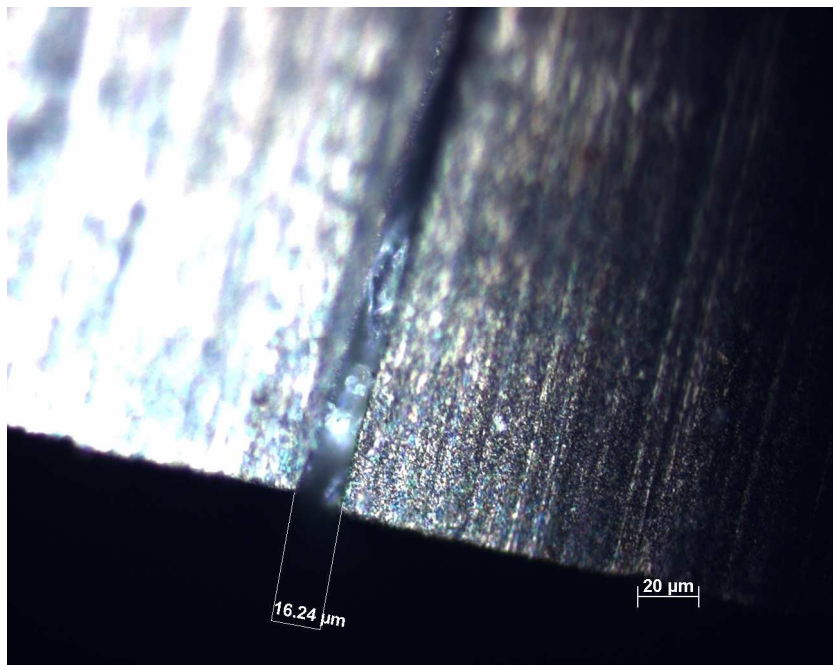


Fig. A7: Macrocrack No.7 which is 16.24μm wide on the side surface of NY15A-1000C-1

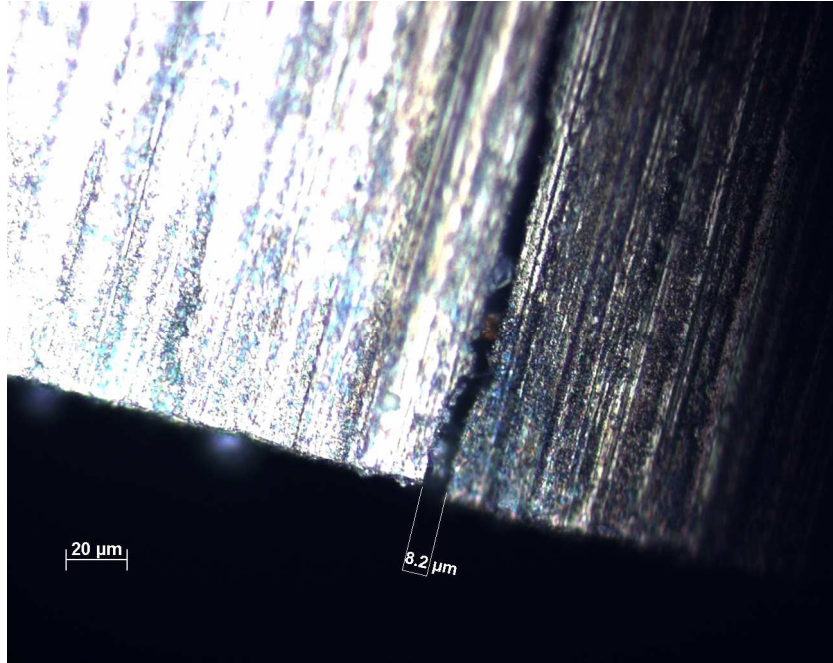


Fig. A8: Macrocrack No.8 which is 8.2μm wide on the side surface of NY15A-1000C-1

The widths of the openings of macro cracks from No.1 to No. 8 were summed up in Table A1. The total width of opening is 100.19μm.

Table A1: Sum of the opening displacements of No.1 to No.8 macrocracks on the side surface of NY15A-1000C-1

Crack No.	Width of the opening (μm)
1	7.98
2	4.83
3	5.04
4	3.99
5	2.94
6	50.97
7	16.24
8	8.20
Sum	100.19

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