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No. 21

Microstructural Measurements on Ceramics and Hardmetals

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Microstructural Measurements on Ceramics and Hardmetals

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Abstract:

This guide is intended to review the importance of microstructure in determining the properties and performance of technical ceramics and hardmetals. It also promotes good practice in characterising those microstructural features which are relevant to materials performance in order that more informed choices of material can be made for specific applications.

Microstructural parameters are described. They are typically characterised in several ways, including measures of grain size, crystallite texture, porosity, and phase volume fractions, as well as the detection of occasional features such as cracks, abnormal grains and inclusions. The importance of microstructural characterisation of these classes of material is reviewed, and possible measurement methods and methods of preparation of test-pieces for making the measurements are described. Based on information taken from the technical literature as well as data generated during NPL research programmes, correlations between microstructural parameters and properties are discussed.

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Note:

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Microstructural Measurements on Ceramics and Hardmetals

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Executive summary

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As with all classes of materials, the properties and performance of hard materials such as ceramics and hardmetals are determined by their microstructures, so evaluation of the microstructure is an important tool for property control, quality assurance and trouble shooting. This NPL Measurement Good Practice Guide reviews the relationships between microstructure and properties for hard materials, and describes methods for microstructural investigation.

A review is also given of parameters which permit microstructures to be described, including grain size and phase volume fraction. The methods of analysing microstructural images are discussed, incorporating statistical limitations of sampling and analysis. Some of the more difficult issues for this materials sector are briefly discussed, such as distributed grain sizes, grain shape and homogeneity, with some possible routes for overcoming the difficulties.

Particular emphasis is placed on procedures for the preparation of suitable polished sections, including the importance of ensuring that during the polishing process using a sequence of abrasive grits of diminishing size, adequate depth of removal is used to reduce the presence of preparation artefacts in the final surface, such as grain pluck-out. Methods of revealing the structure of the material once a suitable polish has been achieved are also described, including various etching methods, relief polishing and interference film microscopy. Annexes A and B deal separately with appropriate techniques for ceramics and hardmetals respectively.

1. Objectives

The properties and performance of advanced technical ceramics and hardmetals are governed by the detail of their composition and microstructure. General physical characteristics, such as density, elastic properties, thermal expansion, thermal conductivity, etc., are governed by average microstructure, while mechanical properties such as strength and toughness are often governed by local properties, particularly the extremes of the microstructural features or the abnormalities. In both classes of material, an examination of the microstructure reveals much about the material, its method of manufacture and its likely properties, so microstructural quantification is increasingly being employed as a quality assurance tool, or as an aspect of material qualification or specification.

In order to quantify microstructure, the first step is the adequate preparation of the material for investigation, i.e. the revealing of microstructural features in an appropriate manner. The next step is to apply appropriate techniques for determining the parameters required. Finally, the results have to be interpreted in the light of specifications or requirements for a particular application or function.

This guide provides an overview of the relationships between microstructure and material properties, and of the current position concerning microstructural measurement applied to ceramics and hardmetals, methods of obtaining data including specimen preparation and uses of the data.

2. Microstructure/property relationships

2.1 Ceramics

2.1.1 Introduction

The mechanical performance of a ceramic is determined primarily by its composition and microstructure, but is modified by the surface finishing procedure applied. Table 1 lists some of these factors and the directions in which properties are shifted as these factors are changed.

Unlike the situation for hardmetals for which properties can be closely related to microstructure for WC/Co type materials (see 2.2), for ceramics there are usually many more variables, particularly compositional ones, which make predictions of performance from microstructure difficult. Nevertheless, in any one compositional type, there are some general trends which may influence choice of product, so understanding the microstructure is important. Since the applications for which ceramics are considered make ever-increasing demands on the materials, many different approaches to formulation are tried in order to achieve the properties required.

Table 2 lists the main types of commercially available ceramic materials for mechanical and thermomechanical applications (Morrell (1985)), and the directions in which developments are moving in order to improve performance and reliability. Although the methods used to enhance properties vary, there are certain common requirements. It is usual in manufacture and handling to aim for low porosity (unless porosity is a deliberate feature) and for the avoidance of inclusions and cracks or chips.

Table 1 - Factors influencing properties of ceramics

Property:	**Controlled by:**	**Improved by:**
Tensile/flexural strength	Chemical composition Grain size Porosity Abnormalities/inclusions Machining Residual stresses	Selecting high-modulus phases Decreasing Decreasing Removing Finer grit sizes Annealing
High-temperature strength	Secondary phase composition	Removal of glassy phase forming components
Elastic properties	Chemical composition Porosity	Selecting high modulus phases Reducing
Fracture toughness	Composition Phase morphology	Selecting intrinsically tough phase types, transformation toughening Developing elongated grains; particulate, platelet or whisker reinforcement
Hardness	Composition Porosity	Selecting intrinsically hard phase types, minimising secondary phases Minimising porosity
Abrasion resistance	Composition Grain morphology	Selecting harder types of material Choosing finer grain sizes
Thermal expansion	Phase composition	Modified by selecting appropriate material types
Thermal conductivity	Phase composition	Select high thermal conductivity phases; minimising secondary glassy phases
Corrosion resistance	Phase composition, especially any continuous secondary phases	Choosing appropriate high-purity materials, or ones free from continuous secondary phases

Of these materials, **high-alumina ceramics** represent the largest group, covering a very wide range of product types and compositions. Most manufacturing organisations have several generic types of alumina material for general purposes, as well as those designed for specific applications (Morrell (1987)). They tend to be coded or cited by their content of aluminium oxide; in general, the less aluminium oxide present, the greater the quantity of secondary

Table 2 - Principal types of monolithic forms of advanced technical ceramics and development directions

Ceramic type:	**Example applications:**	**Development directions:**
Alumina	General purpose, insulators, abrasion resisting parts, sliding wear parts, ceramic armour, sodium vapour lamp envelopes, crucibles, high-temperature tubing, electronic substrates, surgical implants	Principally improvements in processing, corrosion resistance, and mechanical reliability
Alumina/zirconia	Strength and impact resisting parts, cutting tools	Control of zirconia behaviour
Zirconia (Y_2O_3 partially stabilised type, TZP)	Dies, wear parts, knives, ferrules for optical fibre links surgical implants	Control of porosity and grain size
Zirconia (MgO, CaO, Y_2O_3 partially stabilised types)	Dies, wear parts, valves, electrochemical devices	Cost reduction
Zirconia (cubic stabilised type)	High-temperature applications	
Silicon carbide, silicon containing	Wear parts, seals	Process modifications to reduce costs
Silicon carbide, sintered	Wear parts, seals	Liquid phase sintering methods
Silicon nitride, porous, reaction bonded	High-temperature applications in metal casting, crucibles, welding	
Silicon nitride, dense, sintered or hot-pressed	Rolling bearing elements, high-temperature mechanical devices, engine parts, welding jigs, cutting tools, applications needing high strength	Control of grain structure, elongation of grains for self-toughening, removal of secondary phases, reduction in processing costs
Boron carbide	Wear parts, bearings, ceramic armour	
Boron nitride (hexagonal, hot-pressed)	Special applications, crucibles, machinable	
Aluminium nitride	Electronic heat sinks	Improve thermal conductivity
Glass-ceramics	Tailorable materials for seals, joints, special purpose devices, machinable materials	

phases present, and the lower the strength, stiffness and refractoriness of the product. Many materials were originally designed for electrical purposes, and may not have ideal properties for mechanical or chemical corrosion applications. Special purpose varies include:

- High-purity(> 99.9% Al_2O_3), coarse-grained (30 – 200 µm grain sizes) materials for high-temperature applications;
- High-purity (> 99.9% Al_2O_3), coarse-grained (25 – 50 µm grain sizes) but translucent materials for sodium vapour lamp envelopes;
- High-purity (> 99.7% Al_2O_3), fine grained (<2 µm grain sizes), for surgical implants (*e.g.* to ISO 6474);
- Medium purity (95 – 98% Al2O3), medium-grained (5 – 15 µm grain sizes), with secondary components designed for good metallisation through the 'molybdenum-manganese' process;
- Medium purity (95 – 98% Al2O3), medium to fine grained (3 – 8 µm grain sizes) with secondary phases designed for chemical corrosion resistance.

A subclass, often referred to as **zirconia-toughened alumina (ZTA)**, contains unstabilised or partially stabilised zirconia particles which act to improve strength and toughness. Such materials are used for arduous service conditions, such as cutting tools and armour. The normal zirconia phase transformation is suppressed by enclosure in an alumina matrix, but is released by proximity of a crack, and helps to impede their propagation. Other non-oxide additions can also be used to increase hardness and toughness, such as titanium carbide (used for cutting tools) and silicon carbide, either in whisker form (for cutting tools) or in ultrafine particulate form (for developmental, so-called nanocomposite ceramics).

The properties of conventional alumina are very versatile, so only when these properties are inadequate is it generally necessary to employ an alternative type of product, *e.g.* when:

- strength or toughness are inadequate;
- when the thermal expansion coefficient is too high or too low, or needs to be matched to another material;
- when the thermal conductivity is too high or too low;
- when thermal shock resistance needs to be improved;
- when the corrosion resistance is inadequate;
- when electrical properties are inappropriate.

There are many other types of advanced technical ceramic available from specialist manufacturers, but most tend to be more expensive because alumina is a relatively cheap raw material compared with the component powders needed for these other types. The widely available class of **zirconia** ceramics has been extensively researched over the last 20 years or so, extending the traditional so-called fully or cubic-phase stabilised material (FSZ) into versions which have much improved strength and toughness by exploiting the phase transformation behaviour in incompletely stabilised compositions. Most **partially stabilised**

materials (PSZs) have much improved strength and toughness at ambient to moderate temperatures. Their microstructures have either retained tetragonal phase precipitates in a cubic matrix, or mostly ultrafine tetragonal phase grains, the latter often described as **tetragonal zirconia polycrystals** (TZP).

For improved thermal shock resistance, strength and toughness, silicon nitrides can be used. These materials have found a number of niche applications, for which properties have been improved by focusing on particular features. For example, in developing silicon nitride based bearings and cutting tools, the grain size and degree of grain elongation significantly affect mechanical properties, especially toughness, fatigue life and modes of wear. For very high temperature use, control of phase composition and the elimination of secondary glassy phases has received much scientific attention even if such materials are not yet widely exploited.

For a combination of hardness, corrosion resistance and thermal shock resistance, dense silicon carbides offer cost-effective solutions. There are two main types. The reaction bonded type has a small amount of residual free silicon phase which limits high-temperature performance. The sintered type has minimal secondary phases, but may contain residual porosity (or even controlled porosity levels). More recent developments to reduce sintering temperatures by use of liquid-phase sintering provide improved ambient temperature properties, particularly toughness.

Materials availability is constantly changing as processing improves and costs are reduced. For example, as the demands for improved strength increase, the maximum size of permitted strength-limiting flaws such as large grains, pores, inhomogeneities and inclusions decreases, placing more stringent demands on consistency of raw materials, cleanliness of operation, and repeatability of process condition. Although substantial research efforts have been applied to the development of a range of techniques for detecting the flaws which limit properties and reliability[1], including highly specialised instrumental methods for non-destructive evaluation, locating such strength limiting features quantitatively and nondestructively for QA purposes remains difficult to achieve. In cases where strength of the component is critical to successful operation, mechanical proof-testing remains the best option where feasible to perform.

2.1.2 Strength

Strength normally declines with increasing grain size according to the traditional Hall-Petch relationship ($\sigma_f \propto d^{1/2}$, where σ_f is the fracture stress and d is the effective grain diameter), which operates on the basis that the boundaries of individual grains, or pre-existing cracks in individual grains, define the effective defect size. However, this appears to break down with materials of fine grain size for several possible reasons:

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[1] Fluorescent dye methods can be used to detect surface connected cracks. Fractography using optical microscopy or scanning electron microscopy can be sued to identify large grains, inclusions and large pores after fracturing, and to examine the spatial distribution of these features within a component. The specialised instrumentation methods include X-ray imaging, Ultrasonic imaging, acoustic emission, thermal imaging and laser scattering. These are beyond the scope of this Guide.

- other types of microstructural feature, such as large pores, delaminations or inclusions, provide larger ‘flaws’;
- there may be internal stress resulting from the manufacturing process;
- machining, abrading or impacting surfaces can induce damage which may be rather deeper than a single grain;
- the environment may permit the extension of existing surface-connected features when under stress.

For ceramics of simple microstructure which do not involve any toughening or reinforcing mechanism, such as aluminas, optimum strength is usually achieved by using fine powders of high purity and fabrication methods which yield fine-grained microstructures with minimal porosity. For more complex ceramics which involve toughening processes or reinforcing species, the microstructures need to be carefully controlled during processing in order to optimise strength.

Caution is therefore needed in the interpretation of strength data, and note needs to be made of all the conditions of manufacture and preparation of test-pieces in order to provide an appropriate interpretation.

2.1.3 Fracture toughness

Compared with other types of material, ceramics have very little toughness in an engineering sense. Nonetheless, relative toughness of ceramic products is an important parameter influencing usability in certain applications. The toughness of a ceramic is governed by its microstructure, but the relationship between toughness and microstructure is far from straightforward. In some materials, particularly coarser-grained ones, toughness may be related to crack length, an added complication. In alumina ceramics, short-crack toughness can change with secondary glass phase composition as a result of thermal expansion mismatches between this phase and the alumina grains, and may decrease as the amount of secondary phase decreases. In zirconias, the phase change mechanism strongly influences apparent toughness. In silicon nitrides, improved toughness can be generated by growing coarse prismatic grains of high aspect ratio in situ during manufacture.

Because of the great importance of improving toughness, a number of toughening mechanisms have been widely studied. These include transformation toughening, microcracking, porosity, laminated structures, bridging mechanisms by fibres or whiskers, and crack deflection by dispersed phases or particulate additions. In general, these techniques provide mechanisms of absorbing more energy during fracture, but often at the expense of reduced ultimate strength.

2.1.4 Hardness

The hardness of a ceramic is determined by the phases present and the microstructure. In aluminas and silicon nitrides, hardness decreases with higher volume fractions of residual glass and increasing porosity. In silicon nitrides, the presence of retained alpha silicon nitride increases hardness. In sub-micrometre sintered alumina and zirconia, decreasing grain sizes leads to increases in hardness. It should be noted that the literature on hardness is confusing. Hardness is often determined at low indentation forces in order to minimise cracking, but smaller indentations are prone to larger fractional errors of measurement, apparent hardness tending to increase with declining indentation force, especially at forces of less than 10 N.

2.1.5 Wear resistance

The mechanism of abrasive wear of a ceramic is governed by the hardness and toughness of the ceramic and by the conditions of loading and contact. Different ways of wear testing produce very different results, and may even produce different rankings among the same group of materials. For a given class of material, fine-grained ceramics are reported to be more abrasion resistant than coarser grained ones, although this is not always true, and factors such as porosity and minor phase composition can provide a marked influence. Even if other factors of composition and porosity are removed, wear rates and mechanisms can change with grain size, as reported by Miranda-Martinez *et al.* (1994) and Davidge and Riley (1995). These authors tested a range of high-purity fully-dense alumina ceramics and found a Hall-Petch type relationship (Figure 1) showing increasing wear resistance with reducing grain size.

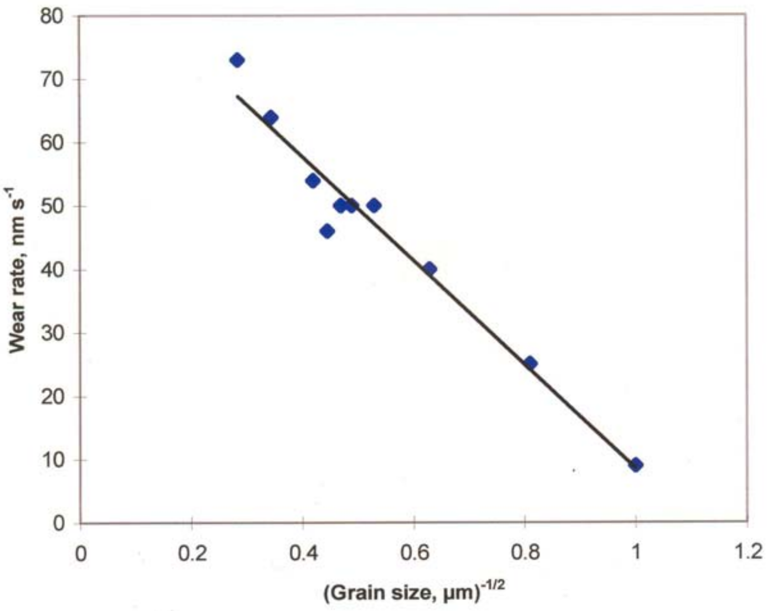

Figure 1 *Effect of grain size on the erosive wear of high-purity fully dense alumina ceramics (after Miranda-Martinez et al. (1994)).*

Another factor is the level of internal stresses between grains or continuous phases of different types lead to different behaviours. Thus while some trends can be identified, it is not feasible to define any completely general relationship between microstructure and wear resistance. An example of this is the addition of silicon carbide particles to an alumina which influences thermal residual stresses and causes a marked change in erosion resistance (Figure 2, Twigg *et al.* (1997)).

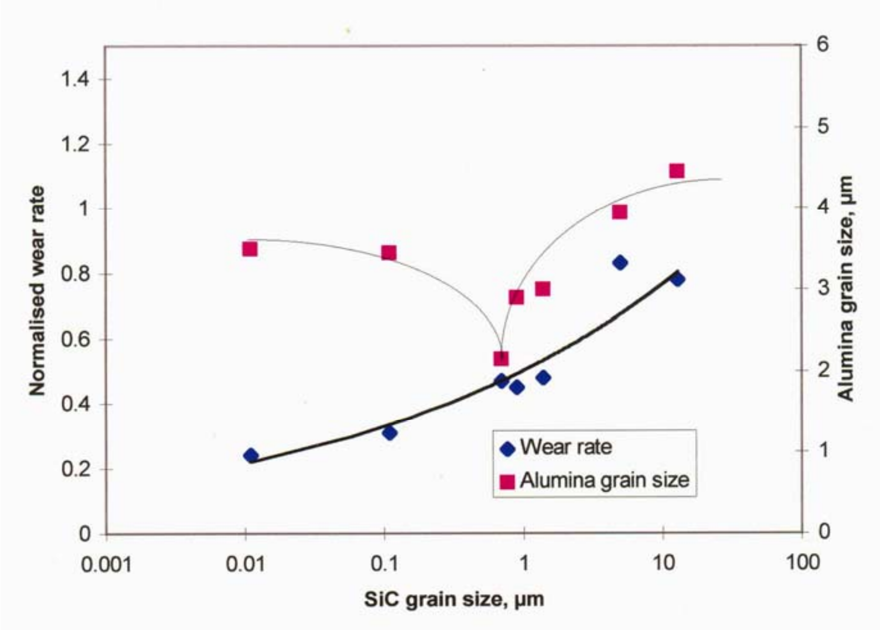

Figure 2 *- Effect of silicon carbide particle size on the erosive wear of alumina/silicon carbide materials made by hot-pressing (after Twigg et al. (1997)).*

2.1.6 High temperature properties

The important high temperature properties are hot strength, hot hardness, creep resistance and chemical inertness. These are usually optimised when the residual glassy phase content is minimised. Creep resistance improves with increasing grain size, the opposite trend to that for short-term strength.

2.2 Hardmetals

2.2.1 Introduction

In many respects there are similarities between liquid-phase sintered ceramic and hardmetal microstructures, except that in hardmetals there are two interpenetrating continuous phases, one metallic and one a hard phase such as a carbide or carbonitride. The metallic phase is usually based on a transition metal, such as Co, Ni or Fe, or an alloy of these, but always has some of the carbide phase in solution. The hard phase can be of a single type, *e.g.* tungsten carbide (hexagonal, WC), titanium carbide (cubic, TiC), tantalum carbide (cubic, TaC) or of mixes of these. The primary microstructural parameters of interest are the composition, size and volume fractions of these two types of phase.

2.2.2 Composition

If the ***hard phase*** is tungsten carbide, it is generally stoichiometric WC with none of the binder phase in solid solution. If molybdenum is added, it can partition itself between the hard phase and the metallic 'binder' phase resulting in a (W,Mo)C structure. If the hard phase is a cubic carbide, such as TiC or TaC, or a carbonitride such as Ti(C,N), it can be non-stoichiometric to different degrees, and this affects properties. Such phases are best characterised by crystallographic lattice parameter measurements, because the major constituent of the binder phase (Co, Ni, *etc.*) does not dissolve in the cubic phases. If there are mixes of hexagonal and cubic structures, the W and Mo atoms partition between the two types, giving, for example, WC or (W, Mo)C plus (Ti, Ta, W)C (known collectively as γ–phases). The choice of hard phase composition is dictated primarily by mechanical property requirements (see below).

The ***binder phase*** can contain elements of the hard phase in solid solution. For example, in WC/Co hardmetals, the Co binder phase is an alloy of (Co, W, C). In this case the amounts of W and C are determined by total composition, and have a very significant effect on properties (Roebuck (1984)). Characterisation of the binder phase composition requires either lattice parameter measurements, transmission electron microscopy coupled with highly local energy dispersive X-ray analysis, or magnetic measurements (Roebuck (1999)).

2.2.3 Microstructural scale

The ***hard phase*** grains are usually in the size range 0.1 to 10 µm, and are primarily controlled by the size of the starting hard phase powders and the processing conditions, *i.e.* liquid-phase sintering, which leads to some grain growth. Some examples are shown in Figures 3 and 4. The size of the hard phase is generally measured by a line intercept technique to give a mean linear intercept size, although industrially, classification by visual comparison with reference micrographs remains commonplace (BS EN 24490, ASTM B390, ISO 4499 (currently being revised by ISO TC199/SC4)).

The size of the ***binder phase*** regions is controlled by the volume fraction of the phase and the size and shape of the hard particles, since it essentially fills the space left between the hard grains. A measure of the size can be obtained also by the linear intercept method or, particularly in the case of WC/Co hardmetals, can be inferred from measurements of coercivity because this property is related to the WC/Co interphase area (Roebuck (1995)), which correlates directly with volume fraction and the mean linear intercept size. There are some uncertainties in these relationships due to variations in the Co-W-C composition, and to internal stresses, factors which are not yet quantitatively understood.

The ***phase volume fractions*** are frequently calculated from known (full, pore-free) densities based on the input composition used for manufacture, but clearly it can be checked by using the line intercept or point counting methods.

2.2.4 Selection and control of properties

Composition, binder phase volume fraction and hard phase grain size are thus the main parameters used by the hardmetal manufacturers to define property targets, in particular:

- Strength
- Fracture toughness
- Hardness
- Wear resistance
- Stiffness
- Fatigue resistance

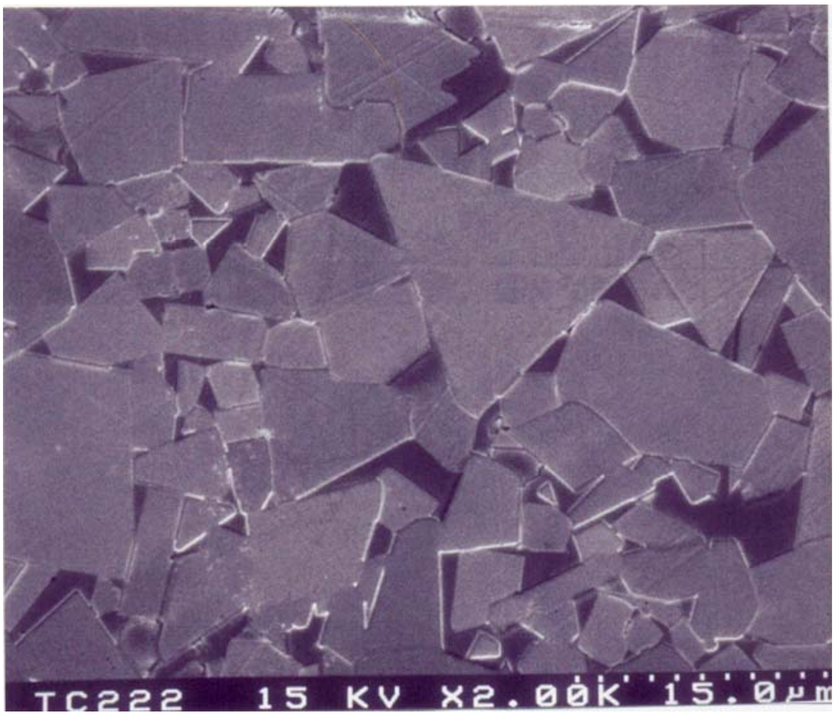

Figure 3 *- Scanning electron micrograph of a coarse-grained hardmetal containing 6 wt% Co showing well defined angular grains.*

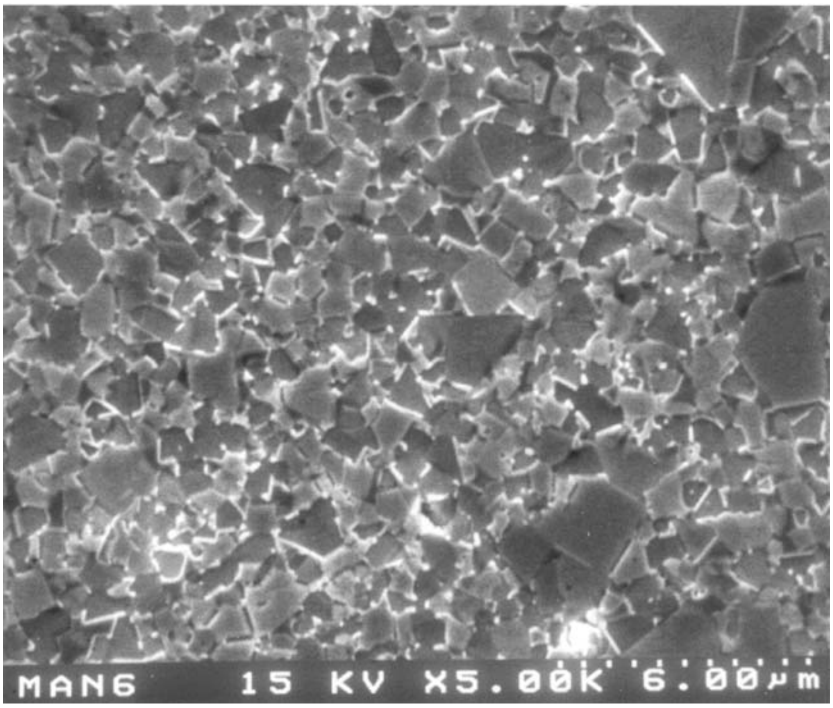

Figure 4 *- Scanning electron micrograph of an ultrafine grained hardmetal containing 6 wt% Ni showing less well defined grains than in the coarser-grained hardmetal.*

and their variation with temperature. In addition the following physical properties can also be tailored to some extent using these variables:

- Thermal expansion coefficient
- Thermal conductivity
- Thermal diffusivity
- Electrical conductivity

The manner in which the principal mechanical properties are influenced by composition, volume fraction and grain size is summarised in Table 3, while Table 4 gives their influence on thermal and electrical properties.

Table 3 - Influence of microstructure on mechanical properties of hardmetals

Property	Hard phase size increasing	Binder phase volume fraction increasing	Sensitivity to composition of	
			Hard phase	Binder phase
Strength				
Compression	Decreases	Decreases	Very sensitive	Insensitive
Tension (flexure)	Little effect	Little effect	Sensitive	Sensitive
Fracture toughness	Increases	Increases	Sensitive	Sensitive
Hardness	Decreases	Decreases	Very sensitive	Insensitive
Wear resistance				
Abrasion	Decreases	Decreases	Sensitive	Insensitive
Erosion	???	???	???	???
Fatigue	???	???	???	???
Stiffness	Insensitive	Decrease	Sensitive	Insensitive

??? = the factors involved are not well understood

Table 4 - Influence of microstructure on thermal and physical properties of hardmetals

Property	Hard phase grain size increasing	Binder phase volume fraction increasing	Sensitivity to composition of	
			Hard phase	Binder phase
Thermal expansion	Insensitive	Increases	Mildly sensitive	Insensitive
Thermal conductivity/ thermal diffusivity	Decreases			
Specific heat capacity	No effect	Increases	Sensitive	Mildly sensitive
Electrical conductivity	Increases	Insensitive	Sensitive	Sensitive
Density	Insensitive	Decreases[1] Increases[2]	Sensitive	Sensitive

1 if Ta or W based hard phase 2 if a Ti based hard phase

2.2.5 Factors affecting strength

As with ceramic materials, it is important to differentiate between tensile and compressive strength behaviours of hardmetals. Both tests are covered by ISO standards (ISO 3327 = BS EN 23327, ISO 4506 = BS EN 24506 respectively, Roebuck *et al.* (1996)). Considering first compression tests, it is possible to obtain very repeatable stress/strain curves for hardmetals to identify the extent of ductility, and the test discriminates very well between the different microstructural variables. However, it is expensive to carry out since strain gauges are required for strain measurement, and well-aligned stiff test jigs in a high-capacity loading machine are needed to ensure that ductility is detected. For the most part, therefore, hardness tests (see below) are substituted. However, hardness tests do not strictly give information on ductility, and hardness can vary between different grades of hardmetal for the same flow stress. This is equivalent to the materials showing different levels of toughness for the same level of hardness.

Typical compression strengths of hardmetals are in the range 2.5 GPa to 8 GPa, *i.e.* are among the strongest of materials. In contrast, in tension or in flexure, hardmetals tend to show more-brittle behaviour, and strengths are typically in the range 1.5 GPa to 4 GPa depending on a number of factors (Roebuck (1997a)). As with fine-grained ceramic materials, the results of flexural strength tests are particularly sensitive to the geometry of the test-piece and the method of its preparation. Preparation of the test-piece by diamond grinding introduces compressive residual stresses into the surface which can increase the apparent flexural strength by a factor of up to two (Roebuck (1996a, 1996b)) if fracture origins are at or very close to the surface[2]. Until more consistent flexural strength test procedures are agreed and widely employed, it will remain difficult to separate conclusively the role of microstructural parameters. Since the influence of grinding stresses appears to be more marked in finer grained materials, there is increasing use made of ever finer grain sizes.

2.2.6 Fracture toughness

Fracture toughness is considered to be an important parameter controlling hardmetal applications, so it is somewhat surprising that there is as yet no international standard for its measurement. However, recently a VAMAS intercomparison exercise on a wide range of hardmetals has provided useful underpinning science that will accelerate the development of standards (Roebuck and Bennett (2004, 2005)). There appears to be a reasonably straightforward relationship between microstructure and toughness in that as the binder phase volume fraction and the grain size increase, so does the toughness. This is related to the size of the binder phase regions, which can be characterised by the mean linear intercept method, but there are also secondary effects due to binder phase composition. The primary toughening mechanism is through ductile fracture of binder phase ligaments behind the advancing crack

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[2] Most good-quality fine-grained hardmetals that have been hot isostatically pressed show very few microstructural abnormalities, such as large pores, so strength tends to be controlled by surface machining flaws or normal microstructural failure.

front (Sigl and Fischmeister (1988)). Hard phase fracture can also make a contribution, particularly in coarse-grained WC-based hardmetals. The cubic phases are more brittle, and are less effective in this capacity. As the grain size decreases, particularly in WC/Co hardmetals, the toughness declines to an asymptotic limit corresponding to interfacial WC/WC boundaries with a value of about 7 MPa $m^{1/2}$. For high binder-phase content, coarse-grained materials, toughness levels as high as 25 to 30 MPa $m^{1/2}$ can be obtained, although such results tend to be strongly method dependent. However, an improvement in toughness is usually accompanied by an increase in ductility and a loss in strength.

2.2.7 Hardness

Hardness is primarily determined by the type of hard phase, and its grain size and volume fraction. Binder phase composition may have a secondary effect; for example nickel-bonded WC is slightly less hard than the cobalt-bonded versions for the same hard phase grain size. In the simple WC/Co hardmetals, there is a Hall–Petch type relationship between hardness and grain size (*i.e.* hardness $\propto$ (grain size)$^{-1/2}$) which is contributing to the commercial drive towards finer grain sizes. However, it is unclear whether this type of relationship is still present when the mean linear intercept grain size is less than 0.2 μm, or whether hardness reaches an asymptotic level equivalent to the trend observed in fracture toughness measurements.

2.2.8 Abrasion resistance

Although a rather severe test intended for ranking materials for rock drilling applications, the ASTM B611 test using wet alumina grit to abrade a test sample is widely used. The amount of wear occurring in the test is directly related to hardness. With increasing hardness up to 2100 HV30 the wear volume in this test decreases, *i.e.* resistance to abrasion increases. A similar trend is observed when the alumina grit is replaced with silica grit (Gee *et al.* (1999)), although wear rates are rather lower. Because of the relationship between hardness and grain size, increasing grain size and binder phase volume fraction leads to worsening abrasion resistance. There are few data available to evaluate the effects of adding cubic carbides, but replacing WC with TiC leads to a ten-fold reduction in abrasion resistance for the same hardness. Replacing Co with Ni reduces hardness slightly for the same volume fraction added, and leads to a slight decrease in abrasion resistance. Changing the binder phase chemistry in WC based materials has little effect in tests in pH neutral water, although at different pH levels, there is some evidence to suggest that the binder phase chemistry may play an important role.

2.2.9 Elastic properties

Elastic properties of WC/Co hardmetals have been shown to be independent of grain size, and controlled solely by the binder phase volume fraction according to a rule of mixtures type relationship (Doi *et al.* (1970), Morrell (2002)). Similarly, substitution of WC by other hard phases produces small changes in elastic moduli.

2.2.10 High-temperature properties

At the present time it is not possible to predict elevated temperature properties from changes in microstructure because, notwithstanding the difficulties of undertaking testing at elevated temperatures, there are few studies which have systematically changed the binder phase content and the hard phase type and size. For example, there is conflicting evidence of the relationship between hard phase grain size and strength. As the temperature is increased, the trend of strength increasing with decreasing grain size has been reported to invert as creep mechanisms at interfaces start to dominate deformation processes (Mari *et al.*(1999)). Binder phase chemistry almost certainly plays a larger part than in room temperature tests as the differences in properties between simple Co, Ni or Co/Ni binders and alloyed binders such as Ni-Cr-Mo become more apparent.

2.2.11 Property maps

Simple regression equations have been developed at NPL (Roebuck *et al.* (1999b), Roebuck *et al.* (2001), Roebuck (2004a)) for WC/Co hardmetals to map three of the above mechanical properties: hardness (HV30); toughness (by the Palmqvist indentation crack length method (Roebuck *et al.* (1999d))); abrasion resistance (ASTM B611); as well as density and coercivity as functions of WC mean linear intercept grain size and Co binder phase volume fraction. The intention of developing these maps is to provide a simple guide to property expectations based on composition and microstructure. It should be noted that although the data upon which the maps are based come mostly from systematic measurements made at NPL on materials from a number of sources, there is usually some scatter associated with uncertainties of measurement, and the nominal nature of the declared composition. Factors such as grain size distribution or carbon content have been ignored, but may contribute to the scatter. The maps are shown in Figures 5 to 9.

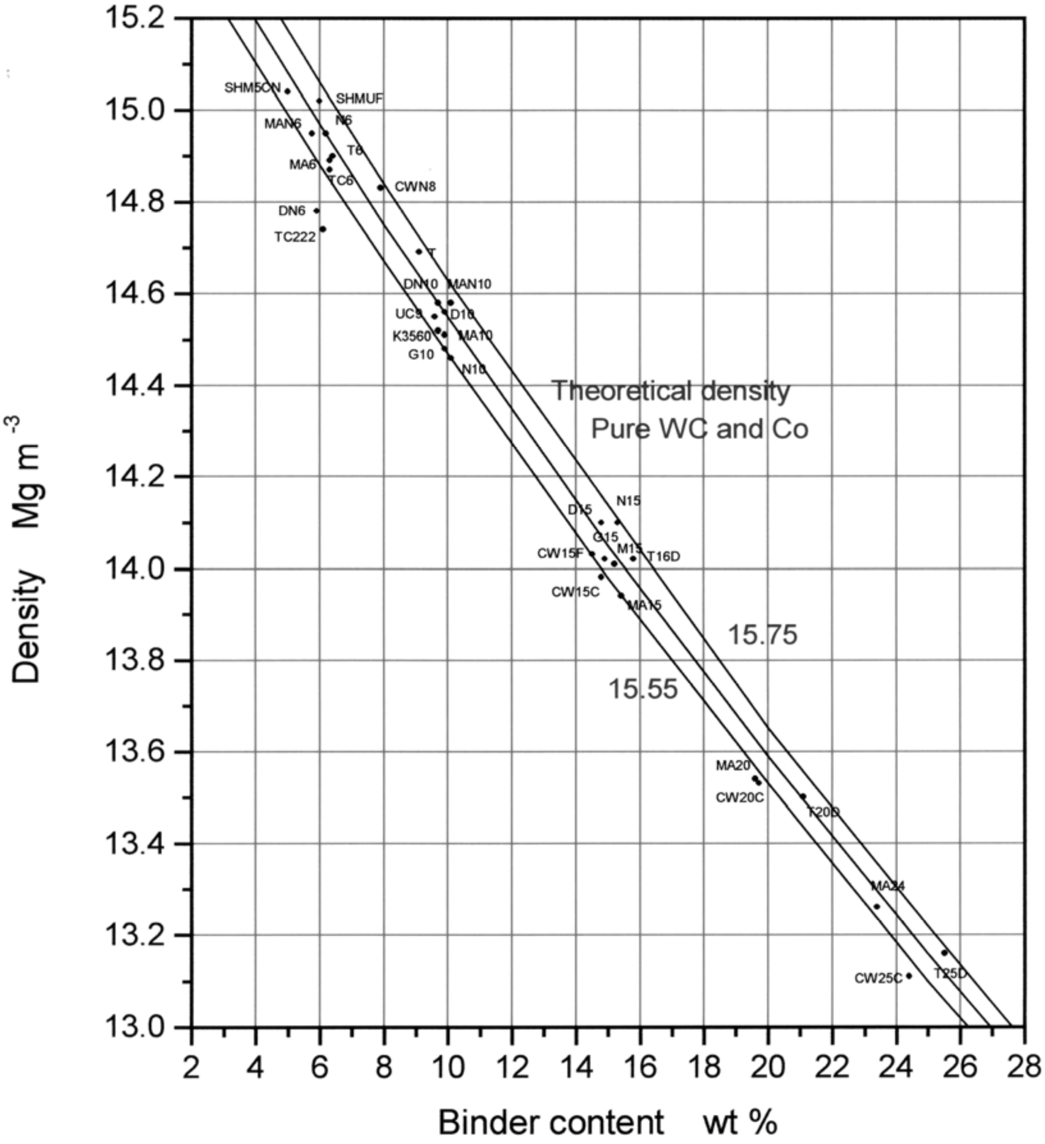

Figure 5 *- Density as a function of cobalt content for WC/Co hardmetals comparing experimental measurements on individual products with theoretical predictions. The three lines represent trends computed using the rule of mixtures approach with zero porosity and assuming different values of 15.55, 15.65 and 15.75 Mg m^{-3} for the theoretical density of WC alone.*

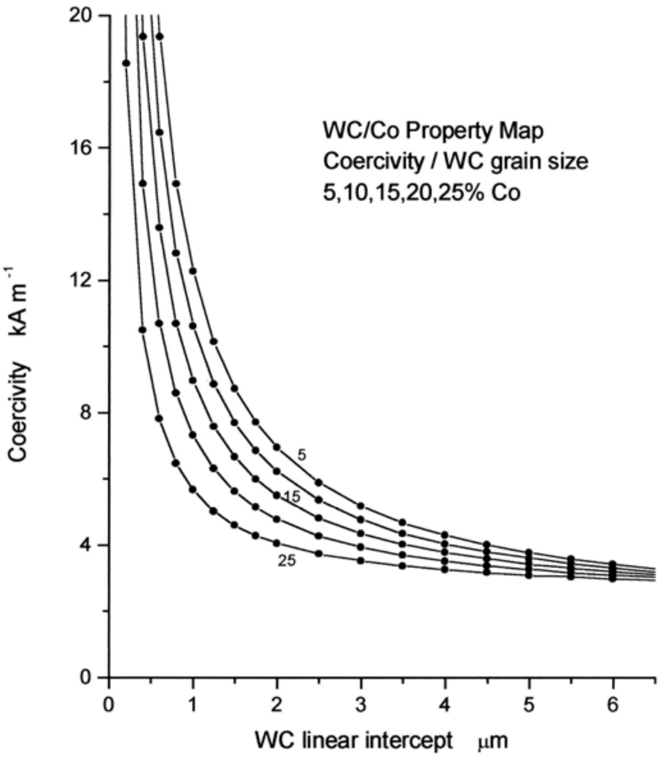

Figure 6 *- Property map showing fitted trends of coercivity as a function of WC mean linear intercept size for different cobalt contents in WC/Co hardmetals.*

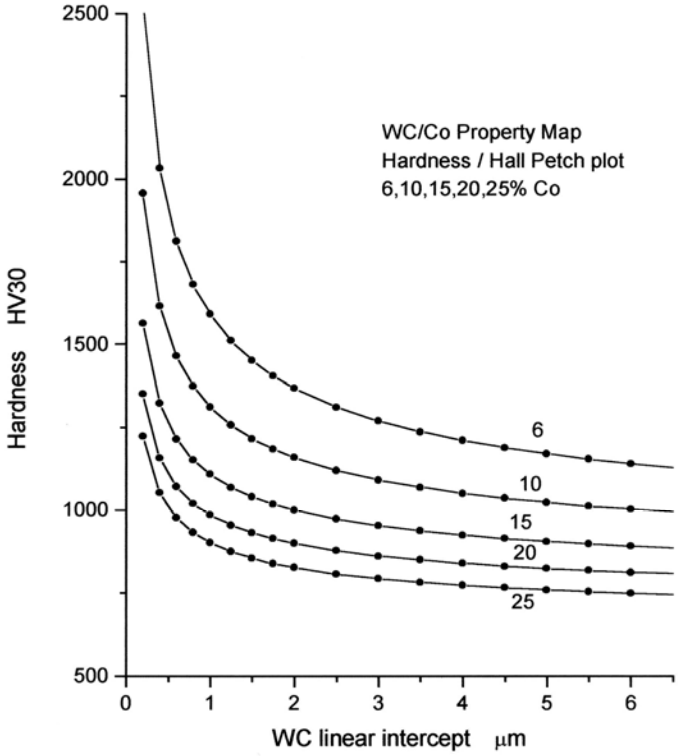

Figure 7 *- Property map showing fitted trends of hardness as a function of WC mean linear intercept size for different cobalt contents in WC/Co hardmetals.*

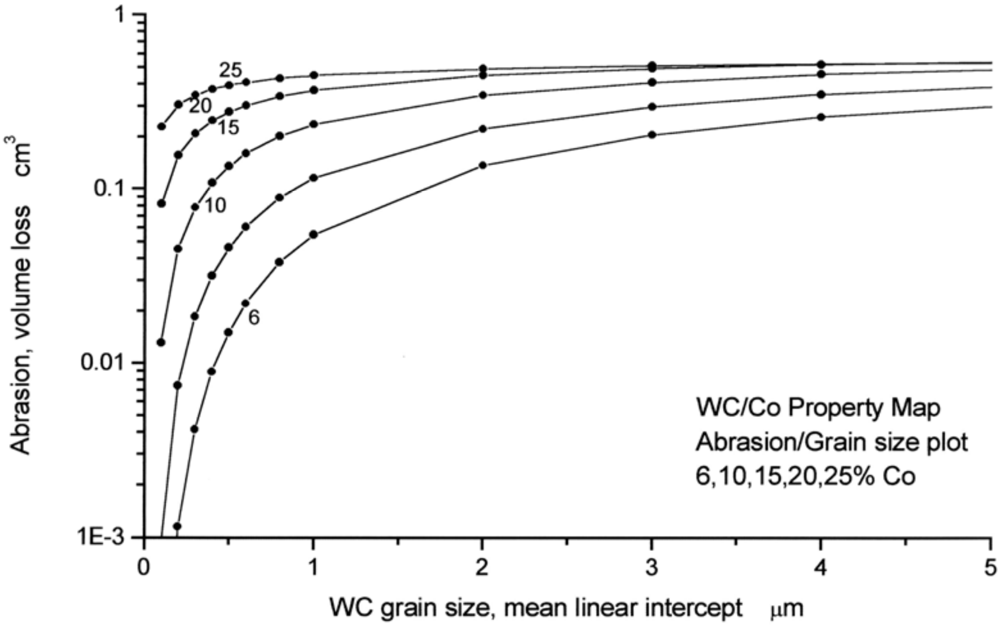

Figure 8 *- Property map showing fitted trends of ASTM B611 abrasion resistance as a function of WC mean linear intercept size for different cobalt contents in WC/Co hardmetals.*

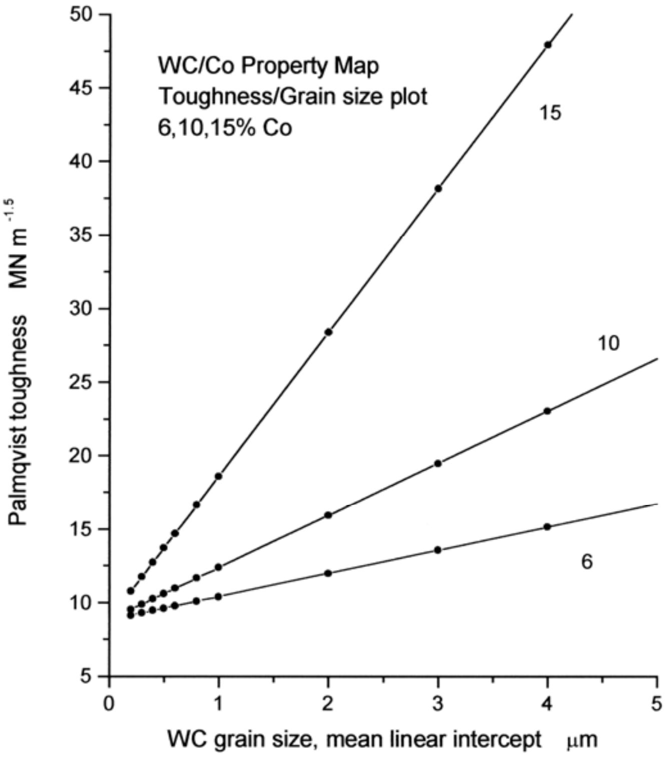

Figure 9 *- Property map showing fitted trends of Palmqvist toughness as a function of WC mean linear intercept size for different cobalt contents in WC/Co hardmetals. Note that the Palmqvist test is unsuited to measurements on materials containing more than 15 % Co.*

3. Microstructural preparation techniques

In this section, some of the general issues associated with preparing materials for microstructural evaluation are given, and supplemented by Annexes A and B which give detailed information on appropriate techniques for ceramics and hardmetals respectively.

3.1 Sampling

Microstructural investigations typically deal with very small areas (volumes) of material. There is often an implicit assumption that any one area selected for evaluation will be representative of the whole, but this is often not the case. The manufacturing process may well introduce spatial variations in the microstructure as a result of density variations (giving variations in porosity), grain orientation effects, or composition variations due to atmospheric interactions in processing (giving variations in phase type or size). It is important not to ignore the processing history of the material, and to select appropriately the positions of sections, and the areas within sections which are subsequently evaluated.

The procedure to be adopted often depends on the purpose of the investigation, and some examples are given in Table 5. In each case, the examined areas of each section will also need to be appropriately sampled, *i.e.* whether truly random positions are used, or whether a systematic set of positions is required in order to examine any trends. In the latter case it is important also to ensure that any apparent differences seen are statistically significant compared with the random variation of the microstructure from place to place.

Table 5 - Sampling procedures for preparing sections

Objective:	**General procedure:**
Quality assurance	Sampling procedure to be agreed with the customer in a manner relevant to the product
Bulk microstructure	Randomly selected section, images prepared remote from surfaces
Near surface effects	Prepare sections in a known relationship to surface e.g. normal to the surface, or parallel to the surface at a known depth
Atmosphere effects	As for near surface effects
Texture effects	Parallel or perpendicular to specific processing directions

3.2 Sectioning

Ceramics and hardmetals normally need to be sectioned using a diamond impregnated cutting disc (Annexes A and B). In order to minimise the depth of damage, it is worth performing this step in as controlled a manner as possible, *i.e.* to produce a flat surface with minimal damage. Techniques will vary, but thin slow-speed saws with controlled feed tend to give the best cut surfaces. The grit size should be no greater than D151 (classification contained within ISO 6106: *Abrasive products – Grain sizes of diamond or cubic boron nitride*). An alternative for hardmetals and some electrically conducting ceramics is electro-discharge machining (EDM), but subsequent polishing routines need to ensure removal of the EDM affected layer, which may be up to 0.5 mm deep.

3.3 Preparing a polished section

Normally the sampled piece needs to be mounted in a mounting medium (plastic or resin). Thermoset plastics are usually the best because they form a hard rigid mount, but are unsuited to weak or porous materials. The use of liquid resins which are subsequently cured offers the best option for weak or friable materials. Adding a vacuum impregnation step helps to fill open porosity in deliberately porous materials, and provides support to thin walls. However, all resin systems tend to shrink on curing, and perfect impregnation is almost impossible. To ensure traceability of the mounted sample:

Make sure the sample is identified by labelling or inscribing on the mount.

Polishing techniques are similar for both classes of material are involve the following series of steps:

flattening by coarse-grit diamond or silicon carbide grinding;
lapping or fine grinding by fine-grit diamond or silicon carbide;
polishing by a sequence of finer diamond grits;
optional final stage (*e.g.* relief polishing).

Different materials behave in different ways to these various steps, so there is no universal recipe for polishing. Some examples are given in Annex A and B. Often, with a new or unknown material it is necessary to make some trials and to modify existing procedures until acceptable results are obtained. For most laboratories, an important additional criterion is to achieve acceptable quality of surface finish in the minimum time. To do this it is important to minimise the amount of material which needs to be removed at each stage while still removing damage from previous stages. The rule of thumb is therefore:

Select laps and grits which minimise damage, and in particular, avoid heavy grinding with coarse grits at the start of the process.

It is important to minimise scratches in the final surface. The best outcome is often achieved through cleanliness, avoiding cross-contamination of laps. Unfortunately, scratching may reappear after etching, particularly in hardmetal materials (an example is given in Annex B), so it is worth spending the effort in polishing effectively, rather than just achieving a superficially scratch-free surface.

In some ceramic materials, such as alumina, grain pluck-out is a problem which can be difficult to avoid. For materials which are prone to this effect, adequate removal of damage from prior grinding and lapping stages is essential, since if damage persists, pluck-out seems to be made easier. For the polishing stages, hard napless polishing cloths generally perform better than soft cloths, since they are less compliant and present a more uniform pressure on the specimen.

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In contrast with this, if it is required to achieve differential polishing between phases, then soft polishing cloths are better than hard ones, since the greater compliance means that softer phases are preferentially removed. The hard grains thus stand proud and are more readily identified. The technique is commonly known as **relief polishing** (see Annex A for an example), but is done only in the final stages of polishing.

3.4 Etching techniques

The objective of etching is to produce topography of the otherwise featureless polished surface so that details of the microstructure, particularly grain boundaries and different phases, can be readily seen. There is a variety of etching techniques appropriate to ceramics and hardmetals, but an appropriate choice depends very much on the material and what needs to be revealed. As summarised in Table 6, etching can be avoided in some cases, but not in others. Annexes A and B give some example procedures.

Note: Microstructural preparation and etching techniques may require toxic or hazardous chemicals. Personnel must be adequately trained, and facilities and precautions as laid down in relevant safety guidelines in place at the laboratory concerned must be observed. In the UK these are the Health and Safety at Work Act and the Control of Substances Hazardous to Health (COSHH) regulations. Safe disposal of chemicals should also meet local regulations.

There are some alternatives to etching. One is interference film optical microscopy, which works well with coarser-grained hardmetals particularly where they contain cubic carbides, and with non-translucent ceramics. The technique involves evaporating or sputtering a uniform oxide film (*e.g.* Fe_xO_y) onto the polished surface (Quested and Bennett (1988)). Different interference colours are generated over each grain type as a result of different phase shifts at the film/material interface. Different phases are readily distinguished by colour rather than topography or reflectivity (the eye is very good at distinguishing colours but much less good with shades of grey).

Table 6 - When to etch

To reveal:	Using:	In ceramics:	In hardmetals:
Grain boundaries	Normal optical microscope	Yes	Yes
	Differential interference contrast microscopy	Use relief polishing	Use relief polishing
	SEM, secondary electron image	Yes	Yes
	SEM backscattered electron image	No	No
Second phases	Normal optical microscope	Usually (SiC/Si is an exception)	Sometimes, *e.g.* η-phase, γ-phases
	Differential interference contrast microscopy	Use relief polishing	Use relief polishing
	SEM secondary electron image	When atomic no. differences are small	Yes usually
	SEM backscattered image	No	No
Porosity	Any	No	No

4. Microstructural measurements

4.1 Parameters and relationships

4.1.1 Grain size

This most fundamental of parameters is one of the least trivial to understand and measure. All microstructures are three-dimensional assemblages of grains which either completely fill the available space, or partially fill it, the remaining space comprising continuous or isolated secondary phases. When a two-dimensional section is prepared for evaluation we see a slice through the microstructure which although representative of the three-dimensional structure, does not replicate it because different grains are sliced through at different heights. The lateral dimensions and areas of these slices are thus more widely spread than the original grain diameter. In this way a completely uniform structure of equal-sized regular space-filling shapes will have an apparent spread of sizes when evaluated in two dimensions.

The average value computed from measurements of individual grains will thus be rather different from the true three-dimensional grain size. In fact in stereological terms, it can be shown that the result of an apparent average grain size determination from a 2D section needs to be multiplied by about 1.7 to obtain the true 3D average grain diameter (assuming spheres, Hilliard (1968)).

Having said this, seldom is a 3D size reported. Since all measurements are made on 2D sections, results tend to be expressed as 2D-determined parameters. The most common of these is the arithmetic **mean linear intercept size**[3]. If randomly positioned lines are drawn across an image of a single-phase microstructure, this parameter can be computed by dividing the length of the lines by the number of intersections between the lines and grain boundaries (Heyn method). This technique ignores texture to the grain shape, and provides a simple and quick-to-make measure purely by counting. As an alternative to lines, circles can also be used provided that the radius of the circle is at least 10 times that of the typical grain size. An alternative is to count the number of grains appearing in a given area of microstructure, and from this compute the average grain area, and hence an equivalent circle diameter as a measure of grain size (Jefferies method). The techniques have been long established in standardised procedures, in particular, ASTM E112, which is aimed principally at metallic materials. More recently, CEN EN 623-3 has been prepared specifically for advanced technical ceramics. This uses the Heyn method with lines or circles, and has been tested for effectiveness and consistency in an international round robin (Dortmans *et al.* (1993)).

For hardmetals, only a comparative terminology of describing grain size is available as a formal standard (BS EN ISO 24499), but this is currently under development by ISO TC199/SC4 to include a section that includes and explains the linear intercept method to make it qualitative. As newer grades of hardmetal are developed with ever finer grain sizes, such a terminology is becoming confusing, and it is becoming necessary to adopt a more scientific approach, which is discussed in detail in *NPL Measurement Good Practice Guide No. 22: The metallographic measurement of hardmetal grain size*.

As mentioned above, linear intercept counting methods do not generally discount any discrete secondary phases which are counted along with the primary phase. If there is a continuous secondary phase, such as a glassy phase in a ceramic or a binder phase in a hardmetal, its presence is ignored. For small volume fractions of secondary phase, typically up to 5% by volume, this simplification has a negligible effect on the result, but above this level there is an increasing error introduced. EN 623-3 requires that for more than about 5 % by volume of secondary phases, the individual intercept lengths are measured, rather than the number of intercepts simply counted. The counting can be performed for each phase, and separate mean linear intercept distances can be computed.

Mean linear intercept size determination is not easy to operate in random orientations by computer-based automatic or semiautomatic image analysis for a various reasons, the principal ones being:

1. With the available programming utilities, it may not be possible to place randomly orientated lines across the image. If only horizontal line scans are possible, bias may

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[3] As distinct from geometric averaging.

creep into the results, especially if the material has any texture of grain shape.

2. It may not be possible to obtain adequate grain boundary contrast to ensure that the intersection is counted. The human eye/brain combination is excellent at identifying where grain boundaries are when they are poorly delineated by etching. Weak contrast, or discontinuous delineation, such as often occurs in scanning electron micrograph images, may be poorly detectable by software controlled counting routines. Human intervention may be needed to ensure that all boundaries are identifiable[4].

Because in computer image processing, the image is broken into discrete pixels of various intensities, images are characterised by pixel counting. This makes the counting of the areas of grains much easier. An alternative measure of grain size can be that based on apparent grain area, typically expressed as the mean circle diameter, or the average diameter of circles of equivalent area to that of the angular-shaped grain slices. The recent exploration of hardmetal microstructures using electron backscattered pattern detection (EBSP, Morrell and Roebuck (2007), Mingard *et al.* (2008)) provides a useful tool for categorically determining grain areas. Whichever method is used, care needs to be taken concerning the method of averaging. Whereas mean linear intercept size is purely a number-based average, the mean circle diameter can in principle be obtained either from the average of measured grain areas, or from the average of the individual circle diameters, or by counting the number of grains in a given area. These results may be slightly different. In addition, care needs to be taken to account properly for the finite width of grain boundaries.

4.1.2 Grain size distribution

A measure of the homogeneity of a microstructure is the width of the distribution of grain sizes. As with the mean linear intercept size, what is measured is really the distribution of the sizes of the random grain sections, so the distribution width tends to broaden compared with the true three-dimensional grain shape. It is usually found that grain size distributions measured using the linear intercept method, but recording the individual intercept lengths rather than the total line length, are approximately log-normally distributed. If the sizes are ranked in ascending order and assigned a probability, then a plot of lognormal probability against log(grain size) is often close to a straight line. In mathematical terms, the probability density function $f(x)$ is given by (Hahn and Shapiro (1967), Schückher (1968)):

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln(x)-\mu)^2}{2\sigma^2} \right]$$

where x is the grain size parameter, σ is a shape parameter *(i.e.* a measure of the distribution width) and μ is a scale parameter. This function is not readily manipulated to give a

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[4] A small proportion of missing grain boundaries in an image may not have a significant effect on an average grain size calculation, but there may be a shift in apparent grain size distribution.

cumulative distribution, and so output data are often more conveniently plotted on special probability paper (lognormal cumulative probability *vs.* log (grain size)). Most statistical data handling packages have algorithms to approximate the distribution. The slope of the plot is a measure of the distribution width and major departures from non-linearity indicate significant deviations from this distribution.

The same principle can be applied to measures of grain area, but again, care has to be employed when averaging the data, because number averages, linear averages and area averages will all lead to different results (Roebuck *et al.* (1999a)).

4.1.3 Phase volume fraction

In multiphase materials, stereological principles can be used to demonstrate that a random section through a randomly distributed two-phase material will show 2D area fractions of the two phases equal to the 3D volume fractions. Characterisation of a 2D slice should therefore give highly representative result of the true 3D fractions. The simplest way of doing this is to overlay an image of the microstructure with a square grid of points, and to count the proportion of the points which lie over each of the phases. This is amenable to manual counting, if a little tedious, but is equally applicable to automatic image analysis if the two phases can be produced with significantly different contrast levels so they can be readily distinguished. Distinctions based solely on shape, or on subtle contrast effects, are much more difficult to make by automatic techniques, and human intervention is usually necessary to identify each phase type. Counting can be done also on a phase area basis, with appropriate partitioning of grain boundary are between the phases.

For materials which contain significant levels of porosity, this too can be treated as a 'phase' for the purposes of measurement, and is the only convenient technique for determining volume fractions of total porosity in multiphase materials (see below).

The point counting method has been documented in a CEN standard for ceramics, and has been successfully evaluated through an international round robin (Bennett *et al. (*1997)). However, there are some limitations, especially for very small volume fractions where large areas must be evaluated in order to obtain statistically significant numbers of counts, generally at least 100. In addition, if one of the phases being counted is a continuous phase, *e.g.* a glassy phase, which is present in narrow layers between grains, correctly counting such a phase depends on correctly identifying its presence in association with the etched profiles of phase boundaries. It may be better to employ unetched samples and to rely purely on phase contrast.

4.1.4 Other measures

For simple microstructures, the above methods are usually sufficient, but there are a number of other measures that may occasionally be required:

1. **Anisotropy:** particularly in ceramic materials which have processed by wet methods,

or which contains whiskers or platelet reinforcements, the microstructure may possess a texture which gives directional properties. It is important to ensure that when characterising such microstructures the sections employed are in appropriate orientations relative to the axes of the texture, otherwise misleading results can be obtained.

2. **Grain aspect ratio:** the choice of raw materials and manufacturing conditions, particularly in ceramics, may result in a microstructure in which the grains are not equiaxed, but have a preferred shape, such as plates, or rods. There are a number of possible measures of grain shape, including area/perimeter ratios and longest/shortest axis ratios, but of course the act of sectioning may not reveal the true shape. Measured aspect ratios are thus on average usually less than the true aspect ratio unless there is strong grain alignment within the plane of the section.

3. **Grain roundness or angularity:** as distinct from grain aspect ratio, this parameter is a measure of the grain boundary length in relation to its area, *i.e.* a measure of whether grains have smooth or tortuous boundaries.

4. **Contiguity:** This is a measure of the degree to which phases are continuous throughout a multiphase structure. It is not widely used, but has particular relevance to both ceramics and hardmetals in which hard grains may have partial direct bonding affecting, for example, high temperature properties or electrical conductivity. Contiguity, C, can be expressed as the fraction of grain surface area A_{gg} which is in direct grain-grain contact:

$$C = \frac{A_{gg}}{A_{gc} + A_{gg}}$$

where A_{gc} is the grain surface area in contact with a secondary continuous phase. It can also be shown (Roebuck and Bennett (1986)) that there is a relationship between this parameter and the respective mean linear intercept grain sizes, d, and phase volume fractions, V:

$$d_c = \frac{1}{1-C} \cdot \frac{V_c}{V_g} \cdot d_g$$

where the subscripts c and g refer respectively to the continuous phase and the grain phase. The contiguity, which can have values between 0 (for completely isolated grains) to 1 (no secondary phase) can thus be readily computed from linear intercept and phase volume fraction determinations.

5. **Homogeneity:** this can be characterised as, for example, the consistency of grain size,

or the adequacy of dispersion of a second phase or porosity within a matrix. One possible measure of this is the distribution of distances between phase particles. A wide distribution would be indicative of a tendency for the second phase to 'clump'.

Many materials have near-surface microstructures which are different from those in the bulk of the item, often as a consequence of interactions with the environment during processing. In such cases it may be necessary to identify a spatial trend in microstructural parameters. This is best tackled by evaluating a series of sections parallel to the surface at known depths[5], so that in each section a statistically relevant number of grains can be employed (typically <100), whereas in a cross-section of the item, the microstructure may change laterally in too steep a manner to be effectively numerically characterised.

6. **Largest feature:** This is perhaps the most difficult of tasks. Strictly, it is impossible to guarantee that the metallographer has found the largest feature in the material. Only the largest feature in any section might be identified, and clearly this represents only a very limited volume of material (a slice of roughly one grain thickness). The larger the area evaluated, the larger the largest feature is likely to be, suggesting that a probabilistic approach could be taken. However, for most purposes, large features, such as pores or large grains, are relevant principally from the strength point-of-view, and if mechanically significant they are much more likely to be found in a strength test than by random sectioning. Fractography can then be used to locate, identify and dimension the fracture origin.

4.2 Preparing images for measurement

4.2.1 General requirements for characterisation techniques

For all the methods of analysis the issue of the extent of acquisition of data needs to be considered in terms of the statistical significance of any deductions that might be made. While no hard and fast rules can be given, recent Monte Carlo type assessments have shown that there is a law of diminishing returns when increasing the number of observations in order to improve the reliability of the average results. A balance needs to be struck between the total effort involved and confidence in the result. An added issue is 'sampling'. A single micrograph normally represents a small area of the prepared sample, and there is a risk that the structure within it may not be representative of the whole. Counting should thus be made over several micrographs to reduce the risk. However, if the homogeneity of product is to be investigated, micrographs from individual locations need to be analysed more intensively in order to deduce any differences between locations. Some recommendations are made concerning measurement statistics:

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[5] Measuring the thickness of the thin layer removed from the surface is not trivial. For small distances, perhaps the best method is to place an array of indentations in the test-piece, and to use their diminishing size as a measure of depth of removal by later polishing. For larger distances, a micrometer may be sufficiently accurate.

Mean linear intercept grain size (Dortmans *et al.* (1993)):

At least 100 grains in total should be counted in order to achieve a result accurate to about ±10%, but it will require about 400 grains in total to halve the uncertainty. At least three randomly selected areas should be chosen and analysed.

Pore or second phase volume fraction (Bennett *et al.* (1997)):

If a manual method is used such as grid intersection counting, the main difficulty comes with small volume fractions to ensure adequate counting statistics. If the manual method is used, at least 100 counts of grid intersections which overlie the phase of interest need to be obtained to achieve a result accurate to about ±10%, and this may require a number of micrographs. If automatic or semiautomatic image analysis is employed, then each individual micrograph is intensively evaluated, and fewer micrographs might be required than with the point counting method in order to achieve the same statistical confidence.

Making enough counts is very important in obtaining reproducible results from random sampling of a test-piece. If individual intercept sizes are measured, then a useful technique which ensures that reproducibility is obtained in any one circumstance is to compute ‘cumulative running average’ grain sizes or phase volume fractions. As measurements are made, they are cumulatively added and divided by the number so far. When the cumulative running average result is plotted against the number of results, initially there will be wild fluctuation, but this settles down with increasing number of results, *i.e.* converges with the true result for an infinite number of measurements (Roebuck *et al.* (1999c)). Counting can be halted when the average result is consistent within a given level of uncertainty (Figure 10).

4.2.2 Measuring average apparent grain size

For manual evaluation, the grain boundaries must be individually sufficiently visible to be counted as intersecting lines or circles drawn on micrographs. For image analysis techniques, the contrast at the boundary must be sufficiently great that the boundary can be distinguished from other topographic features. For both techniques, either a grain boundary etchant or a means of developing differential contrast between adjacent grains is required. Techniques depend very much on the material. Some general guidance and some examples are given in Annexes A and B. In single-phase oxide ceramics, heating to high temperature will encourage the formation of grooving at grain boundaries. In multiphase ceramics, acid or alkaline etching may preferentially remove a grain boundary phase, and this is adequate for low contiguity materials. In non-oxide ceramics and hardmetals, the emphasis is usually on specialised techniques for producing grain contrast. In some materials with crystallographically anisotropic hardness, relief polishing using a final polish on a soft lap, followed by Nomarksi interference microscopy can reveal grain boundaries quite well, but at some risk of grain edge rounding. Some general guidance is given in the Annexes. Some materials pose particular problems, and need specialised approaches.

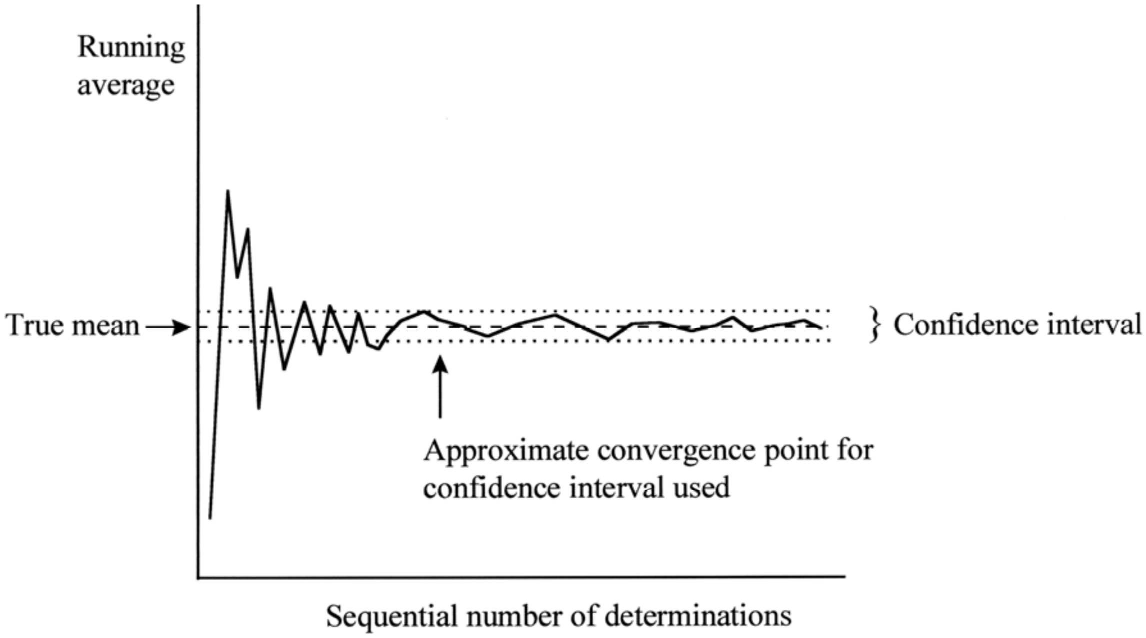


Figure 10 *- Running average technique to determine convergence of the mean result to a given level of confidence.*

4.2.3 Measuring grain size distribution

The requirements are basically the same as for determining an average grain size, except that images need to be taken at a sufficient magnification so that individual intercept lengths can be determined with sufficient accuracy. For the manual method using visual observations with a steel rule to make measurements from a micrograph, intercept lengths can usually be measured to ± 0.2 mm, so to achieve better than 10% accuracy, all grains should appear to be larger than 2 mm in the micrograph. In the case of image analysis using the line intercept method, grain boundary contrast needs to be sufficient, or to be capable of adequate enhancement, in order to clearly identify the centre of the boundary. For grain area determination by pixel counting, systematic errors can be involved if the boundary width if detection is based solely on intensity levels. Boundaries may need to be manually enhanced or demarcated in order to clearly and correctly position them.

4.2.4 Measuring phase volume fraction

4.2.4.1 General

Correctly assessing phase proportions relies on ensuring a contrast difference between the phases. Preferably this should be done on polished sections which have not been etched, or which are etched in ways which preferentially provide contrast but do not attack grain boundaries, avoiding topographic contrast which interferes with phase contrast. Each class of material and each observational technique require different approaches.

4.2.4.2 Optical image evaluation

If the image is to be evaluated optically, assuming the magnification required is adequate, the following pointers may be useful:

1. For materials of metallic appearance (*e.g.* hardmetals, some non-oxide ceramics), different phases may show sufficient contrast to be clearly visible on an as-polished surface. For example, in reaction-bonded silicon carbide, the free silicon phase always appears white compared with silicon carbide. It also relief polishes a little, depending on the polishing technique employed. In cases where contrast is insufficient, the deposition of a transparent dielectric film, e.g. lead oxide, can be used to provide colour contrast which is different on different phases dependent on the refractive index of the phase and the film thickness. The eye is particularly sensitive to colour, and provided that the film thickness can be made uniform over the required observation area, phases can in most cases be readily distinguished.

2. For ceramic materials which show optical translucence, contrast levels tend to be very poor, and are swamped by scattered internal reflections. In some cases, secondary low refractive index phases can be distinguished from high refractive index crystalline phases based solely on intensity, but in others it is not possible to prepare images which can be reliably analysed. Interference films (as for metallic appearance materials) may help, but colours tend to be weak. Normally, reflective metal coatings need to be applied to achieve useful visualisation of the microstructure, but different phases only become apparent if a suitable etching method has been sued. Reliance has to be placed on geometrical shape or size differences. Consequently, scanning electron microscopy is usually more useful.

4.2.4.3 Scanning electron microscopy

Particularly for finer grained materials (<2 µm), scanning electron microscopy is the practical method of producing images. In order to generate contrast between phases, backscattered electron images are preferred because the intensity is related to the average atomic number of the species in each phase. However, this technique tends to be relatively noisy compared with secondary electron images. In some instruments it is possible to achieve adequate contrast between phases by optimising the secondary electron image detection conditions. Care must be taken to ensure that the test-piece is flat and featureless, because topographic effects will otherwise dominate and confuse phase counting.

An alternative approach is to use mapping of the generated X-rays. This has some limitations because resolution is poorer than backscattered electron images, is typically 1 µm only, and is thus effective only at low magnifications (*i.e.* < 1000X). Other developing SEM based techniques appropriate mainly to electronic conductors include electron backscattered pattern analysis (EBSP, Venables and Harland (1973), Engler and Gottstein (1992), Wilkinson and Hirsch (1997)).

4.2.5 Measuring porosity

One of the major problems in determining porosity in ceramics, but not so much in hardmetals, is in distinguishing between true pores and holes formed by pluck-out of grains during polishing. Some materials are more prone to pluck-out than others, and alumina ceramics can be particularly troublesome in this respect. By using a scanning electron microscope to examine the size and shape of the holes in relation to those of the grains, it is often possible to get an indication of whether or not the apparent porosity is genuine from its shape. Most genuine pores have curved edges, while grain pluck-outs tend to be more angular in shape. In materials in which grain pluck-out is a problem, the general rule in surface preparation is to minimise damage produced by coarse grits, either by avoiding using them all together or by ensuring that subsequent finer grits remove enough material to eliminate previously induced damage, and to continue polishing until the apparent porosity level is at a minimum

Porosity measurements are conveniently made using photographs of a polished surface before any etching process is carried out. For translucent ceramics it is possible to improve contrast by applying a reflective coating, for example a sputtered gold film.

For single-phase impervious ceramics where the density of the phase is known, an alternative method of obtaining the true porosity level is by via apparent density measurement, for example by weighing in air and immersed in a liquid. If the material contains some open porosity, then both open and closed porosities can be determined. For multi-phase materials, or materials with phases of unknown density, there is clearly some error in this method.

4.2.6 Characterising continuous phases

Many ceramic and hardmetal materials contain continuous phases between clearly identifiable grains. In some cases these are obvious on microstructural examination, for example:

1. In a conventional 90% alumina ceramic which is fired to a relatively low temperature, all grains of alumina are surrounded by a clearly visible thick layer of structureless glassy phase.

2. In a 20% Co hardmetal, a substantial fraction of the hard phase grains such as tungsten carbide is surrounded by the continuous cobalt-based binder phase.

In materials where the proportion of species constituting a secondary phase is less than about 5%, this phase becomes difficult to identify except at very high magnification, or through use of transmission electron microscopy coupled with lattice imaging. The morphology of the phase depends on its compositional, and hence surface energy, relationship to the primary crystalline phases. In many cases, the phase collects primarily at three-grain junctions as a triangular-section pipe, but also as thin inter-grain films a few nm thick. In some materials where grain–grain bonding occurs during firing, these films break down to permit formation of direct grain bonding, for example in some coarser-grained alumina products and many hardmetals.

In terms of surface preparation, one of the major problems encountered is differential polishing of the phases, which tends to round the edges of the hard grains which stand proud of the secondary phase surface. This leads to contrast variations across grains which can confuse image analysis. The phenomenon can be minimised by using hard laps which preserve optimum surface flatness throughout the polishing cycle, and by minimising the use of soft compliant laps which tend to enhance relief polishing.

Quantifying the distribution of continuous phases is difficult, and really depends on the purpose for which the information is needed:

Phase volume fraction: Clear delineation of all continuous phase area is needed, but this is generally an optimistic requirement. With less than 10% by volume secondary phase, up to 50% of it could be in narrow regions between grains that simply cannot be counted in a statistically significant fashion.

Average inter-grain phase width: Some magnetic properties of hardmetals are considered to result from the binder phase domain size, which is related to the binder phase widths. High magnification is generally needed to usefully resolve widths, either using SEM or TEM. Assumptions have to be made concerning the angle of the section relative to the plane of the boundary.

It can be readily appreciated that meaningful data are very difficult to acquire and interpret.

4.3 Problem issues

4.3.1 Distributed grain sizes

There is increasing interest in both ceramic and hardmetal materials concerning the use of deliberately size distributed grain structures. The manufacturing route involves mixing precursor powders of very different sizes, and if correctly processed should result in a wide, possibily multimodal, distribution. Correctly detecting this distribution for quality assurance purposes remains something of a problem for the following reason. When a section is prepared, large and small grains are randomly sectioned. This means that the grain area seen is generally smaller than the maximum grain section, and further if a line intercept method is used to compute grain sizes, the lines on average do not cross the widest part of the section. The net consequence is a broadening of the apparent intercept size distribution compared with the true situation. Even if there are two apparently distinct sizes of grain visible to the naked eye, the acquired data plotted as a distribution may well appear as a single continuous smooth distribution. Much information is lost in firstly preparing the 2D section of the the 3D structure, and then in using 1D lines across the 2D surface. Determining distributions of 2D grain areas is likely to be more reliable than determining the distribution of line intercepts.

In addition, there is the issue of counting statistics. If the determination of grain sizes or volume fractions of coarse and fine grains is required, sufficient of each type must be counted in order that both are statistically representative. If the sizes are widely different, *e.g.* 20 μm grains surrounded by 1 μm grains, the statistics are improved by counting at both high and low magnification rather than at a single intermediate magnification. At least 100 grains of each size type must be counted in order that the results are representative of the sample as a whole, irrespective of the number of micrographs required to achieve this target. If the data can be acquired by image analysis rather than manual techniques, it may not be possible simply to separate the two visually apparent size fractions. Alternative measures of grain size may have to be used, such as grain area or equivalent circle diameter. The important aspect is to ensure that the counting statistics are sufficient to provide consistent answers.

4.3.2 Characterising whiskers and fibres

Determining the sizes or volume fractions in materials containing **continuous fibres** generally poses no problems, especially if the fibres have round cross-sections. Usually the fibre architecture is known, and sections can be prepared perpendicular to fibre directions in order to determine volume fractions. Fibre diameters are also readily computed, even if the section is considerably off-axis.

However, the situation concerning determining the **aspect ratio** of short fibres or whiskers in reinforced materials is much less straightforward. Fibre or whisker axes tend to be orientated according to the method of manufacture. In many cases they lie in planes perpendicular to the direction of application of pressure during processing, *e.g.* as result from sedimentation, layering processes, spraying processes or hot-pressing. If a section is prepared within this plane, then generally a fibre or whisker is seen as a longitudinal section, and its length and width can be determined. However, if the fibres or whiskers are more randomly orientated in three dimensions, many, if not most, will be sectioned across their narrow dimensions and their lengths will not be apparent in the sections. The apparent aspect ratios will be seriously under-estimated. Thouless *et al.* (1988) demonstrated the nature of the problem theoretically for a distribution of random length cylinders in random orientations when characterised by 2D sections. The topic has been discussed by Park *et al.* (1994) in relation to SiC whisker reinforced alumina. There appears to be no simple solution to achieving direct results from 2D sections because the matrix material cannot generally be removed to release the fibres or whiskers. The alternative approach is to characterise the fibres or whiskers before manufacturing the composite, and to assume that aspect rations are unchanged by subsequent processing.

4.3.3 Detecting extreme features

The volume of material effectively sampled by examining a cross-section is in practice rather small. If features are common and widely distributed, any random section will normally find such features, but at volume fractions of less than 0.1%, the chances of occasional large pores, large grains or inclusions being found on a single small section is somewhat remote. If the feature being sought is mechanically significant, it is probably best to use a mechanical test first and to identify the position of the extreme feature using fractography (Morrell (1999)). The fragments can then be reassembled, mounted in resin and sectioned appropriately in order to examine them in a systematic manner. This approach cannot always be justified, but it in many cases it will remove the needle-in-the-haystack problem.

4.3.4 Measures of anisotropy and homogeneity

4.3.4.1 Homogeneity

Most materials are intended to be homogeneous or to have deliberate microstructural gradients in particular regions. Local microstructural inhomogeneity can arise from inadequate precursor mixing processes or compaction, and can lead to inhomogeneity in grain sizes, orientations or phase proportions, leading to local variations in properties. Quantifying homogeneity on the scale of, say, 10 grains, is limited by the random nature of grain structures, but there are possibilities over longer distances. If n limited areas of a section are analysed for the total number features of interest, the individual values N_i will be distributed about a mean value $\overline{N}$ with a standard deviation σ given by (Gurland, 1968):

$$\sigma^2 = \frac{1}{n}\sum_{i=1}^{n}(N_i - \overline{N})$$

which is a measure of homogeneity from region to region. Clearly sufficient number of regions of sufficient size have to be evaluated to gain confidence in this result, which needs to be compared with the standard deviation for a purely random distribution. A particular case of interest for many of the newer materials is the homogeneity of distribution of reinforcing particles. One measure is the average distance between the centres of such particles exposed in a section. It can be shown (Gurland (1968)) that throughout a volume, this distance, λ_V, is related to the mean number of particles per unit volume, N_V, by:

$$\lambda_V = 0.554 N_V^{-1/2}$$

The equivalent case for particles in a plane (e.g. in a section), is given by:

$$\lambda_A = 0.500 N_A^{-1/2}$$

where N_A is the number of particles per unit area.

4.3.4.2 Mutual orientation effects

If the grains in a material have a natural elongated or plate-like habit, orientation effects can often be seen in products processed by directional methods, such as extrusion or slip casting provided that the subsequent firing and grain growth does not totally alter the structure. Quantification of grain size and shape can be achieved by using the line intercept method in specific process-related orientations, rather than the normal random orientations. It should be noted that true crystallographic orientation is usually not revealed by ordinary microstructural sectioning (*cf.* the situation with whiskers or fibres). In order to evaluate this aspect, more complex techniques are required, including:

- X-ray diffraction texture patterns (*e.g.* Sandlin et al. (1993))
- optical birefringence studies of thin sections viewed in transmitted polarised light microscopy (*e.g.* Clinton *et al.* (1986))
- electron channelling patterns (EBSP) in the SEM (*e.g.* Wilkinson and Hirsch (1997))

For the particular case of whisker orientation effects, Pezzotti *et al.* (1990) used a polar plot method proposed by Saltikov (1958), the basis of which is as follows. On a micrograph of a section prepared in a known relationship to a processing direction, a series of parallel lines are placed at a variable angle. The number of intersections of whiskers per unit length of line over the area of the micrograph is then determined as the set of lines are rotated, and plotted as a function of angle. Random orientation should produce a circular or near circular distribution, whereas mutual orientation gives a dumbbell shaped distribution. Using this method on sections of different orientations, Pezzotti *et al.* found that a hot isostatically pressed SiC whisker reinforced Si_3N_4 was had an effectively isotropic distribution. The method should also be applicable to grain shape analysis in anisotropic materials, such as extruded alumina.

Park *et al.* (1994) developed a method which requires prior knowledge of the length distribution of whiskers in the starting material. Assuming the whiskers survive processing into a ceramic body intact, the two dimensional length distribution seen on a plane at a given angle to a processing direction can be computed assuming a Gaussian distribution of whisker angle out from a processing plane. These theoretical results can be compared with those from evaluated two-dimensional sections at various angles to the processing plane. Using this technique they compared uniaxially hot-pressed and hot isostatically pressed SiC whisker reinforced aluminas with the theoretical distribution results, and determined the distribution parameters.

4.3.4.3 Minor phase dispersion

The simplest measure is the scatter of nearest neighbour distances between the centres of dispersed grains of a given type. A broad distribution, particularly with a tendency to show short distances approaching the phase grain size, indicates that there is some clumping of grains, rather than a uniform distribution. To undertake this, micrographs have to be prepared and analysed by identifying grain centres and measuring distances.

5. Bibliography

Bennett, E.G.; Dortmans, L.J.M.G.; Hendrix, M.; Morrell, R.; De With, G. (1997), "CEN/VAMAS Study of phase volume fraction measurement - A preliminary review of results", *Euroceramics IV*, 2111–4; see also Hendrix, M.; Bennett, E.G.; Morrell, R.; Dortmans, L.J.M.G.; De With, G., "CEN/VAMAS phase volume fraction round robin", *Brit. Ceram. Trans. J.*, 1998, **97**(6), 293–300.

Clinton, D.J.; Morrell, R.; McNamee, M. (1986), "Textures in high-alumina ceramics", *Br. Ceram. Trans. J.* **85**, 175–9.

Davidge, R.W.; Riley, F.L. (1995), "Grain-size dependence of the wear of alumina", *Wear*, **186-187**, 45-49.

Doi, H.; Fujiwara, Y.; Miyate, K.; Oosawara, K. (1970), "A systematic investigation of teh elastic moduli of WC/Co hardmetals", *Met. Trans. A,* **1**, 1417-25.

Dortmans, L.J.M.G.; Morrell, R.; De With, G. (1993), "Round robin on grain size measurement for advanced technical ceramics", *J. Eur. Ceram. Soc.* **12**(3), 205–13.

Engler, O.; Gottstein, G. (1992), "A new approach to texture research: local orientation determination with EBSP", *Steel Research*, **63**(9), 413-8.

Gee, M.G.; Gant, A.J.; Byrne, W.P.; Roebuck, B. (1999), "Abrasion and reciprocating wear of hardmetals and ceramics", NPL Report CMMT (A) 166, February 1999.

Gurland, J. (1968), "Spatial distribution of discrete particles", in *Quantitative microscopy*, edited by DeHoff, R.T.; Rhines, F.N., McGraw Hill Book Co., New York, 278–90.

Hahn, G J.; Shapiro, S.S., "Statistical models in engineering", John Wiley and Sons, New York, 1967.

Hilliard, J.E. (1968), Measurement of volume in volume" in *Quantitative microscopy*, edited by DeHoff, R.T.; Rhines, F.N., McGraw Hill Book Co., New York, 45-127.

Mari, D.; Bolognini, S.; Feusier, G.; Viatte, T.; Benoit, W. (1999), "Experimental strategy to study mechanical behaviour of hardmetals for cutting tools", *Int. J. Refr. Hard Mater.*, **17**, 209-25 (see also *Proc. In. Conf. Science of Hard Materials,* Lanzarote, Spain, 1998).

Mingard, K.P., Roebuck, B., Bennett, E.G., Gee, M.G., Nordenstrom, H., Sweetman, G., Chan, P. (2008), “Comparison of EBSD and conventional methods of grain size measurement of hardmetals”, submitted to *Proc. 9th Int. Conf. Science of Hard Materials*, Jamaica, March 2008.

Miranda-Martinez, M., Davidge, R.W., Riley, F.L. (1994), “Grain size effects on teh wet erosive wear of high-purity polycrystalline alumina”, *Wear*, **172**, 41-8.

Morrell, R. (1999). “Fractography of brittle materials”, *NPL Measurement Good Practice Guide No. 15.*

Morrell, R. (2002). “Determining elastic moduli of hardmetals”, *NPL Measurement Note* MATC (MN) 33.

Morrell, R., Roebuck, B. (2007), “Quantitative challenges in characterising the mechanical properties of hard materials”, *J. Metrological Soc. India*, **22**(3), 153-6.

Park, Hyoung-Yoon; Kim, Hyoun-Ee; Kim, Doh-Yeon (1994), “Evaluation of whisker alignment in axisymmetric SiC_w-reinforced Al_2O_3 composite materials”, *J. Amer. Ceram. Soc.*, **77**(11), 2828–32.

Pezzotti, G.; Tanaka, I.; Okamoto, T. (1990), “Si_3N_4/SiC-whisker composites without sintering aids: I, quantitative evaluation of microstructure”, *J. Amer. Ceram. Soc.,* **73**(10), 3033-8.

Quested, P.N.; Bennett, E.G. (1988), “Interference film microscopy”, *Microscopy and Analysis*, May 1988.

Roebuck, B.; Cottenden, A.H.; Almond, E.A. (1984), “The influence of composition, phase transformation and varying FCC/HCP phase contents on the properties of dilute Co-W-C alloys”, *Mater. Sci Eng.*, **66**, 179-84.

Roebuck, B.; Bennett, E.G. (1986), “Phase size distribution in WC/Co hardmetal”, *Metallography*, **19**, 27-47.

Roebuck, B. (1995), “Terminology, testing, properties, imaging and models for fine-grained hardmetals”, *Int. J Refr. Hard mater.*, **13**, 265-79.

Roebuck, B.; Gee, M.G.; Morrell, R. (1996) “Developments in testing and mechanical properties of hard materials”, *Powder Metall*, **39**(3), 213-8.

Roebuck, B. (1996a), “Bend strength tests for hardmetals, Part 1”, *VAMAS Tech. Rep. 22-1,* June 1996, National Physical Laboratory.

Roebuck, B. (1996b), “Bend strength tests for hardmetals, Part 2”, *VAMAS Tech. Rep. 22-2,* June 1996, National Physical Laboratory.

Roebuck, B. (1997a), “Effect of test-piece geometry on flexural strength of representative hardmetals and cermets”, *Proc. 14th Plansee Seminar,* May 1997, Reutte, Austria, pp 352-65.

Roebuck, B. (1999), “Magnetic coercivity measurements for WC/Co hardmetals”, *NPL Measurement Note CMMT (MN) 042*, April 1999.

Roebuck, B.; McCormick, N.J.; Day, A.; Bennett, E.G. (1999a), “Measurement of WC grain size distribution”, *NPL Report CMMT (A) 141,* January 1999.

Roebuck, B.; Bennett, E.G.; Byrne, W.P.; Gee, M.G. (1999b), “Characterisation of baseline hardmetals using property maps”, *NPL Report CMMT (A) 172*, April 1999.

Roebuck, B.; Bennett, E.G.; Dickson, A. (1999c), “The measurement of uncertainty in grain size distribution – Interlaboratory exercise I – Reference images”, *NPL report CMMT (A) 154,* May 1999.

Roebuck, B.; Bennett, E.G.; Lay, L.A.; Morrell, R (1999d), “Palmqvist toughness for hard and brittle materials”, *NPL Measurement Good Practice Guide No.9.*

Roebuck, B., Gee, M.G., Morrell, R. (2001), “Hardmetals – microstructural design, testing and property maps”, *Proc. 15th Plansee Seminar*, Reutte, Austria, 29 May-1 June 2001, edited by Kneringer, G., Rödhammer, P., Wildner, H., Vol. 4, pp245-66.

.

Roebuck, B. and Bennett, E.G. (2004), “Assessment of toughness tests for hardmetals”, *Proc. PM 2004, World Conference on PM*, Vienna, Austria, edited by Danniger, H., Ratzi, R., EPMA, Shrewsbury, UK, 2004, pp .

Roebuck, B. (2004a), “Extrapolating hardness-structure property maps in WC/Co hardmetals” *Proc. 8th Int. Conf. Science of Hard Materials*, San Juan, Puerto Rico, November 2004, and *Int. J. Ref. Metals and Hard Mater.* **24** 101-8.

Roebuck, B, Bennett, E.G. (2005), “Hardmetal toughness tests”, VAMAS Report No. 48, NPL, March 2005.

Saltikov, S.A. (1958), *Stereometric Metallography*, Metallurgizdat, USSR, 1958.

Sandlin, M.S.; Lee, F.; Bowman, K.J. (1993), “Simple geometric model for assessing whisker orientation in axisymmetric SiC whisker reinforced composite”, *J. Amer. Ceram. Soc.*, **76**(6), 1522-8.

Schückher, F. (1968), “Grain size”, in *Quantitative microscopy*, edited by DeHoff, R.T.; Rhines, F.N., McGraw Hill Book Co., New York, 201-265.

Sigl, L.S., Fischmeister, H.F. (1988), “On the fracture toughness of cemented carbide”, *Acta Metall.*, **36**(4), 887-97.

Thouless, M.D.; Dalgleish, B.J.; Evans, A.G. (1988), “Determining the shape of cylindrical second phases by two-dimensional sectioning”, *J. Mater. Sci. Eng.*, **A103**, 57-68.

Twigg, P.C.; Alexandre, G.; Davidge, R.W.; Riley, F.L.; Roberts, S.G. (1997), “The wet erosive wear of polycrystalline alumina with silicon carbide particles inclusions”, *Euroceramics V, Vol. 3, Key Eng. Mater.*, **132-6**, 1520-23

Venables, J.A.; Harland, C.J. (1973), “Electron backscatter patterns”, *Phil. Mag.*, **27**, 1193-1200.

Warshaw, S.I.; Norton, F.H. (1962), “Deformation behaviour of polycrystalline alumina”, *J. Amer. Ceram. Soc.*, **45**(10), 479-86.

Wilkinson, A.J.; Hirsch, P.B. (1997), “Electron diffraction based techniques in the scanning electron microscope, *Micron*, **28**(4), 279-308.

Annex A: Preparation of ceramics for microstructural measurement

A.1 Sectioning

A specimen having a surface area of about one square centimetre is usually convenient for embedding and polishing. If the sample of material to be tested is much larger than this, it is necessary to use a cutting machine having a bonded diamond wheel to prepare the specimen. For exceptionally hard and tough ceramics, such as cubic boron nitride, a smaller specimen should be used to achieve practical subsequent polishing times. The thickness should be at least 3 mm so that it can be effectively mounted.

Since certain ceramic fabrication processes lead to anisotropic microstructures, it is prudent to make a record of the orientation of the surface to be polished in relation to the original sample shape.

A.2 Embedding

Before polishing it is usually convenient to embed the specimen in a mount to improve handleability, either by using cold-setting resins or by hot mounting in bakelite or other thermoplastic material using a die and mounting press. The latter method has the advantage of providing a mount of regular shape, having flat and parallel faces, but this can also be achieved with resin mounts by machining the faces flat and parallel in a lathe before grinding and polishing. In either case the identity of the specimen should be inscribed on the mount.

Since it may be necessary to remove the ceramic from the mount after polishing in order to etch it, care should be taken to place an identification on the specimen before embedding. The mount can usually be cut off using a hacksaw. If a transparent acrylic resin is used for mounting, it can later be removed by heating in a furnace at about 650 °C provided that suitable fume entrapment facilities are available. This is convenient for oxide ceramics which are to be thermally etched, but inappropriate for non-oxides which are prone to oxidation.

A.3 Preparing a flat surface

The aim in surface preparation is to produce a flat and scratch-free surface which is truly representative of the material. This is accomplished by a sequence of grinding and polishing steps using a series of diminishing grit sizes until an acceptable finish is obtained. A common problem in the preparation of polished ceramic surfaces is that the early stages can cause sub-surface damage, so that tear-out occurs later. It may then be difficult to distinguish between tear-out and porosity. Care is therefore needed in selecting a procedure which will minimise such effects.

The first step is to obtain a planar surface. If an as-received surface is being prepared, the outer zone should be removed, since it may not be representative of the bulk of the material, having been exposed to the atmosphere during sintering. Planar grinding may be carried out using water-cooled bonded diamond discs, or a slurry of loose diamond abrasive on a platen. The former method is quicker, but is more likely to produce sub-surface damage. The use of loose abrasive such as 30 μm diamond on a shock-absorbing platen (for example tin/plastic composite) helps to prevent sub-surface damage and is therefore preferable.

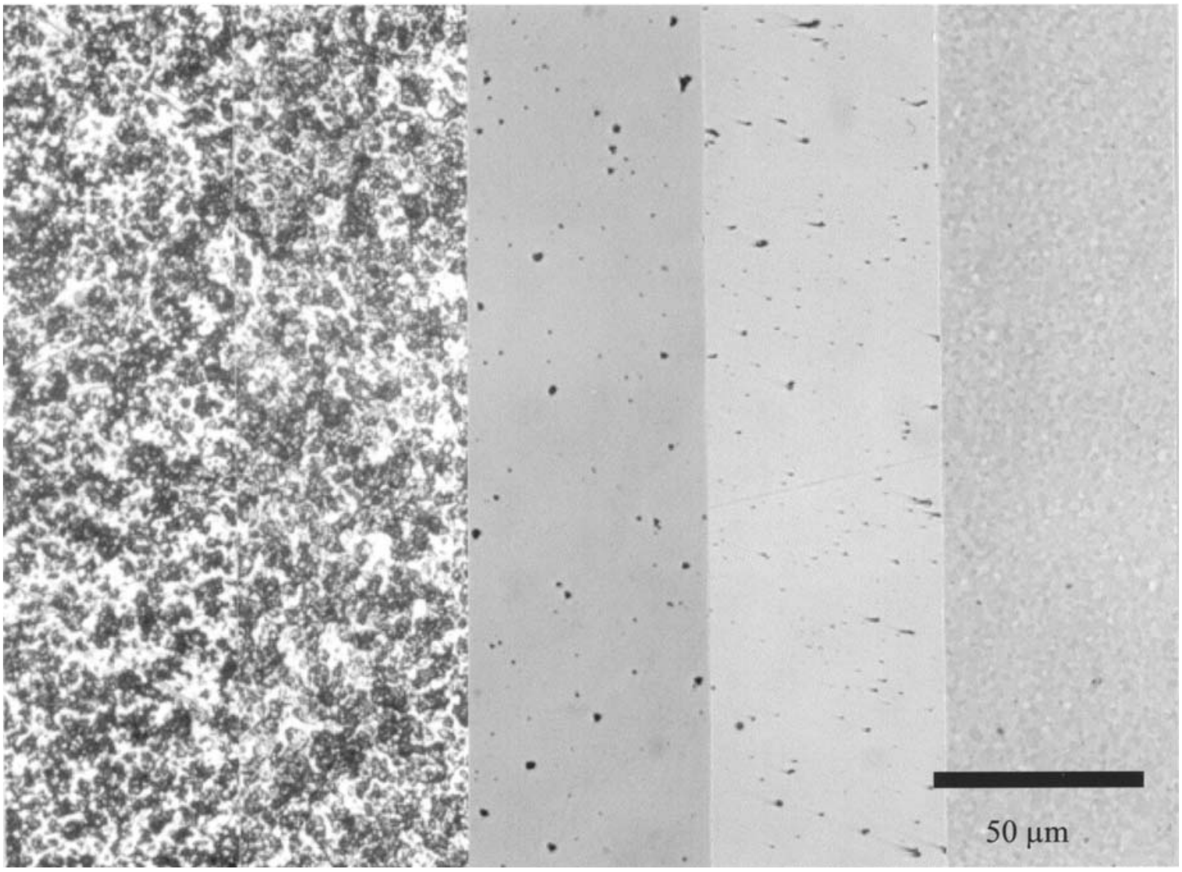
A.4 Polishing

After grinding to form a planar surface, polishing is carried out using a series of increasingly fine diamond abrasives on suitable cloths. A sequence of 30 μm, 6 μm, 1 μm and 1/4 μm diamond gives good results with most ceramics. It is generally accepted that the thickness of the layer to be removed by each abrasive size should be at least half the diameter of the grit used in the preceding step. It is not possible to give guidance on loads to be applied, but excessive loads should be avoided. The depth of removal of material can be monitored by measuring the diagonal size of a Vickers hardness indentation before and after a polishing stage; the depth removed is about one seventh of the reduction in the mean diagonal length.

A lap such as a tin/plastic composite can be used for the first stage, and napless cloths are suitable for the other stages. The use of napped cloths is not advisable for polishing ceramics, since they can cause pluck-out, and unwanted relief polishing. A final chemical polishing stage using alkaline colloidal silica on a napless cloth gives excellent results with many ceramics. The different stages in polishing of a high-purity alumina bioceramic are shown in Figure A.1.

In some ceramics the structure can be revealed by relief polishing, which should be done as a final stage using a napped cloth. The relief effect is produced by differences in wear resistance between different phases, or between different crystallographic orientations of a single phase. Figure A.2 shows an aluminium nitride in which relief polishing has been used to reveal individual grains.

An optical microscope should be used to monitor the progress of polishing, continuing until there is no further change in appearance. A stable appearance indicates that any pits observed are genuine porosity, rather than pluck-out caused by the polishing procedure (Figure A.3)



30 *µm* 6 *µm* 1 *µm* ¼ *µm* *final*

Figure A.1 - *Stages in polishing an alumina bioceramic, left to right, diamond, the final stage also having been given a final alkaline colloidal silica polish to provide slight relief.*

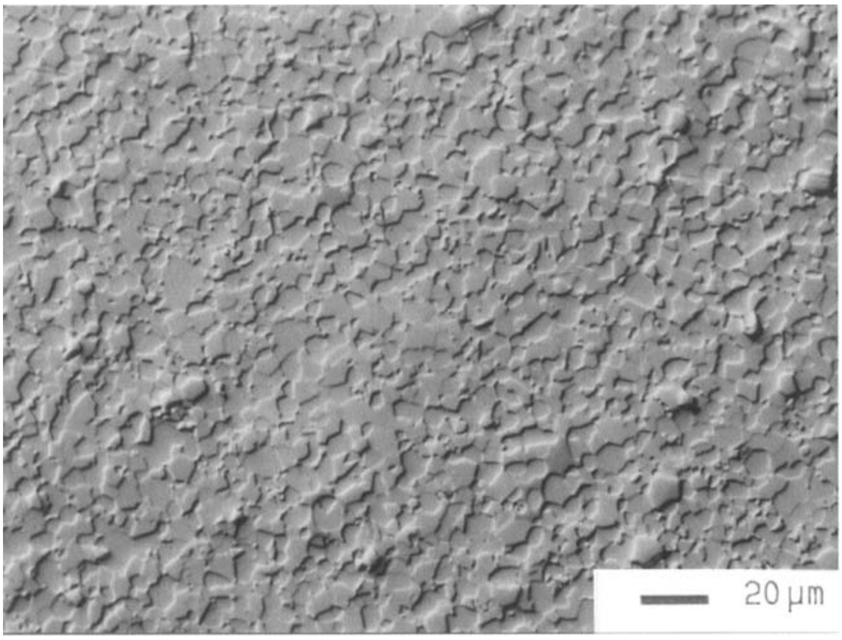


Figure A.2 - *Microstructure of an aluminium nitride produced by relief polishing.*

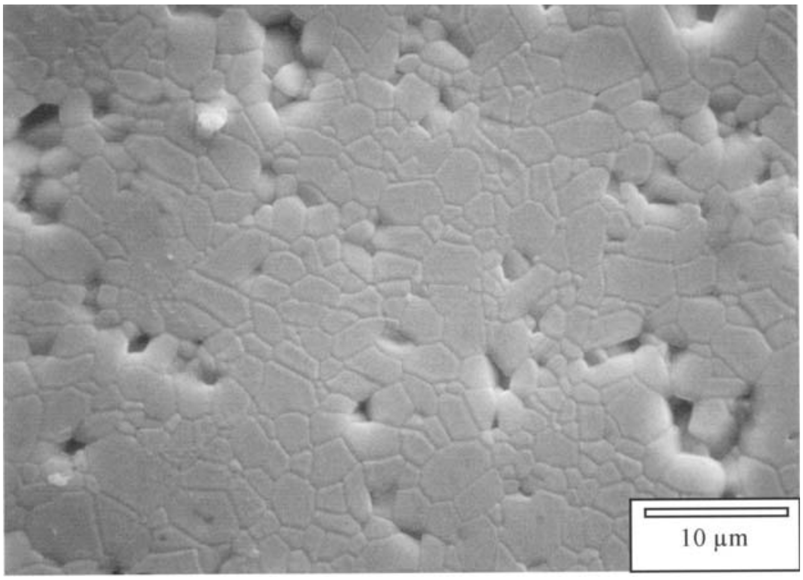


Figure A.3 *- High-purity fine-grained alumina suffering from grain pluck-out in polishing before thermal etching at 1410 °C for 10 minutes. Not the grain-shaped 'pores'.*

A.5 Etching

A.5.1 General

Unless relief polishing is effective, it is usually necessary to carry out an etching procedure to reveal grain boundaries before the true microstructure is visible. Etching methods vary from one type of ceramic to another. With an unknown material some experimentation is often required. There are two basic approaches, 'thermal etching' and chemical etching, both having wide application, but some materials need more specialised approaches, such as fluorine plasma etching (*e.g.* silicon nitrides) or electrolytic etching (*e.g.* boron carbides).

In 'thermal etching', which involves heating the polished test sample to high temperatures, grooving occurs where grain boundaries intersect the polished surface, and some filling of residual scratches across grain surfaces can advantageously also occur. Thermal etching is widely useful for oxide ceramics because the treatment can be carried out in air in a simple small furnace. Although in principle it can be applied to non-oxides as well, they require a vacuum furnace or a controlled atmosphere furnace with a low partial pressure of oxygen to suppress oxidation. It is therefore less widely reported for non-oxides, and chemical etching is more commonly used for such materials.

Chemical etching is used to attack one or more phases preferentially and thus produce contrast. Typically, continuous secondary phases can be revealed by this process, an example being the use of hydrofluoric acid to reveal continuous silicate phases. However, the directly bonded boundaries between major phase grains usually cannot be revealed because many ceramics are very resistant to attack by commonly available chemicals. Methods of causing severe attack are often needed to produce differential etching rates between grains (*e.g.* hot concentrated orthophosphoric acid on high-purity alumina), but such methods are quite difficult to control. A further disadvantage of chemical etching in comparison with thermal etching is that it tends to cause the reappearance of scratches, because the sites of damage are more actively attacked by the etchants.

The literature on etching procedures is widely scattered, but an NPL/Institute of Ceramics monograph (reference A.1) summarises some of the more appropriate approaches. A group at the Max Planck Institute in Stuttgart has produced a series of articles giving comprehensive guidance on the ceramographic preparation and etching of different classes of ceramic [A.2-A.11]. Brief details of procedures are given in the following sections.

A.5.2 Oxide ceramics

Thermal etching has been used for a variety of oxide ceramics, including aluminas, zirconias, and zirconia-toughened aluminas. It simply involves heating the polished sample in a furnace, commonly at 150 to 200 °C below the sintering temperature. Grain boundaries become grooved by surface energy driven diffusion, and any scratches are partly filled in. The main risk in thermal etching is that the microstructure will be modified, either by grain growth, by reactions between phases, or by decomposition of the phases present. For this reason the lowest temperature giving the desired effect should be used, and a short exposure time interval such as 15 minutes. Figure A.4 shows a 99.9% alumina bioceramic given a short, relatively low temperature thermal etch which reveals the grain boundary structure sufficiently adequately for SEM observation. Figure A.5 shows the appearance of a similar material over-etched by a prolonged treatment at higher temperature. Boundaries are heavily grooved, and there are many etch furrows revealed on grain surfaces. Such an image is inappropriate for quantitative work because of large variations in contrast, the potential disappearance of smaller grains, or even surface grain growth.

For general-purpose alumina ceramics, temperatures in the range 1250 to 1500 °C have been used, the higher values being used for the most pure compositions [A.9]. A difficulty that can arise with materials containing glassy phases is that this phase melts and can crawl across the polished surface of the alumina grains, leaving a rather untidy appearance. For zirconia-toughened aluminas, treatment at 1400 to 1500 °C is often satisfactory. Figure A.6 shows the result of heating at 1500 °C for 15 minutes.

For zirconia ceramics, the temperature required is determined by the composition and concentration of the additives. Temperatures of 1300 - 1500 °C have been used [A.4]. Figure A.7 shows a tetragonal zirconia polycrystal (TZP) heated at 1360 °C for 60 minutes. With this type of material sintered at low temperatures, care must be taken to ensure that thermal etching does not alter the apparent microstructure. As a guideline, the thermal etching temperature should be at least 100 °C, preferably more than 150 °C below the original firing temperature. Figure A.8 shows a more traditional cubic zirconia product containing a glassy phase which does not need thermal etching to reveal grain shapes.

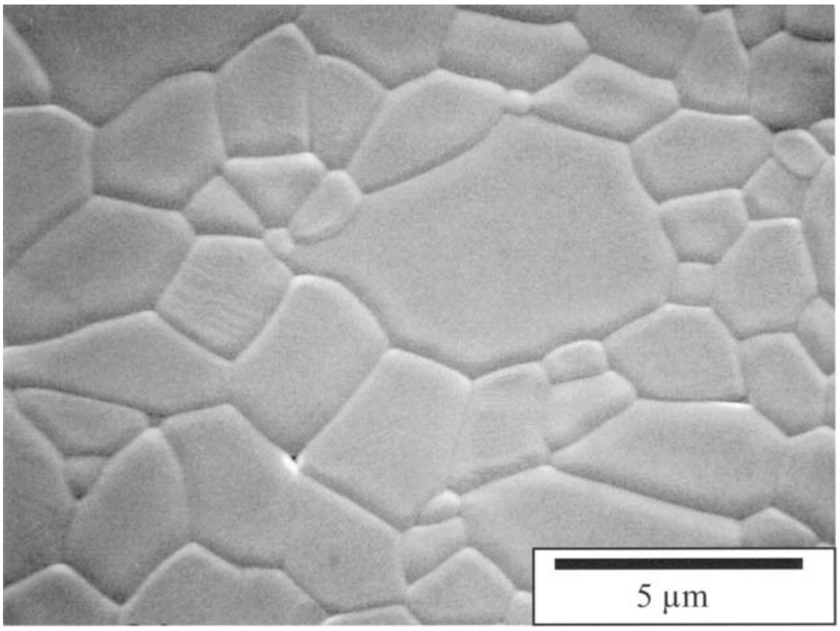


Figure A.4 *- Microstructure of a high-purity alumina used for biomedical purposes revealed by a thermal etch at 1410 °C for 10 min.*

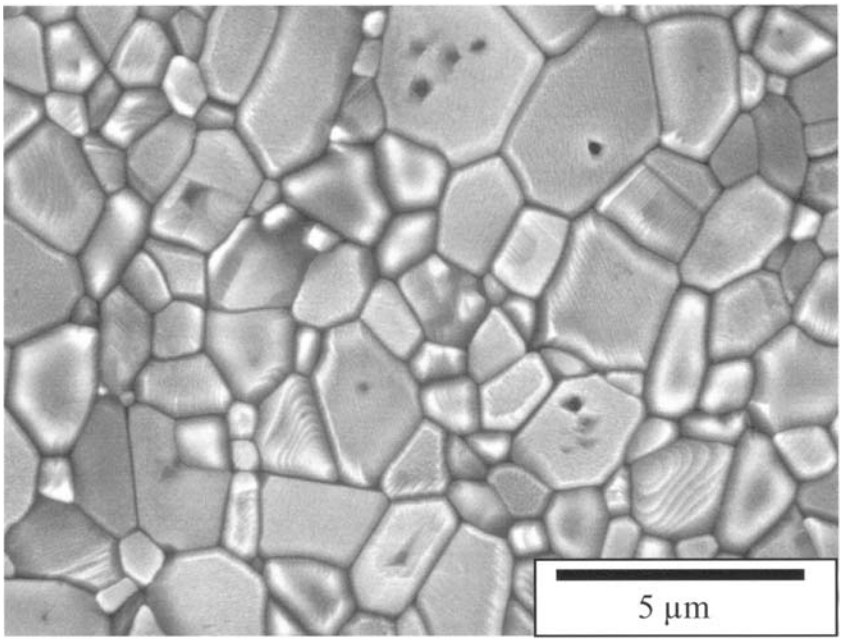


Figure A5 *- Microstructure of a similar alumina to that in Figure A4 revealed by excessive thermal etching at 1500 °C for 2 h.*

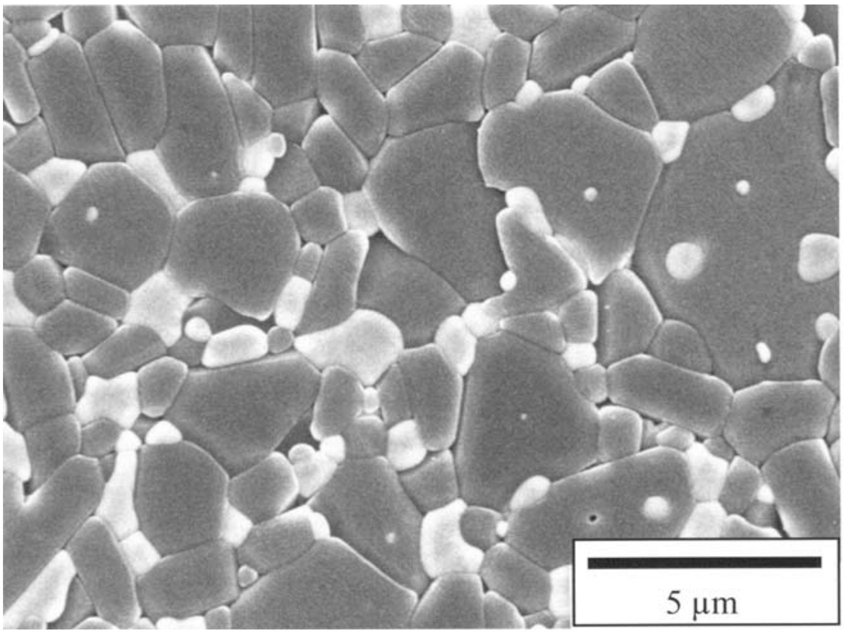


Figure A.6 *- Microstructure of an alumina/zirconia cutting tool material revealed by thermal etching at 1500 °C for 15 min.*

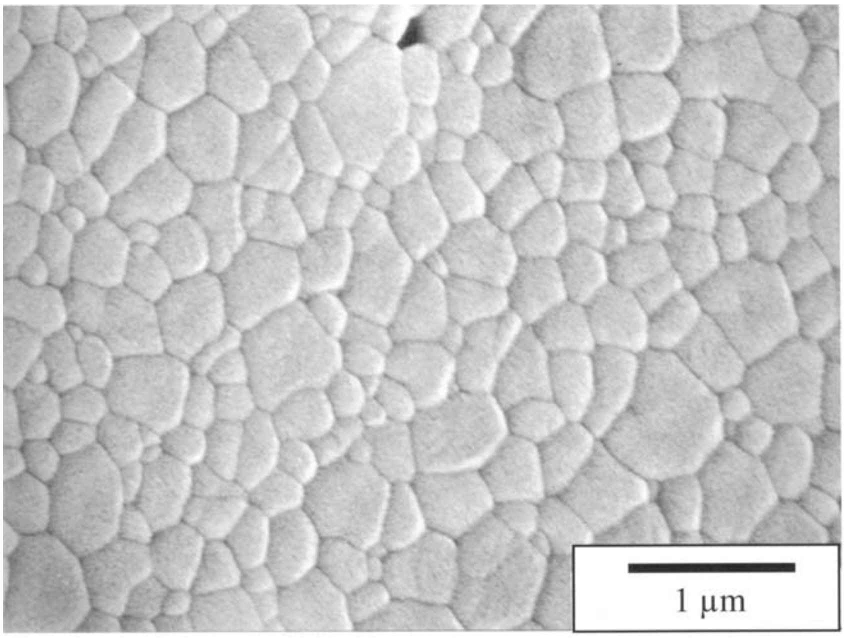


Figure A.7 *- Microstructure of an ytttria partially stabilised zirconia (Y-TZP) material revealed by thermal etching at 1380 °C for 1 h.*

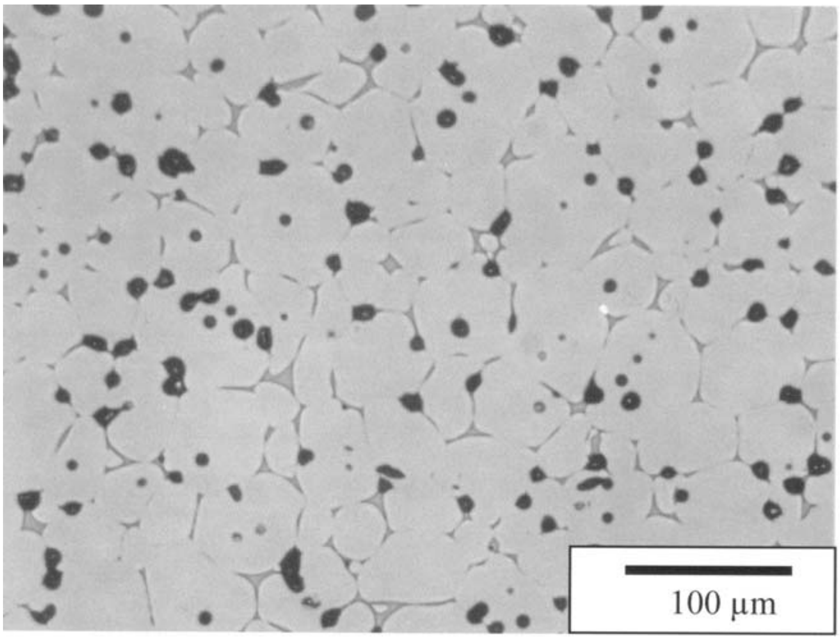


Figure A.8 *- Microstructure of refractory cubic zirconia material where grain boundaries can be inferred without thermal etching from the distribution of secondary glassy phase.*

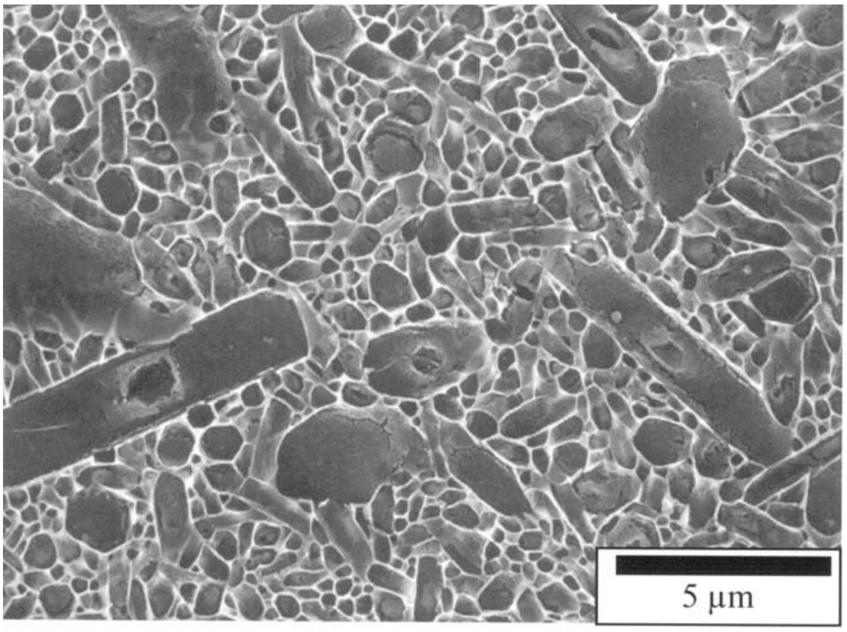


Figure A.9 *- Microstructure of sintered silicon nitride material revealed in the SEM by plasma etching. Note that the contrast is produced by the silicon nitride phase being depressed relative to the grain boundary phases.*

A.5.3 Non-oxide ceramics

For silicon nitride and sialon ceramics the most convenient, repeatable and effective method for revealing grain boundaries is by plasma etching [A.6, A.11, A.12]. The etchant gas used is carbon tetrafluoride containing 5 % oxygen. The gas is decomposed in the plasma to form fluorine-containing species which react with any silicon compound to form gaseous silicon tetrafluoride, which is removed. A typical plasma etching treatment involves warming the reaction chamber using a nitrogen plasma for about 10 minutes, and then admitting the etchant gas and energising the plasma for about 40 seconds using a power level of 150 W. Figure A.9 shows the appearance of a plasma etched silicon nitride.

A similar plasma etching process using carbon tetrafluoride containing 7.8% oxygen has been used for fine-grained silicon carbide ceramics [A.13]. A variety of other methods have been used for silicon carbides [A.3, A.14], including Murakami's reagent, molten salts and electrolytic methods. Murakami's reagent and its modified forms are aqueous solutions containing potassium hexacyanoferrate (III) and sodium hydroxide. A typical etching process involves immersing in a boiling solution of 3 g NaOH and 30 g $K_3Fe(CN)_6$ in 100 ml water for 15 - 20 minutes. The time required depends on the sintering additives and grain sizes.

For boron carbide, electrolytic etching in 1% KOH solution has been used to reveal grain boundaries [A.8]. The conditions used were voltage: 30 - 60 V; current: 3 A/cm^2; cathode: V2A steel; time: 30 - 60 s.

A.6 References

A.1 Clinton, D.J., *A guide to the polishing and etching of technical and engineering ceramics*, Institute of Ceramics, Stoke-on-Trent, UK, 1987.

A.2 Carle, V.; Schäfer, U.; Täffner, U.; *et al.*, "Ceramography of high performance ceramics. Part I: Ceramic etching", *Pract. Metallogr.*, 1991, **28**[7], 359-377.

A.3 Carle, V.; Schäfer, U.; Täffner, U.; *et al.*, "Ceramography of high performance ceramics. Part II: Silicon cabide (SiC)", *Pract. Metallogr.,* 1991, **28**[8], 420-34.

A.4 Schäfer, U.; Schubert, H.; Carle, V.; *et al.*, "Ceramography of high performance ceramics. Part III: Zirconia (ZrO_2)", *Pract. Metallogr.*, 1991, **28**[9], 468-83.

A.5 Predel, F.; Buzin, J.P.; Carle, V.; *et al.*, "Ceramography of high performance ceramics - Part IV: Aluminium nitride (AlN)", *Pract. Metallogr.,* 1991, **28**[10], 542-52.

A.6 Täffner, U.; Carle, V.; Schäfer, U.; *et al.*, "Ceramography of high performance ceramics - Part V: Silicon nitride (Si_3N_4)", *Pract. Metallogr.*, 1991, **28**[11], 592-610.

A.7 Schäfer, U.; Jäger, H., Carle, V.; *et al.*, "Ceramography of high performance ceramics - Part VI: Superconductors", *Pract. Metallogr.*, 1991, **28**[12], 633-48.

A.8 Predel, F.; Telle, R.; Carle, V.; *et al.*, "Ceramography of high performance ceramics. Part VII: Boron carbide (B_4C)", *Pract. Metallogr.,* 1994, **31**[5], 218-33.

A.9 Carle, V.; Trippel, B.; Täffner, U.; *et al.*, "Ceramography of high performance ceramics - Part VIII: Alumina (Al_2O_3)", *Pract. Metallogr.,* 1994, **31**[5], 218-33.

A.10 Telle, R.; Carle, V.; Predel, F.; *et al.*, "Ceramography of high performance ceramics - Part IX: Pores and chips", *Pract. Metallogr.,* 1995, **32**[9], 440-66.

A.11 Täffner, U.; Hoffmann, M.; Krämer, M., "A comparison of different physical-chemical methods of etching for silicon nitride ceramics", *Pract. Metallogr.* 1990, **27**[8], 385-90.

A.12 Chatfield, C.; Norstrom, H.; "Plasma etching of sialon", *J. Am. Ceram. Soc.*, 1983, **66**[9], C168.

A.13 Kim, Y.-W.; *et al.*, "Grain growth and fracture toughness of fine-grained silicon carbide ceramics", *J. Am. Ceram. Soc.*, 1995, **78**[11], 3145-48.

A.14 Cook, S.G.; *et al.*, "Etching and microstructure of engineering ceramics". *Mater. Charact.,* 1995, **34**, 1-8.

Annex B: Preparation of hardmetals for microstructural measurement

NOTE: A new revision of ISO 4499 for harmetal microstructural measurements is in preparation, based on previous work summarised in ASTM standards and some of the work described in this *Good Practice Guide* (B.1 – B.3).

B.1 Sectioning

Since cemented carbides are frequently in the form of small pieces, it is often possible to prepare and examine the whole cross section. When a sample is too large for this, it should be sectioned using a diamond cut-off wheel so that a representative area can be examined. Diamond cutting wheel or electro-discharge machining is commonly used, although the latter may leave a surprisingly large depth of damage, and typically 0.3 - 0.5 mm may need to be removed subsequently.

B.2 Embedding

As with ceramics (Annex A), where possible, specimens should be embedded, either by using cold-setting resins or by hot mounting, to facilitate polishing with minimal rounding of the edges.

B.3 Preparing a flat surface

The first step is to remove an adequate amount of surface skin material (typically about 1 mm) or damage region from cutting (typically 0.1 – 0.5 mm) and to prepare a planar surface. Planar grinding may be carried out using water-cooled bonded diamond discs, or a slurry of loose diamond abrasive on a platen. The former method is more rapid. A typical sequence of grit sizes might be 180, 65 and 20 μm. Skin removal can be achieved quickly starting with 180 μm grit size, the damage from this being removed by smaller grit sizes in sequence. If no skin removal is needed, the process can often start with a 65 or 40 μm grit size. In both cases the residual grinding grooves can be removed typically by using finer diamond grades in resin-bonded wheels.

B.4 Polishing

After grinding to form a planar surface, polishing is carried out using a series of progressively finer diamond abrasives. The main aims are to avoid pluck-out of the hard phase, to avoid preferential polishing of the binder phase, and to reveal the true porosity level, which is often very small. Excessive loads on the sample should be avoided.

The methods adopted in any laboratory will depend on the equipment available. Automatic polishing has advantages if large numbers of samples are being prepared, whereas semi-automatic polishing is more flexible and convenient for small numbers of samples.

For semi-automatic polishing, a sequence of 30 µm, 6 µm and 1 µm diamond is suitable. Napless cloths or other proprietary media are suitable. A final polish with 1 µm diamond on a napped cloth helps to remove scratches, and gives a surface which is satisfactory for optical microscopy. A further polishing stage using ¼ µm diamond on a napped cloth may be required if the specimen is to be examined in a SEM at high magnification. Figure B.1 shows the effect of inadequate polishing revealed later by etching (see b.6), with residual grooves across each grain. Use of such an image in automatic image analysis could lead to significant errors in computed phase volume fractions or grain sizes.

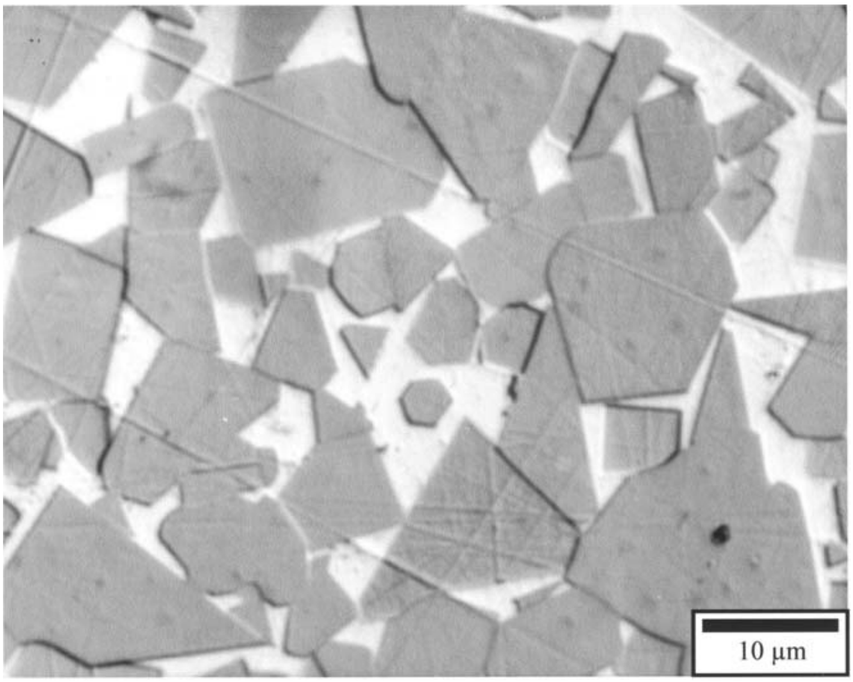


Figure B.1 *– A coarse-grained hardmetal with an inadequate polish. The effects of coarse grinding have not been entirely removed, and are revealed after etching in this Nomarski interference micrograph.*

B.5 Measuring porosity and uncombined carbon

Most hardmetals contain negligible levels of porosity, but inspections are often necessary for quality assurance purposes. If significant porosity is observed in a polished section, determinations can be carried out using the methods given in the standard specification [B.4] which uses comparison images. This standard also covers determination of uncombined carbon. An example of this is shown in Figure B.2.

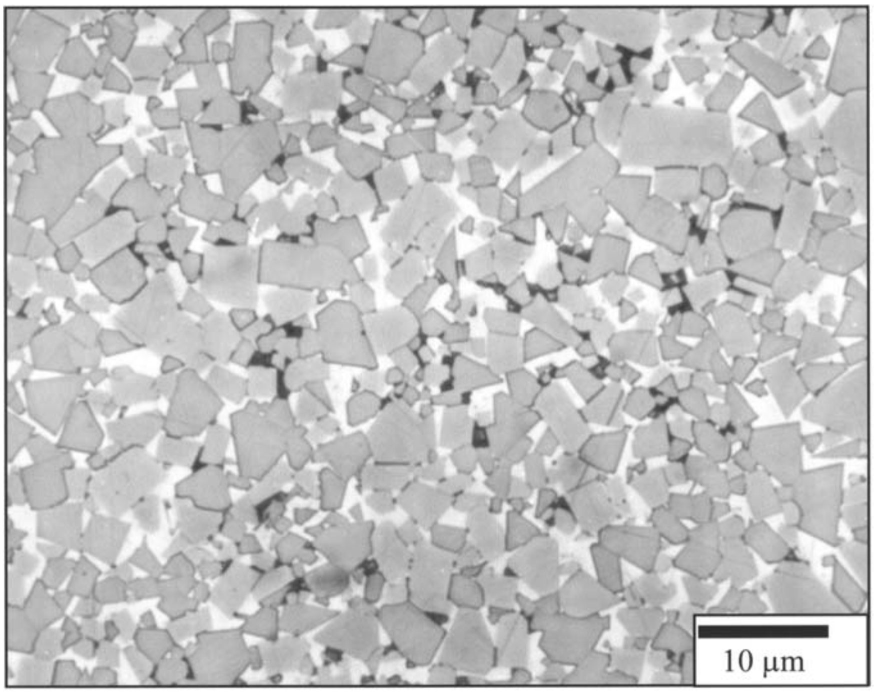


Figure B.2 *- An optical micrograph of a hardmetal containing excess carbon and showing discrete graphite grains.*

B.6 Etching

If a polished section of a tungsten carbide hardmetal is examined optically, the different phases can be observed, but not the shapes and sizes of the grains. The standard methods [B.2, B.3] describe procedures for progressively etching the surface in order to identify the different phases present, which can be quantified using scanning electron microscope techniques [B.5]. The following symbols and definitions are used:

Phase name:	**Definition:**
α-phase	Tungsten carbide
β-phase	Binder (for example based on Co, Ni, Fe)
γ-phase	Carbide having a cubic lattice (for example TiC, TaC) which may contain other carbides (for example WC) in solid solution
η-type phases	Multiple carbides of tungsten and at least one metal of the binder phase

Two etchants are conventionally used:

Etchant:	**Composition:**
A	Freshly prepared mixture of equal quantities of 10 % (mass/mass) aqueous solutions of potassium hexacyanoferrate (III) and potassium or sodium hydroxide (Murakami`s reagent)
B	A mixture of equal volumes of concentrated hydrochloric acid and water

Depending on the phases to be identified, three techniques are can be distinguished:

Technique 1:
This technique etches the α-type phases (WC grains) relative to the binder phase, making the grains appear darker and exposing their angular shape (Figures B.1 and B.3). The specimen is treated with etchant A at about 20 °C for 3 to 6 minutes.

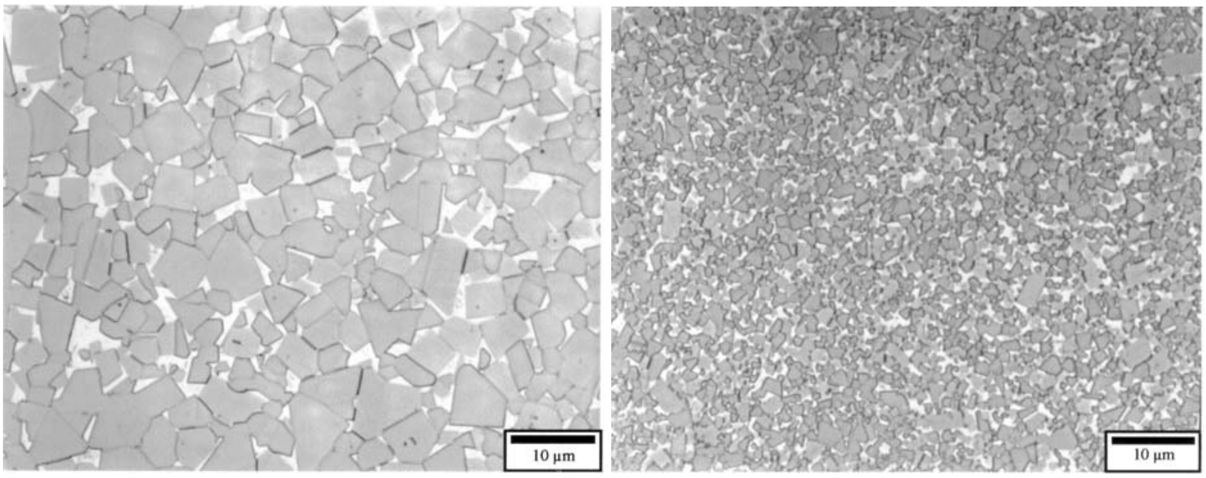


***Figure B.3** – Optical micrographs of (left) a medium grain size 6% Co hardmetal, and (right) a fine grain size 6% Co hardmetal, both after etching using Technique 1 (Etchant A) to darken the WC grains.*

Technique 2:
Several etchants can be used to etch the Co binder (β) phase, including saturated $FeCl_3$ (darkens the Co phase), hydrochloric acid (Etchant B above, removes the Co phase as also shown in Figure B.4), and nital (HNO_3/ethyl alcohol, removes the Co phase). In order to reveal grain boundaries in the Co phase, ion beam etching can be used.

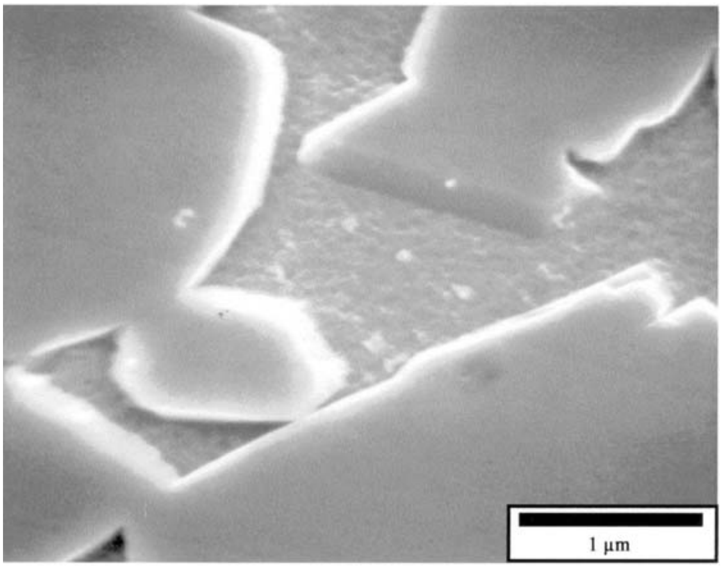


Figure B.4 *– Scanning electron micrograph of a Co-bonded hardmetal etched using etchant B to relieve the binder phase. Note that grain boundaries between carbide grains are not revealed.*

Technique 3:
This technique allows the presence of γ-phases (cubic carbides) to be determined. The phases appear light yellowish brown, and have a typically rounded shape (Figure B.5). The specimen is treated in Etchant A at about 20 °C for 3 to 4 minutes. This is used principally to delineate WC grain boundaries. It is then washed in water and immersed in Etchant B for about 10 s to remove the oxide deposits produced by Etchant A, which also has the effect of etching the binder phase slightly. Next it is washed in water, then in alcohol and dried. Finally it is etched in mixture A for about 20 s, which re-oxidises the γ-phases preferentially.

Technique 4:
This technique enables η-type phases to be determined, as they are coloured orange to brown while other phases are unetched. These phases often appear in rosette form (Figure B.6). The specimen is treated in Etchant A at about 20 °C for 2 to 10 s, and is then flushed immediately with water, without removing the oxide layer. The surface is rinsed with acetone or alcohol and dried without wiping. Contact with fingers should be avoided to prevent contamination by grease.

These four recipes are for conventional WC/Co materials with grains sizes of typically 1 μm or greater. For materials with ultrafine grain structures which need to be observed at higher magnifications in the SEM, etching times must be decreased to reduce the extent of differential etching. For materials bonded with nickel or nickel-based alloys, the following is recommended to preferentially etch the binder phase:

Technique 5:
An electrolytic technique can be applied using dilute hydrofluoric acid (*e.g.* 2 ml of 40% HF solution in 100 ml water) with the test sample being anodic.

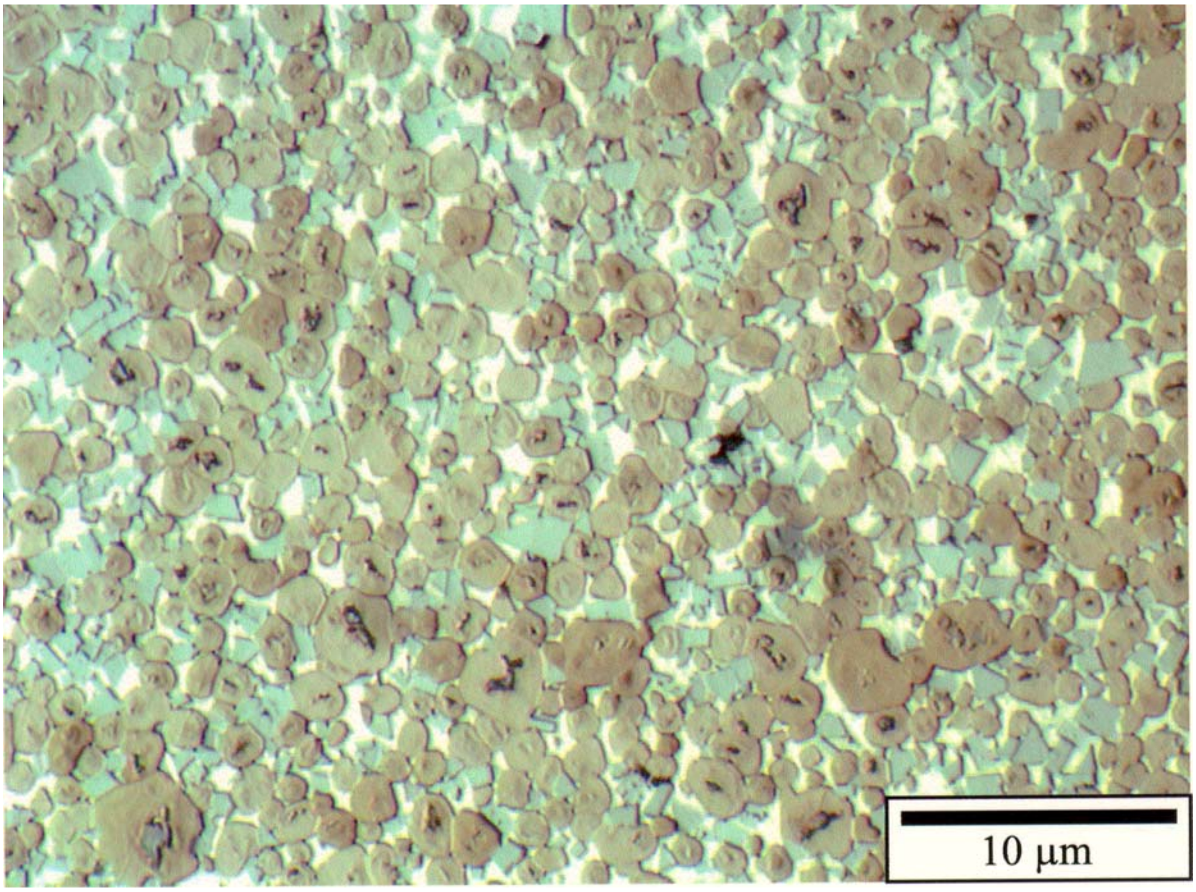


Figure B.5 *- Optical micrograph of a hardmetal containing cubic carbides or so-called γ-phases (the nominal composition was 68% WC, 9% TiC, 11% TaC and 12% Co, all by weight). The WC (α-phase) appears bluish, the binder phase is white, and the cubic carbides (γ-phases) appear brownish with residual cores from the solution-reprecipitation process during sintering.*

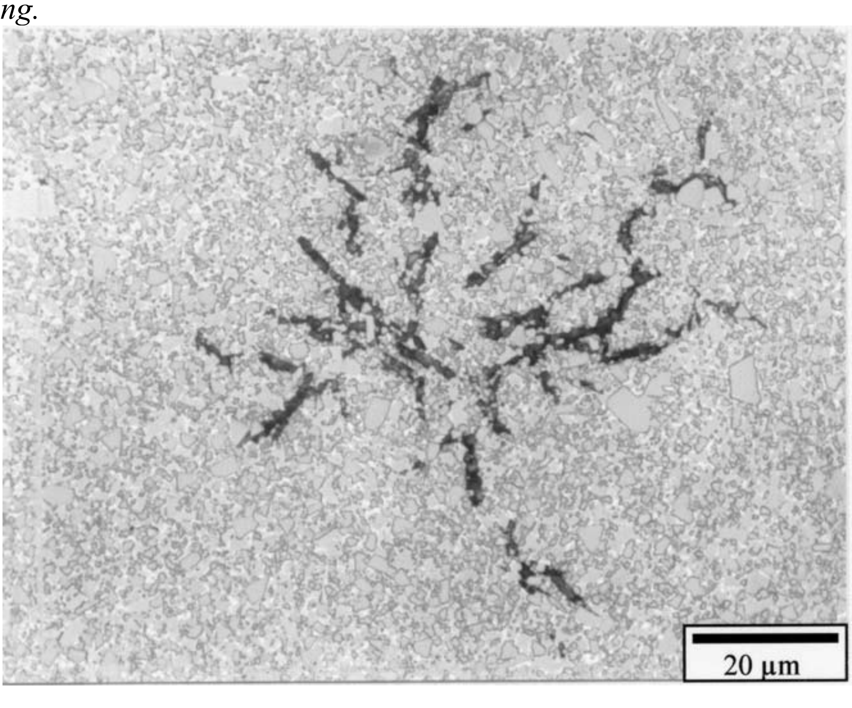


Figure B.6 *- Optical micrograph of a localised rosette of so-called η-phase.*

B.7 References

B.1 ASTM B 665-92 Standard practice for metallographic sample preparation of cemented tungsten carbides.

B.2 ASTM B 657-92 Standard test method for metallographic determination of microstructure in cemented tungsten carbides.

B.3. BS EN ISO 24499:1993 Specification for hardmetals - metallographic determination of microstructure. (Revision in preparation by ISO TC119/SC4, DIS stage in 2007.)

B.4. BS EN ISO 24505:1993 Specification for hardmetals - metallographic determination of porosity and uncombined carbon.

B.5 Nordgren, A.; "Microstructural characterisation of cemented carbides using SEM based automatic image analysis". *Refractory Metals and Hard Materials*, 1991, **10**, 61-81.