

*Measurement
Good Practice Guide*

**The Metallographic
Measurement of
Hardmetal Grain Size**

E G Bennett & B Roebuck

*Meeting
the challenge*

*Surface
engineering*

Casting

*Ceramics
PROCESSING
composit*

NPL 
National Physical Laboratory

Measurement Good Practice Guide No 22

The Metallographic Measurement of Hardmetal Grain Size

E G Bennett and B Roebuck

Centre for Materials Measurement and Technology

National Physical Laboratory

Teddington, Middlesex, UK, TW11 0LW

Abstract: The measurement of hardmetal grain size should in principle be carried out on a regular basis by both the manufacturer and end user as part of a quality control system. However, there is no current standard for grain size measurement of hardmetals. The situation is further confused by the lack of an agreed terminology. Grades of hardmetals which were considered “very fine” a decade ago could be considered to be “medium” grades today and the range of superlatives used to describe the microstructure has become confusing. Also, in many cases, only the mean grain size is measured and no indication of the size distribution is given. In theory, it is possible for two different hardmetals to have the same mean grain size but different mechanical properties, such as fracture toughness, because the size distribution of the WC grains is different.

The method by which the microstructure is quantified can also markedly affect the mean grain size that is measured. For example, if an optical microscope with a poor quality objective lens is used, the resolving power will be inadequate and very small grains cannot be measured. Measurement of the same microstructure with an instrument of higher resolution would consequently result in a smaller mean grain size.

To meet the need for quantification, the present document describes good laboratory practice for measuring the WC grain size of a hardmetal. Recommendations are also given for a method to characterise size distribution. Methods of metallographic preparation and etching techniques are as important as the grain size measurement method, and are included. Technical input for the Good Practice Guide has been provided by powder manufacturers, sintered hardmetal manufacturers, technical institutes and end users. The principal type of hardmetal considered is WC with Co binder. However, the guide can be used for hardmetals that contain cubic carbides or which are based on TiC or Ti(C,N).

© Crown Copyright 2000
Reproduced by permission of the Controller of HMSO

ISSN 1368-6550

January 2000

National Physical Laboratory
Teddington, Middlesex, United Kingdom, TW11 0LW

Acknowledgements

This guide has been produced in a *Characterisation of Advanced Materials* project, part of the *Materials Measurement* programme sponsored by the Engineering Industries Directorate of the Department of Trade and Industry. The advice and steer from the Ceramics and Hardmetals Industrial Advisory Group in reviewing the guide are gratefully acknowledged.

Production of the Guide was supported by contributions from members of an EC Thematic program, HAMMER, in the EC DGXII SMT programme. The authors would like to acknowledge the following; Dr Jörg Bredthauer and Dr Benno Gries of H C Starck, Annika Sandman and Ingrid Reineck of Sandvik Coromant AB, Dr Jacek Komenda of the Swedish Institute for Metals Research, Dr Wolf-Dieter Schubert and Dr Gernot Friedbacher of the Technical University of Vienna. Finally the authors would also like to thank colleague Dr R Morrell for advice on the text and layout of the Guide.

For further information on *Materials Measurement* contact the Materials Enquiry Point at the National Physical Laboratory:

Tel 020 8943 6701
Fax: 020 8943 7160
E-mail materials@npl.co.uk
Internet: <http://www.npl.co.uk>

Note:

This guide contains a range of suggestions for procedures which involve the use of chemicals that may be hazardous to health. It is the responsibility of the individual users of such chemicals to ensure that training is appropriate and that the procedures are safe and in accordance with local regulations. NPL Management Ltd accept no responsibility should any injury result from the use of such procedures.

The Metallographic Measurement of Hardmetal Grain Size

Contents

Executive Summary

1 Guide Outline.....	1
2 Introduction.....	2
3 Metallographic Preparation.....	6
3.1 Sectioning.....	6
3.2 Mounting.....	7
3.3 Grinding.....	7
3.4 Lapping.....	8
3.5 Polishing.....	8
3.6 Cleaning.....	10
3.7 Etching.....	10
4 Calibration.....	13
5 Grain Size Measurement.....	16
5.1 Objectives.....	16
5.2 Systematic analysis.....	16
5.3 Mean grain size by the linear intercept method.....	19
5.4 Distribution types and measurement.....	20
5.4.1 Mathematical representation.....	20
5.4.2 Selection of plotting methods.....	21
5.4.3 Recommendations for grain size distribution measurement.....	28
5.5 Sampling.....	29
5.5.1 Sampling of products.....	29
5.5.2 Sampling of microstructure.....	30
5.6 Measurement errors.....	31
5.6.1 Systematic and random errors.....	31
5.6.2 Smallest measurable intercept.....	32
6 Reporting.....	33
7 Standards and References.....	34
Appendix A: Measurement Case Study.....	36
A1 Arithmetic mean linear intercept.....	36
A2 WC Grain size (intercept) distribution.....	42
Appendix B: Report Proforma.....	45
Appendix C: Polishing Routines.....	47
Appendix D: Names and Addresses of Suppliers.....	50
Appendix E: Definitions and Symbols.....	52

Executive Summary

The properties and performance of hardmetals are directly dependent on the microstructure developed during manufacture, which in turn is controlled by the character of the starting powder batch. Understanding the microstructure is the key to controlling or improving properties, and therefore the measurement of microstructural features, particularly grain size and size distribution is of paramount importance.

The standard method for grain size given in BS5600 : Part 4 : Section 4.13: 1980 and ISO 4499 - 1978 "Powder metallurgical materials and products", is not one of measurement but rather one of comparison against "standard" optical micrographs. The drawbacks of such a method are that, firstly, it is not quantitative and cannot distinguish between similar grades or changes in processing, and secondly, there is a marked trend towards finer grain sizes beyond the scope of the comparative micrographs and leading to confusion of nomenclature between grades.

This guide provides information on setting about achieving qualification of grain size data, including microstructural preparation procedures, optical microscopy and high resolution SEM and reporting to modern quality standards. Procedures which best evaluate grain size distributions are analysed and the best options are discussed. A case study of an example material is evaluated. Much of the work stems from NPL's research programme performed in close liaison with the BHARG and within an EC Thematic Network "HAMMER". This guide is aimed at those developing or undertaking quality assurance on hardmetal materials as a practical guide giving both background information and procedures which can be adopted appropriately for immediate needs.

1 Guide Outline

This guide principally addresses the issue of good practice for the measurement of a mean value for WC grain size. It recommends the use of a linear intercept technique for obtaining data. Grain size distribution is also important and techniques for measurement of this parameter are discussed and recommendations are given for a suitable method.

The guide essentially covers five main topics:

- Metallographic Preparation;
to ensure clear images are produced for measurement.
- Calibration of Microscopes;
to underpin the accuracy of measurements.
- Linear Analysis Techniques;
to acquire sufficient statistically meaningful data.
- Analysis Methods;
to calculate representative average values.
- Reporting;
to comply with modern quality requirements.

The guide is supported by a Measurement Case Study to illustrate the recommended techniques.

These guidelines are intended for:

- The measurement of hardmetal grain size by metallographic techniques only using optical or electron microscopy.
- Sintered WC/Co hardmetals (also called cemented carbides or cermets) containing primarily WC as the hard phase.
- Measuring the grain size and distribution by the linear intercept technique.

The guidelines are not intended for:

- Recommendations on shape measurements. Further research is needed before recommendations for shape measurement can be given.
- Measurements of coercivity are sometimes used for grain size measurement but this current guide is concerned only with a metallographic measurement method. It is also written for sintered hardmetals and not for characterising powders.

2 Introduction

Outline

This Measurement Guide provides advice on good practice to measure WC grain size in a sintered hardmetal. However, it also examines the potential for measurement of size distribution. It draws upon the expertise of raw materials suppliers, manufacturers of hardmetals and research institutes that measure hardmetal grain sizes.

Measurement Rationale

Grain size measurements are required for the following reasons:

- for product design and performance assessment
- for materials selection
- for quality control

At present there is no international standard for the measurement of hardmetal grain size. The key to good measurement lies with the metallographic preparation of a hardmetal surface such that images on which measurements are made reflect the true microstructure. These measurements must also reflect the limiting factors of the imaging technique.

Hardmetals

Hardmetals (sintered carbides or carbonitrides) are composite materials usually comprised of 70-90% by volume of a hard phase (skeleton of either WC, TiC, TaC, Ti(CN) or combinations) and interpenetrated with a transition metal binder such as Co or Ni. Hardmetals are manufactured by a powder metallurgical manufacturing route using powders generally in the nominal size range 0.3–10 μm . These are compacted under high pressure and sintered at high temperature. They are hard, strong and tough. Hardmetals are wear resistant and can maintain their properties at high operating temperatures. They are used for metal cutting, rock drilling and wear parts. For example, for turning, milling and drilling in the mechanical engineering, machine tools, automotive and aerospace industries hardmetals are dominant in cutting steel and cast iron and their share in cutting and forming of non-ferrous metals, composites, plastic, stone, minerals and wood is still growing. The outstanding properties of WC hardmetals are also needed to form hot steels by rolling and to produce synthetic diamonds. Rock drilling tools are used for mining, off-shore oil, geological and civil engineering. The fine scale of the microstructure and high strengths and toughness pose particularly difficult problems for their full characterisation. Important properties of the material, such as hardness, strength, fatigue, wear resistance, fracture toughness and heat conduction depend on the hard phase grain size and distribution and on the amount of binder phase.

Hardmetal compositions are described by the wt% binder phase content, the type of carbide present (WC, TiC etc.), and sometimes by a nominal figure for the grain size of the hard phase. The latter can be measured either by quantitative metallography or by inference from measurements of coercivity. In principle quantitative metallography can be used to measure grain size distribution but at present no standard or agreed method is available. Additionally, there is no agreed metallographic preparation and etching method for the preparation of sections of material on which to make the measurements.

A very wide range of terms are used to describe powders or sintered hardmetals of different sizes. For example, the following have been used in a number of publications and reports.

Extra coarse	Fine	Microfine
Coarse	Very fine	Micrograin
Coarse / Medium	Ultra fine	Nanophase
Medium	Extra fine	Nanograin
Medium / Fine	Submicron	Super fine

None of these terms have commonly agreed or well defined size ranges among users and producers of powders or sintered products. Locally, however, organisations, associations or manufacturers have developed in-house definitions. Unfortunately, although there is some overlap, in general these in-house definitions do not have a one-to-one correspondence.

Powders are available with mean sizes expressed as particle diameters, in 3-D; and mean values are given as the mean of the mass distribution of a batch. By contrast, the most commonly used method to measure the size of WC grains in a sintered product is the linear intercept technique where the mean value is expressed as the arithmetic mean of the number distribution on a 2-D image.

There is no doubt that an agreement on a widely acceptable procedure for the measurement of grain sizes in both powders and sintered materials is of greater importance than the arbitrary choice of names (terminology) for a range of grain size classes. Furthermore, it is clear that any terminology scheme would have to have relevance to most currently available materials as well as accommodating the newer very fine grained hardmetals.

Fine Grain Sizes

The trend towards the fine grained structures started in the late 70's and for over ten years, ever finer grained hardmetals have been produced with a steadily growing market. For example, only the high hardness, stiffness and comparatively good toughness of submicrometre WC/Co hardmetals can succeed in the high technology drilling and machining of printed circuit boards. Due to the ongoing miniaturisation of microelectronic devices the diameter of these microdrills is becoming smaller and smaller. The smallest diameters are now 100 μm (0.1 mm) which is only

200 times the WC grain size of 0.5 μm from which they are made. Materials with even finer mean WC intercepts of 0.2-0.3 μm are being developed which can only be analysed with high resolution scanning electron microscopes (SEMs.) **At present there is no routine method to evaluate such fine structures.** Reliable measurement methods will be crucial in producing materials with consistent results.

The interest in hardmetals with fine grain sizes derives from an understanding that hardness generally increases with a decrease in WC grain size. WC powders with very fine sizes are increasingly becoming available. The use of non-standard terminology can be confusing and benefits could accrue from a rationalisation of the terminology for their description. Their use is also placing new demands on the requirements for testing and characterising of sintered structures. **There is no standard for the measurement of WC grain size.** The required methods are not straightforward and this is particularly the case for very fine grained materials. Measured grain sizes depend strongly on the resolution of the method utilised. The discrimination ability of different methods decreases as the grain size decreases. Comparisons between different procedures become very difficult and this makes it necessary to define the measurement conditions. Clearly the demand for generally accepted and robust techniques becomes even more accentuated in the case of ultrafine grained hardmetals. The result of grain size measurement methods frequently depend on the method of preparation and examination of samples. There is obviously considerable scope for developing new methods of preparation which will be required for these very fine grained materials, and probably even altogether new types of measurement method.

The most direct way to measure the WC grain size is to use quantitative metallography on a polished and etched cross section of the microstructure. Procedures are available for obtaining a mean value for the grain size of single phase materials either by point or area counting, by linear intercept techniques (Heyn method) or by counting the number of grains per unit area (Jefferies method). Measurement on images of microstructures can be performed using optical microscopy for some coarser sized WC hardmetals, but, for many materials, the grain size is too small to be resolved and scanning electron microscopes must be used. In some ultra-fine grain hardmetals the grain size is less than 0.5 μm and good quality images are difficult to obtain using conventional (thermal emission) SEMs. These materials require high resolution instruments such as Field Emission SEMs (FESEM). Even then the images obtained may be open to question of interpretation.

Size Distribution

An issue facing hardmetal manufacturers is the importance of WC grain-size distribution on physical properties. The measurement of coercivity only gives a single value and does not indicate narrowness or spread of distribution. Also, many of the methods of quantitative metallography such as point counting or the number of grains per unit area only return a single value. The effect of size distribution as well as mean size of WC on hardmetal properties has not been extensively researched although widespread views are held by different industry groups on the effects of

distribution width on properties. The question most frequently asked is “*For the same mean grain size, are the properties better for a wide or narrow distribution*”. At present there are no published results which allow an unambiguous answer to be given. Furthermore, there is the additional and related effect of modality. For example, a structure could be imagined in which there are mixed populations of grains with different means and spread. The effects of such a structure on properties are also not known, although at one extreme a material structure can be envisaged in which a few very large grains are dispersed within a uniformly distributed structure. If, for example, these grains are larger than 20–30 μm in a nominally 1 μm mean sized material it has been shown that when subjected to tensile stresses, they can act as fracture initiation sites and thus have an obvious effect on properties. But for less extreme cases, such as for example a 50/50 or 75/25 bimodal distribution, the effect on properties is less clear.

3 Metallographic Preparation

Objectives

- To obtain a plane section suitable for optical or electron microscopy
- To have a repeatable metallographic preparation method
- To reveal a microstructure which is representative of the material and free from artefacts produced by grinding or polishing
- To reveal the WC grain boundaries

Good metallographic preparation is essential to produce a plane polished sample that when etched reveals the true microstructure of the hardmetal. Bad preparation can lead to grain tear out, uneven etching and misleading detail in the microstructure which will effect any subsequent measurement. The following sections detail the stages which are required to obtain a well polished and etched surface of a hardmetal, suitable for quantified measurement of grain size.

Preparation and etching procedures may require toxic or dangerous chemicals. Personnel should be adequately trained, and facilities and precautions as laid down in the relevant safety guidelines in place at the laboratory concerned should 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.

3.1 Sectioning

In many cases the hardmetal sample may have to be sectioned into smaller samples for metallographic preparation. Large samples require longer preparation times due to the high hardness of the material and this in turn results in increased preparation costs. A transverse section is recommended to avoid the problems associated with possible structural variation close to the surface.

Diamond tooling is normally required to cut hardmetals into smaller samples. There is a wide variety of cut-off machines which use blades with diamond embedded on the rim of the disc. Fast cutting times are easily achieved. Wire cutting machines in which diamond is embedded in a wire offer a cheaper method. Very fine slices can be obtained using this method but only at a relatively slow rate of cutting. A faster method is electro-discharge machining, but sufficiently fast machines are not generally suited to a metallographic preparation facility.

3.2 Mounting

Mounting of the sample into a resin has several advantages: it is more suited to automatic preparation, the sample is easier to handle, the specimen codes or identification can be inscribed or written onto the mount. Cold setting and thermo-setting resins are available.

Thermo-setting powders (such as phenolic or diallyl phthalate powders) require a mounting press in which the sample is placed into a chamber, resin is then added, and is melted under pressure. The cycle time for these machines can be quite slow. The advantage is that hazardous chemicals are not used and the resin has an unlimited shelf life.

Cold setting resins (such as epoxy, acrylic or polyester resins) do not require additional equipment apart from the moulds in which the sample is placed and the resin poured on top. The resins normally consist of two parts, a monomer and a catalyst, occasionally a third filler material is used; this may be to increase the hardness or to act as a conductive medium. Various types are available which set in minutes or hours; the quicker setting material reaches relatively high temperatures while the slow setting resin remains cool. Mounting of samples in “quick setting resins” is faster whilst cold setting resin is more economical for batches. However, a drawback is that these resins usually have an associated chemical risk, they have a limited shelf life and they must be stored in cool conditions.

A further consideration is that following metallographic preparation of a flat surface, the hardmetal sample may have to be removed from the mount before etching or placing in the SEM. Cold setting resins can be quite difficult to remove and may require grinding away from the sample.

3.3 Grinding

Whichever method is used to obtain a section of a hardmetal sample, it will have considerable surface and subsurface damage that must be removed. Diamond grinding discs are available from all the main suppliers of metallographic equipment. These come in a range of diamond abrasive sizes and can produce very high rates of material removal from the surface of the sample. They should be used in order of decreasing abrasive size to both remove surface and subsurface damage and to obtain the plane section of the hardmetal sample which is to be polished. At each stage of grinding, the process should be continued until the surface damage (observed by optical examination without magnification) from the previous stage of preparation is removed and then continued for the same amount of time to remove subsurface damage.

If a small sample of hardmetal which has not required sectioning is to be polished, the surface should still undergo the grinding stages. Variation in microstructure which may exist near the surface of a sintered hardmetal such as an increase in the binder content would not represent the true microstructure of the material. Typically, at least 200 µm of material (BS EN 23878 : 1993,

ISO 3878 : 1983)[1] should be removed during the grinding process to obtain a section representative of the bulk microstructure.

The diamond grinding discs are available in several forms; metal bonded, resin bonded, wire mesh and plastic encapsulated. These vary considerably in cost and longevity of use, the resin bonded being the most durable and expensive. Details of these discs are available from the suppliers listed in the appendix.

3.4 Lapping

Occasionally a lapping stage may be incorporated into the preparation procedure immediately after grinding. Lapping is normally carried out on a glass, metal, plastic or composite platen to which diamond abrasive is applied. The key features of lapping are

- The production of a plane surface.
- It is an intermediate step between grinding and polishing.
- The removal of surface damage without imparting substantial further sub-surface damage.
- Relatively high rates of surface removal compared to the same size of diamond abrasive used on a polishing cloth.

Several suppliers provide laps of different compositions depending on the hardness of the material to be prepared. However, this stage of preparation may not be necessary if a coarser size of diamond abrasive is used on a polishing cloth as an additional stage. As with the grinding stages, the time of lapping should be sufficient to remove all the surface damage and then continued for an equivalent length of time to remove subsurface damage.

3.5 Polishing

The terminology for polishing has almost as many problems as those used for describing sintered hardmetal grain size or powder sizes. These terms include :-

Coarse Polishing	Polishing	Pre-polishing
Medium Polishing	Integrity Stages	Fine Grinding
Fine Polishing		

It could be argued that there is only one polishing stage and that is the one in which all surface damage such as fine scratches are removed or, more correctly, reduced to a condition where they cannot be resolved by optical or scanning electron microscopy, and that all previous stages are fine grinding or pre-polishing stages.

Irrespective of the terminology, the polishing stages are normally carried out on a short nap or napless cloth (such as Texmet, DP Pan or similar) with decreasing sizes of diamond abrasive. The abrasive sizes are typically 15 μm , 6 μm , 3 μm and 1 μm for each of the polishing stages. The abrasive may be applied as a suspension, aerosol, paste or other proprietary method.

The suspension is more suitable for automatic polishing machines whereby it is applied as a spray to the polishing cloth at regular intervals. The advantage of the system is that fresh diamond abrasive with good cutting ability is present during the polishing stages allowing fast surface removal. The method is controllable and cost effective.

Aerosol sprays may be used in semi-automatic and manual polishing machines and can also be cost effective. Again, fresh abrasive is easily applied to the polishing cloth to ensure good material removal rates.

Diamond pastes are rarely used nowadays. These had to be applied to the polishing cloth prior to polishing and it is not easy to apply fresh abrasive during use. Control of the usage rate is difficult to determine and use of these pastes can therefore be extremely expensive.

Another important aspect to consider during the polishing stages is the use of lubricants. These perform a dual role. The first is to act as a coolant. During the polishing process, the diamond abrasives are cutting into the WC grains and high temperatures are reached at the cutting point. This may affect the true microstructure of the hardmetal as well as being detrimental to the diamond abrasive, causing it to fragment quickly. The cooling action of the lubricant prevents high temperatures being reached. The second role of the lubricant is to ensure that the abrasive applied to the polishing cloth is used efficiently. During the polishing stage, wear debris is produced as well as the diamond abrasive fragmenting. This can result in the polishing cloth becoming clogged and inefficient. Lubricant should be added at regular intervals such that the wear debris formed becomes fluid enough to be forced to the edge of the cloth and the cloth is cleaned by this action prior to fresh abrasive being added. Automatic and semi-automatic polishing machines use an alcohol based lubricant in most cases. Proprietary lubricants are available for manual polishing techniques.

For each of the polishing stages, the specimen is polished until the surface damage from the previous preparation stage has been removed. The polishing time is then extended for an additional equivalent amount of time to remove the subsurface damage. Failure to remove subsurface damage is soon revealed after etching when uneven etching or grooving can be seen. The subsurface damage is preferentially etched and is revealed as quite broad lines of deeper etching which can be seen with an optical microscope. After each polishing stage, the specimen and specimen mounts (for automatic polishing) must be thoroughly cleaned.

For each of the polishing stages, the time required will depend upon the size of sample and the size and hardness of the mount in which it is contained. Other factors effecting the polishing stage are

those relating to the microstructure of the material, such as grain size and volume fraction of the constituents. Polishing variables are applied force, rotational speed and the rates at which both lubricants and abrasives are applied.

One problem which often occurs is that of polishing very large samples. In this case, the applied load per unit area may be insufficient for the diamond to cut efficiently into the WC grains. A typical immediate reaction is to increase the applied force. However, this can have the opposite effect of further increasing the polishing time by changing the characteristics of proven polishing routines. The abrasive entering the side of the specimen becomes fragmented before reaching the centre of the specimen. As a result, edge rounding of the sample occurs, very long polishing times are required and the process becomes increasingly expensive. The solution where appropriate is to section the sample into smaller areas. An alternative is to grind to a finer initial finish with a resin bonded wheel and smaller diamond abrasive size. In this case, fresh cutting abrasive is constantly being used at all points on the surface of the specimen.

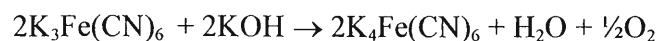
3.6 Cleaning

An underlying principle of metallographic preparation is cleanliness between each of the grinding and polishing stages. This prevents debris and abrasive grit being carried onto the next stage. Detergents and hot water can be used between these stages. Specimens and specimen mounts used for automatic polishing machines can be immersed in an ultrasonic cleaning bath. The specimens and specimen mounts can then be dried either using an alcohol rinse followed by a hot air dryer or oil free compressed air.

However, cleaning of the specimen prior to etching is far more critical. It has been found in many cases that the use of hot water and certain detergents can cause the Co binder phase to stain. It is recommended that cleaning is carried out in an ultrasonic bath using a proprietary detergent in warm water which is known not to effect the Co binder, or alternatively to rinse in acetone. **Cleaning specimens ultrasonically in acetone prior to examination in an electron microscope is especially recommended.**

3.7 Etching

The etchant recommended by the standard for microstructural characterisation of hardmetals (ISO 4499, BS5600) [2] for revealing the microstructure is Murakami's reagent. The reagent consists of potassium ferricyanide and either potassium or sodium hydroxide. These react together to produce potassium ferrocyanide and (nascent) oxygen which attacks the carbide grains and grain boundaries whilst the binder phase is generally unaffected [3] as shown in Fig.1.



As can be seen from the above chemical equation, the reaction starts once the chemicals have been mixed, therefore the reagent must be used fresh. However, solutions of constituents can be prepared and stored separately. Additionally, when etching large quantities of hardmetals, the strength of the reagent will rapidly decrease and fresh solution should be used when times required for effective etching are extended unacceptably.

The Standard BS5600 recommends use of a freshly prepared solution of equal quantities of 10 to 20% (m/m) aqueous solutions of potassium hexacyano – ferrate (III) [potassium ferricyanide] and potassium or sodium hydroxide (10 to 20 g in 100 ml water). The etching time at 20° C is advised to be in the range 3 to 6 minutes.

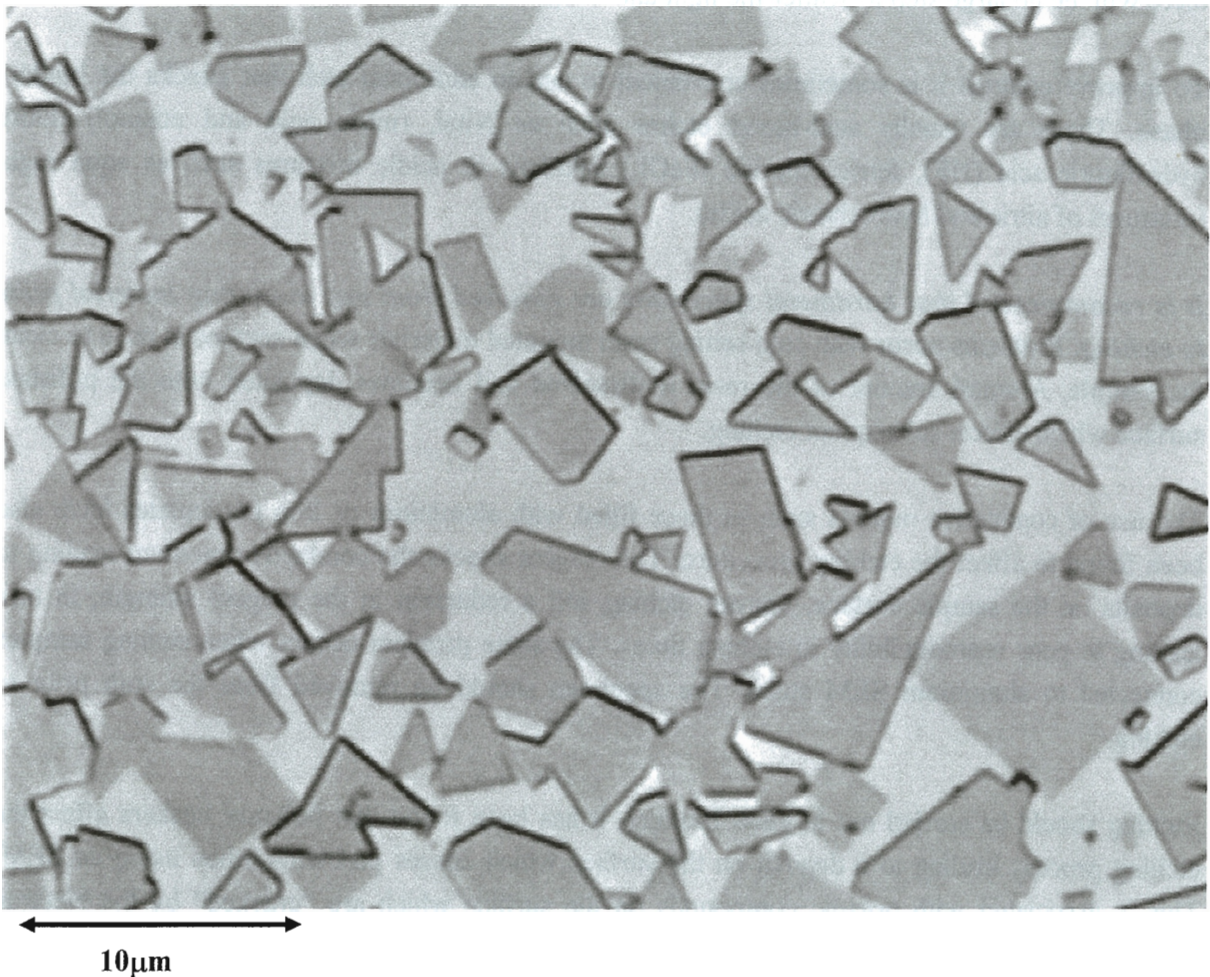


Figure 1 - Coarse grained hardmetal, 25% binder, x100 oil immersion objective. The WC grains (α phase) appears dark grey while the Co binder (β phase) is lighter. The sample was etched for 6 minutes in Murikami's reagent to reveal the grain boundaries which appear dark grey to black. The contrast of the grain edges is due to their angle to the surface at which light is scattered when viewed with an optical microscope.

Van der Voort [3] suggests using 10 g of potassium ferricyanide, 10 g potassium hydroxide at room temperature. An alternative is 5 g potassium hydroxide, 3 g potassium ferricyanide and 100 ml water which is used boiling.

Samuals [4] also advocates the use of boiling potassium hydroxide - potassium ferricyanide.

Murakami's reagent attacks the WC phase. Adjacent grains of WC are attacked at differing rates depending upon their crystallographic orientation relative to the polished surface. Thus, height differences and steps are produced between adjacent grains. Normally incident light in an optical microscope is scattered at these steps and the grain boundaries appear darker. In some cases, the orientation between adjacent grains may be similar such that they etch at the same rate, in this case there will be no large step to scatter the light and the grain boundaries will not appear dark.

To improve contrast it is sometimes convenient to use an additional etch that attacks the binder-phase. These are usually acid-based etches such as Nital, (nitric acid and ethanol) dilute hydrofluoric acid (HF), ferric chloride (FeCl_3) solutions or acidic mixtures such as aqua regia (mixtures of nitric and hydrochloric acids).

It is recommended that hardmetal specimens are removed from any mounting material prior to etching. Problems occur with cold setting resin mounted materials when acetone is used to clean the sample. A small amount of the resin is dissolved and becomes deposited onto the polished surface which effects subsequent etching.

The use of conductive mounts such as those filled with aluminium or iron particulates have also been found to affect the etching procedure. The reagent attacks the conductive medium leading to deposits on the sample surface, uneven etching and a reduction in the reagent strength, in turn leading to poor reproducibility in etching times. The same problem occurs when etching samples connected to aluminium SEM stubs. The specimen should be removed from the stub prior to etching.

Etching should be carried out in glass beakers. It has been found that polymer beakers affect the etching process leading to a deposit on the surface which causes problems when using an SEM. This is associated with organic compounds on the surface which are "cracked" by the electron beam giving rise to carbonaceous deposits that lead to local charging on the specimen surface. This deteriorates the image, and is probably caused by the Murakami's reagent attacking the polymer to form an organic compound which deposits onto the specimen surface.

4 Calibration

Objectives

- to ensure measurements are calibrated and traceable
- to provide confidence in the measurements as part of a quality system
- to ensure that the highest resolution images are obtained

To give reliable quantitative measurements images must be calibrated against a stage micrometer or scale traceable to a National reference standard. Stage micrometers are available for both optical and scanning electron microscopes and suppliers of these stage micrometers can also arrange for calibration. These normally consist of a series of lines which have a nominal spacing. For instance, a graticule for an optical microscope may have a nominal line spacing of 10 μm . However, there can be variations in this line spacing, so the graticule requires a certificate from a recognised or accredited body which states the actual line spacing and the errors of measurement. A typical stage graticule for optical microscopy is shown in Fig. 2.

The most commonly used stage micrometers for SEM's are the SIRA grids. These are ruled lines which form a grid and are available with 19.7 and 2160 lines per mm. However, these must also be calibrated and certified as being traceable to a National Reference Standard.

For images obtained from an optical microscope, an image of the calibration graticule must also be obtained using the same objectives (and internal magnification step changers or zoom position) and illuminating technique. The microscope must be set up for Köhler illumination to obtain the maximum resolution [5].

The resolving power of an optical microscope [5] or minimum distance d in μm which can be seen in monochromatic light is given by

$$d = 0.6\lambda / \mu \sin\theta \text{ or } 0.6 \lambda / \text{N.A.}$$

where:

- λ is the wavelength of the illuminating light, in μm
- θ is the half angle of the aperture of the objective
- μ is the refractive index of the surrounding medium, 1 for air.
- N.A. is the numerical aperture of the objective.

The highest resolution is obtained using an oil immersion objective which can have a N.A. as high as 1.25 (compared to 0.9 for a dry objective). Thus for a x100 oil immersion objective with a N.A. of 1.25, a monochromatic light source of 0.5 μm (500 nm), the smallest theoretical distance which can be resolved is 0.24 μm . In practice it is found that there is a higher limit of about 0.5 μm , limited by aberrations from various sources.

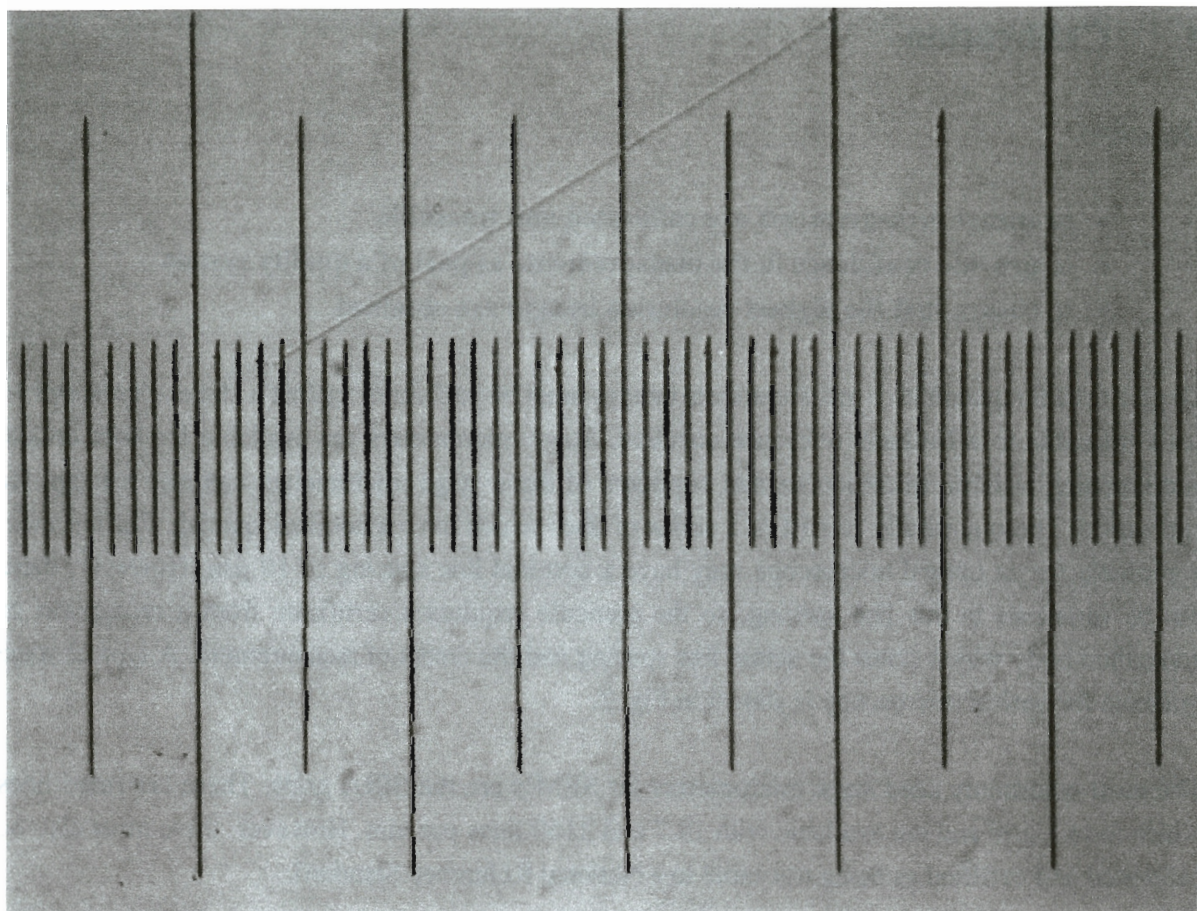


Figure 2– Calibrated stage micrometer for optical microscopy

The resolving power of objectives available on a typical research optical microscope are shown in Table 1. **It is recommended that the highest N.A. objectives available are used for maximum resolution.**

Table 1 - Resolution of optical microscopes, wavelength of illumination, 500 nm.

Objective magnification and type	Numerical aperture	Resolution, μm
x5, Plan Fluotar	0.15	2.00
x10, Plan Fluotar	0.30	1.00
x20, Plan Fluotar	0.50	0.60
x50, Plan Apochromatic	0.85	0.35
x100, Plan Apochromatic	0.90	0.30
x100, Plan Fluotar, oil immersion	1.30	0.23

For images obtained from a scanning electron microscope, images of the graticule should be obtained under the same conditions (accelerating kV, working distance, illumination aperture) as those used for the hardmetal. Typical resolving powers of SEMs are 20 nm and 1.5 nm for

FESEM's. However, the resolving power is dependent upon the working conditions of the electron microscope as well as the type of material being imaged.

Image analysis scales or stage micrometers are available for both optical and scanning electron microscopes. These contain artefacts of known size and shape and can also be calibrated and made traceable to national standards. An advantage of these scales is that they can be used for performing a check on the magnification calibration of images. Similarly, images obtained can be checked for distortion caused by tube cameras attached to optical microscopes or astigmatism of the electron beam of a SEM. Calibration in both X and Y directions is recommended to check for image distortion or when using semi automatic or automatic image analysis. In the absence of distortion, calibrated artefacts should not change in size or shape irrespective of the position within the image field.

5 Grain Size Measurement

5.1 Objectives

- to define measurement techniques
- to define the linear intercept method
- to define distribution types and measurement
- to recommend the method for grain size distribution
- to define methods of sampling
- to determine measurement errors

5.2 Systematic analysis

The most direct way of measuring the WC grain-size is to polish and etch a cross-section of the microstructure and then to use quantitative metallographic techniques to measure a mean value for the grain size, either by area counting or by linear intercept techniques. The linear intercept technique is popular because it produces size distribution information. It is often found that the measured number distribution of intercepts is lognormal in form, which gives a straight line when plotted on lognormal probability paper. An alternative is the measurement of the sectional grain area. However, this is not yet commonly used or well developed.

There are six ways by which the mean size of the WC grains can be defined (these are shown schematically in Fig 3) as combinations of Dimension and Type:

Dimension: by length (of a line across a 2D section of a grain);
by area (of 2D sections of grains);
by volume (of individual grains);

Type: by number or by size.

A number average is obtained by counting each measurement of the parameter of interest (length, area or volume) and dividing the total value of the parameter (length, area or volume) by the number of this parameter counted.

A size average is obtained by measuring the cumulative value of the parameter (length, area or volume), normalised by the total value of the parameter (length, area or volume) and plotting this against the parameter. The value of the parameter at a cumulative probability of 0.5 (50%) is defined as the size average.

Thus, there are six possible combinations for defining a WC grain size

grain length parameter	-	by number or by size
grain area	-	by number or by size
grain volume	-	by number or by size

These six parameters can also be expressed as distributions as shown in the schematic diagram in Fig 3.

The value most used to date has been a length parameter. This can be obtained in several ways, for example, by parallel lines or circles as described in ASTM E - 112, Standard Test Methods for Determining Average Grain Size:

by linear intercept	called the Heyn method from a straight line drawn across the structure
by equivalent circle diameter	this is obtained by measuring grain areas and then taking the diameter of a circle of equivalent area

* An additional method is that by Jefferies where the number of grains per unit area can be counted. This can, if required be converted to an equivalent circle diameter.

It must be noted that

- Point / area counting provides no information on distribution.
- Jefferies method is not intended for use on multiphase materials such as hardmetals.

The recommended technique for measurement of hardmetal grain size is the linear intercept method.

Grain size and size distribution

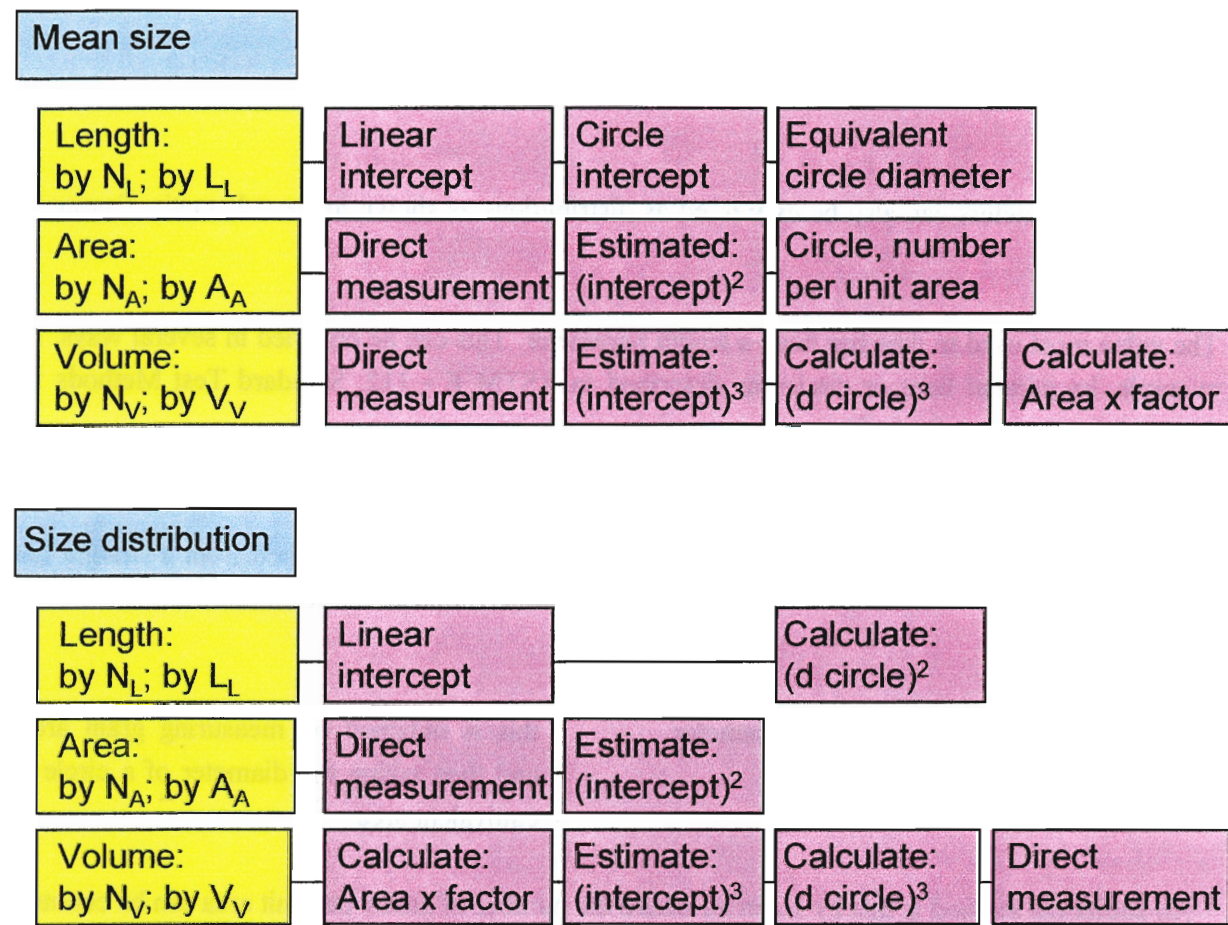


Figure.3 – Systematic analysis of methods for characterising grain size and distribution

5.3 Mean grain size by the linear intercept method

It is recommended that the arithmetic mean linear intercept is used as the parameter to define WC grain size. This is the simplest procedure to use and has the added advantage of providing data that can be used to quantify distribution width.

This method requires a straight line to be drawn across a calibrated image. In a single – phase material the length of line (L), starting at a random position, traversing a number of grain boundaries (N), and ending at another random position, is measured. The mean linear intercept distance is thus:

$$\ell = L/N$$

As can be seen from the above equation, only the mean linear intercept distance is calculated, there is no information obtained on grain size distribution.

For a nominally two-phase material such as a hardmetal (α and β phase), the linear intercept technique is less straightforward because each phase has to be measured independently, but it can provide information on grain size distribution. A line is drawn across a calibrated image of the microstructure of an hardmetal. Where this line intercepts a grain of WC, the length of the line (l_i) is measured using a calibrated rule (where $i = 1, 2, 3, \dots, n$ for the 1st, 2nd, 3rd ... n^{th} grain). It is advisable to count at least 100, preferably at least 200 grains in order to reduce the statistical scatter to below 10%.

The mean linear intercept grain size is defined as:

$$\bar{l} = \Sigma l_i / n$$

Where:

- $\bar{l}$ is the mean linear intercept grain size.
- l_i is the measured length of each individual intercept.
- Σl_i is the sum of the measured length of each individual intercept
- n is the number of WC grains intercepted.

Hardmetal grain sizes fall in the range 0.1 – 10 μm . Because of the uncertainties of measurement it is good practice to report the mean linear intercept grain size to one decimal place for values $>1.0 \mu\text{m}$ and to two decimal places for values $<1.0 \mu\text{m}$. i.e., the results are reported to two significant figures such as 3.4 μm or 0.18 μm .

A worked example is given in Appendix A.

5.4 Distribution types and measurement

5.4.1 Mathematical representation

As indicated in section 5.1 intercept data can be plotted systematically by a number of methods in order to compare and contrast the different ways in which cumulative distributions of sizes can be displayed and examined [6-13], in particular by using distributions based on either number or size probabilities.

Cumulative distribution of values by number:

$$P_i = \frac{\sum_{j=1}^i n_j - 0.5}{N_d}, \quad (A) \text{ for areas or estimated areas} \quad (1)$$

$$P_i = \frac{\sum_{j=1}^i n_j - 0.5}{N_A}, \quad (A) \text{ for areas or estimated areas} \quad (2)$$

Cumulative distribution of values by size:

$$P_i = \frac{\sum_{j=1}^i d_j}{\sum_{j=1}^N d_j}, \quad (B) \text{ for intercepts} \quad (3)$$

$$P_i = \frac{\sum_{j=1}^i A_j}{\sum_{j=1}^N A_j}, \quad (C) \text{ for areas or estimated areas} \quad (4)$$

where N_d is the total number of intercepts, d_i , counted

N_A is the total number of grain areas, A_i , counted

If area is estimated from intercepts squared then $N_d = N_A$

$\sum_{j=1}^i n_j$ is the cumulative number of intercepts or areas up to the i^{th} data point

$\sum_{j=1}^i d_j$ is the cumulative length of intercept up to the i^{th} data point

$\sum_{j=1}^N d_j$ is the total cumulative length of intercept

$\sum_{j=1}^i A_j$ is the cumulative area up to the i^{th} data point

$\sum_{j=1}^N A_j$ is the total cumulative area.

For example:

- the data can be shown as cumulative probability plots with the ordinate (y) given a linear scale or by using probability paper. The latter method expands the extremes of the distribution and contracts the central regimes.
- the data can be plotted as cumulative probability plots with the abscissa (x) on a linear or logarithmic scale. Historically, this has been the preferred method for plotting WC size distribution data [14,15], where a number probability is used for the ordinate and the size is plotted as log size on the abscissa. It has been found that linear intercept measurements plotted in this way have a log-normal distribution, giving a straight line when log-normal probability paper is used. The equation for log-normal probability is:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp \left[\frac{-\left(\ln(x) - \ln(\mu_g)\right)^2}{2\sigma^2} \right] \quad (5)$$

where σ is a measure of the distribution width and μ_g is the geometric mean (Fig. 4). This does not plot conveniently mathematically, but many software packages have numerical approximations to the function, permitting σ to be determined. However, for materials with mixed size distribution [16] it is not so convenient to use a single value of σ . The use of probability paper generally gives a straight line for data for current commercial hardmetals, indicating that the parameter, σ , is the width of the lognormal distribution. Linear intercept measurements of WC grains have lognormal distributions.

- a further refinement is to normalise the abscissa values, i.e. normalised intercept or normalised area. This is obtained by dividing by the number or size average.
- the data can be plotted as intercepts, or areas, either by number (A) of the i^{th} ranked data or as cumulative length of intercept (B) or cumulative area (C). Area can be estimated by squaring the intercepts. For A, B and C the mathematical expressions used to calculate cumulative probability, P_i are given by equations (1) and (2).

5.4.2 Selection of plotting methods

There are several questions to be asked of these different types of data plots.

- *Do the data reveal differences more clearly when plotted using a linear abscissa rather than logarithmically? Are there advantages in using normalised data for the intercept values?*

When intercept distribution data are plotted against intercept or area on a linear abscissa the distribution is compressed for the small sizes and expanded for the large sizes. This representation possibly reflects what is seen when the eye/brain interprets the microstructures with a bias towards the larger sizes. It enables differences to be seen more easily for large grains but not for the grains at the small end of the distribution. In conclusion, both plots could have a role to play depending on the kind of information required. Normalised abscissa values have some advantage when comparing materials with different mean values. It is possible to see more clearly differences in distribution widths.

- *Is there any benefit in plotting the ordinate on a linear scale rather than on probability paper?*

The probability plots expand the distribution at each end and effectively weight the information so that perhaps an exaggerated effect of differences in large or small grains is observed.

- *Is there an advantage to plot the data as distance or area fractions (ie size fraction) rather than by number fraction? Is it number fractions or is it size fractions that are related to properties?*

It has been shown [6,10] that there are advantages to using areas rather than intercepts because the differences in distribution type for materials with narrow and wide distributions are more pronounced. Areas can be estimated by squaring the values of the intercepts. Some typical plots of the different kinds of distributions are shown in Fig 5, including number and estimated area probability plots against intercept and normalised intercept axes.

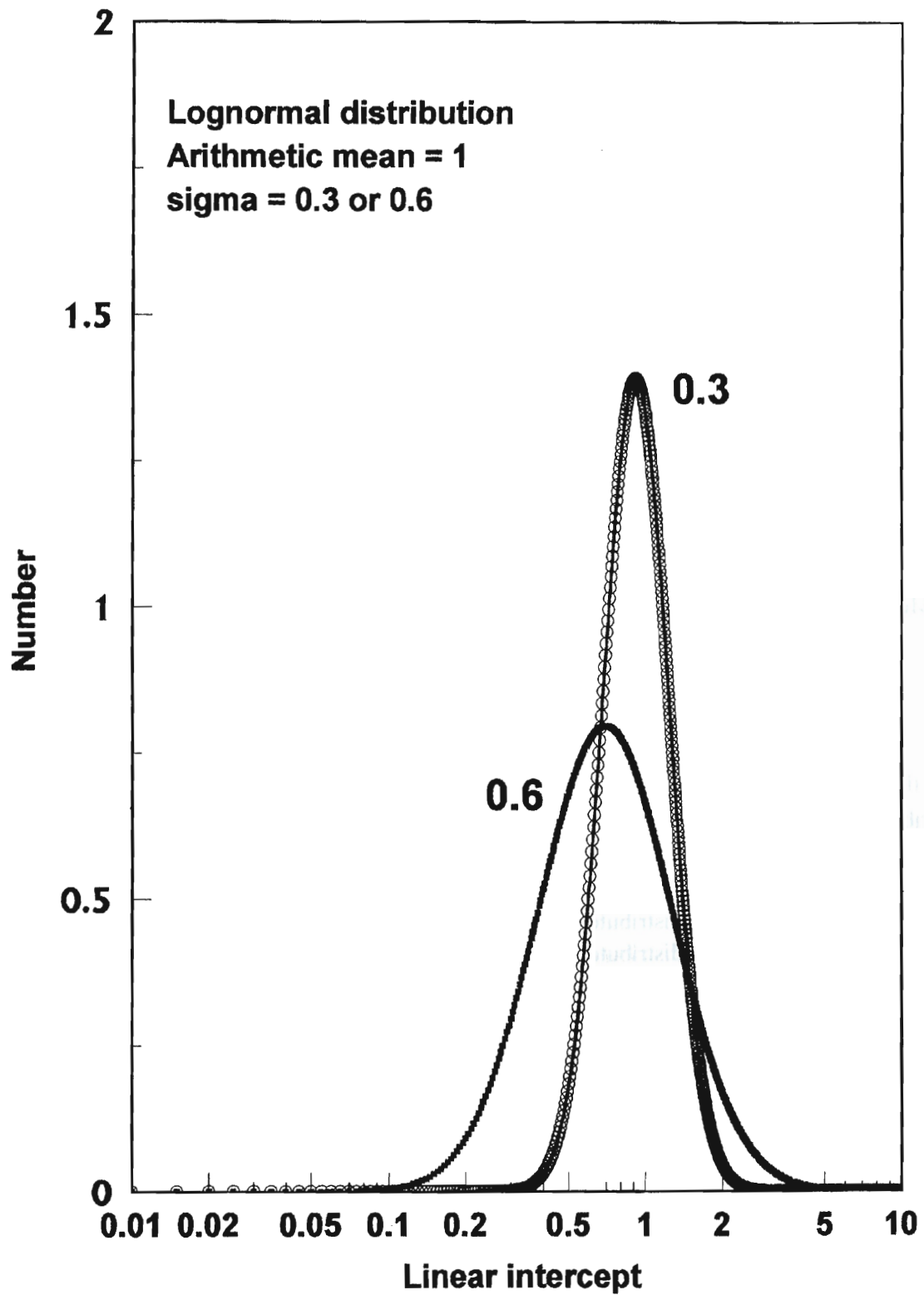


Figure 4 - Lognormal number probability distributions

Computer simulation has been used to assess the effectiveness of the linear intercept or area measurement techniques and its relevance to three dimensional structures [12-14]. A computer programme was written that runs on a standard PC. The program contains various shapes such as a tetrakaidecahedron, a cube, a cylinder, a rod, a tetrahedron and a trigonal prism. These shapes were used to explore the consequent distribution of 2-D intercepts and areas that can be generated from the 3-D shape. The program generates statistical data on each shape for a specified number of sections. The data includes information on areas, intercept lengths, vertices and numbers of sides. The program can be run with single sizes of shapes or with normal (a Gaussian) or lognormal distributions (with different distribution widths and mean values). The data are generated by randomly sectioning the shape (distribution).

Several aspects of the measurement of distribution data using intercepts have been investigated [14] with the tetrakaidecahedron model shape, including:

- Estimating areas using squared values of intercepts;
This was validated as a useful method of obtaining information on area distributions from intercept lengths.
- Measurement of small intercepts;
It was found that small intercepts were not important when data was plotted as size probabilities.
- Quantification of distribution width using model lognormal distributions.

For the latter, a model tetrakaidecahedron was used to generate size probability data for three distributions:

- single sized
- lognormally distributed, $\sigma = 0.3$
- lognormally distributed, $\sigma = 0.6$

The data are plotted in Fig 6 as cumulative size probability (estimated area - based on squaring the intercept values) against normalised intercept (i.e. intercepts normalised by the number mean linear intercept). This comparison plot was then used to decide how uniform a particular structure was in 3-D. The plots are then compared with measurements on the hardmetal microstructures.

Thus, it has been concluded [14] that the most convenient distribution by which to discriminate the distribution widths of the real microstructures was that based on:

Estimated area probability *plotted against* Normalised linear intercept

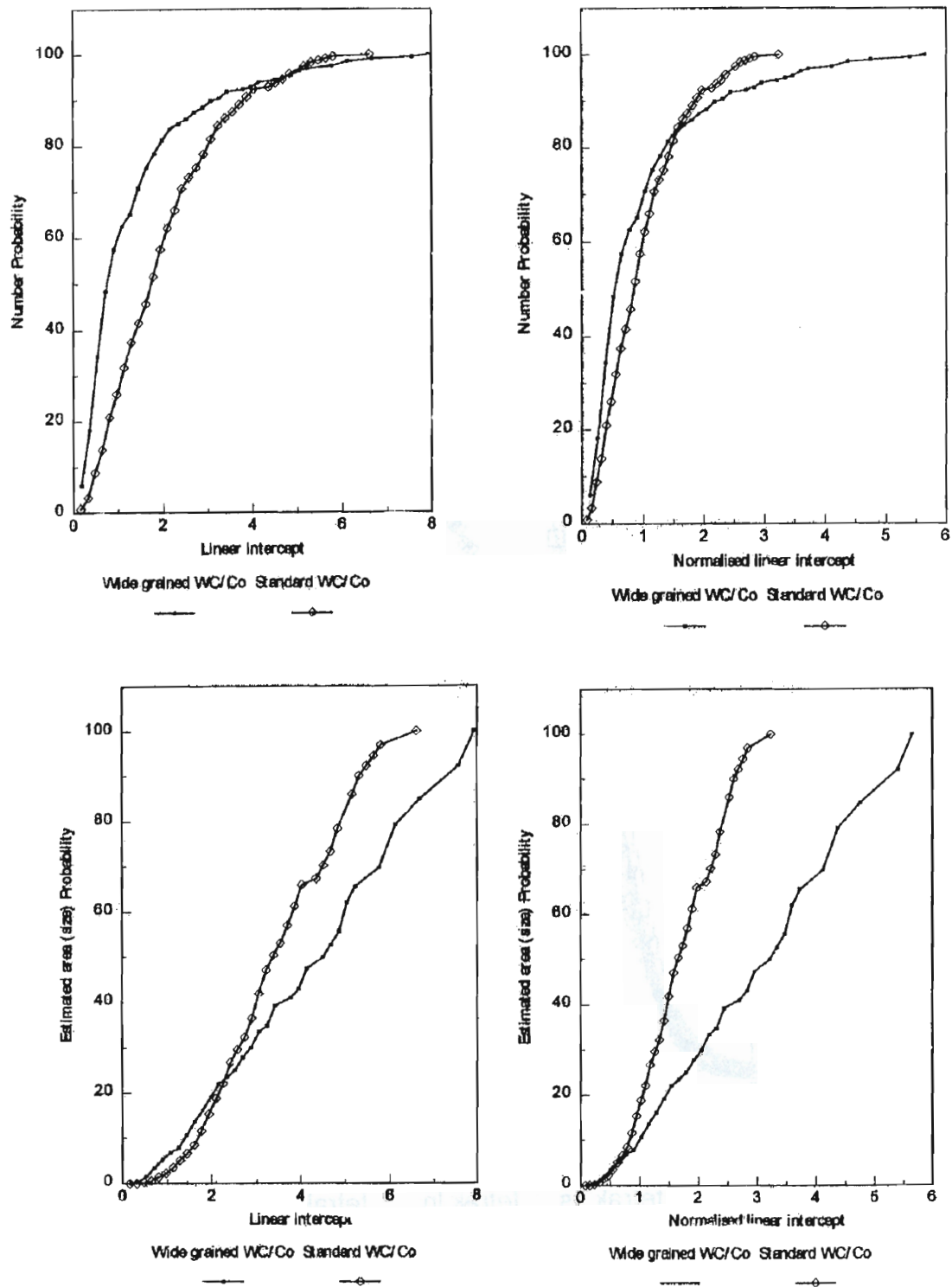


Figure 5 - Different types of distribution.

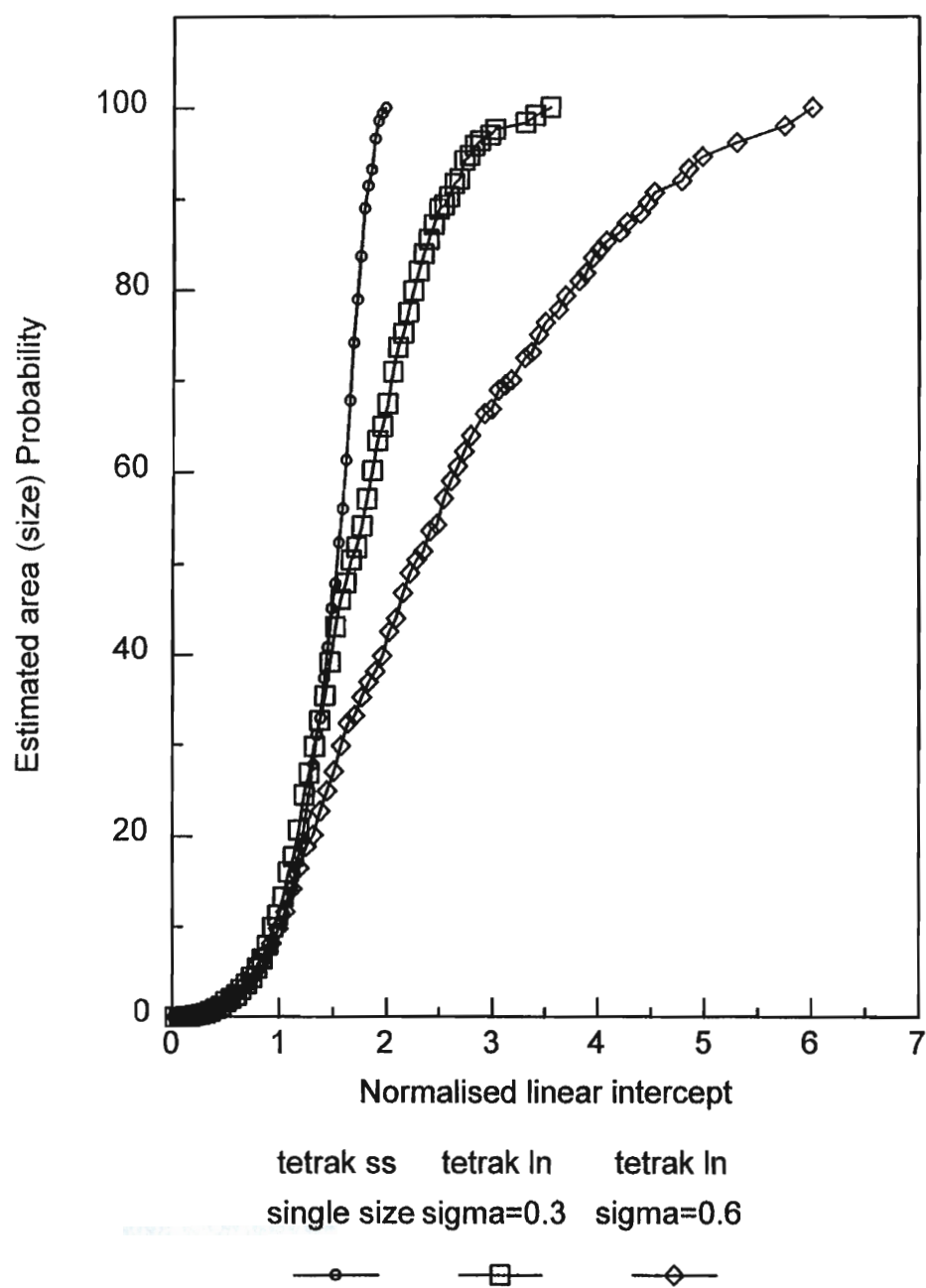


Figure 6 - Reference plot for size distribution comparisons

Fig. 7 shows data from a commercial hardmetal plotted against data from the tetrakaidecahedron model with different values of sigma. These plots indicate that a shape equivalent to the tetrakaidecahedron lognormally distributed in 3-D with a sigma of 0.3 gives the closest fit to measurements on conventional structures. The plots in Fig. 7 are very useful in answering the question "how uniform is a particular distribution". The data shown are for sigma values (measure of distribution width) of 0.01, 0.3 and 0.6. Clearly the nearer is a measured distribution to that corresponding to a distribution with a sigma of 0.01 then the more uniform is that structure.

A worked example is explained in Appendix A.

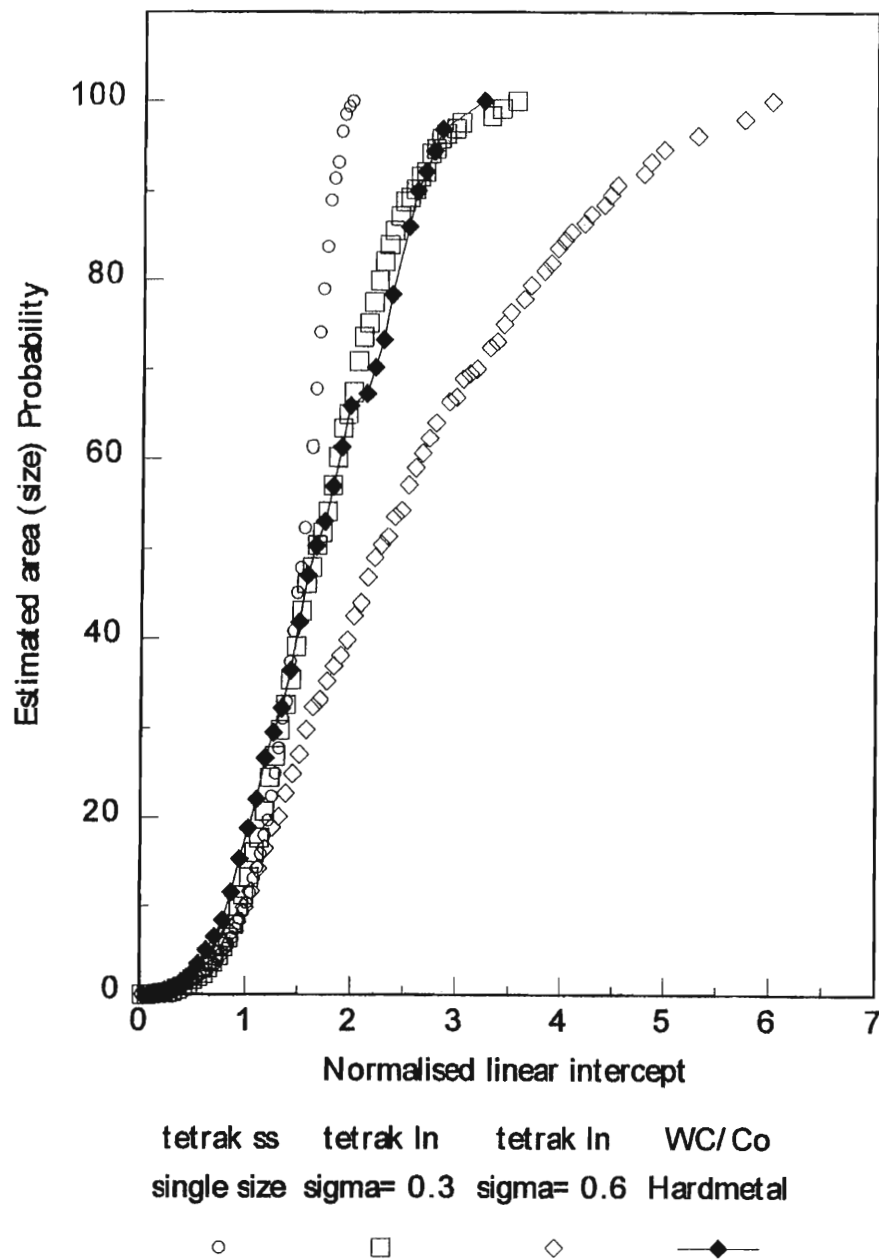


Figure 7 - Comparison of hardmetal grain size distribution data and reference plot.

5.4.3 Recommendations for grain size distribution measurement

A suitable procedure for measuring the size distribution of grain might be:

- Prepare a representative 2-D polished and etched section.
- Measure at least 200 intercept lengths in μm .
- Rank the data by size.

- Square the individual intercept data to get an estimate of individual grain areas.
- Calculate cumulative size probabilities, by dividing each (estimated) area increment by the total (estimated) area.
- Calculate an arithmetic mean linear intercept in μm (number average of intercept lengths).

NB: This value can be quoted as the mean grain size, while recognising that it was obtained from measurements on a 2-D plane. It should not be converted to a 3-D size.

- Normalise the intercept values by dividing by the arithmetic mean intercept.

There are now two ways to plot the data:

- (a) For direct measurements of size distribution plotted against size.

In this case:

- Plot the cumulative size probability (estimated area) against estimated area (intercept squared).

- (b) For comparing the distribution widths of different materials.

In this case:

- Plot the cumulative size probability (estimated area) against the normalised linear intercept

Fig. 6 can be used as a reference plot to estimate how wide is the distribution. Fig. 6 gives equivalent data from a tetrakaidecahedron shape with lognormal distributions of $\sigma = 0.01, 0.3$ and 0.6 . A σ value of 0.01 is equivalent to a structure with all grains the same 3-D size.

5.5 Sampling

5.5.1 Sampling of products

Sampling is the procedure whereby an item of hardmetal or a region within an item is chosen for testing. Random sampling is defined such that in selecting an individual from a population each individual in the population has the same chance of being chosen [17].

In the Standard BS EN 24489 : 1993, ISO 4489 : 1978: Sintered hardmetals - Sampling and Testing [18], paragraph 4 states that “For confirmation of the grade of hardmetal, it is usually sufficient to take a test sample of one unit” for the following tests:-

Determination of coercivity	ISO 3326
Determination of density	ISO 3369
Determination of hardness HRA	ISO 3738
Determination of hardness HV	ISO 3878

and tests which may be carried out in special cases :-

Determination of microstructure	ISO 4499
Determination of porosity and uncombined carbon	ISO 4505

5.5.2 Sampling of microstructure

Sampling for microstructural purposes has to be carefully considered depending on the reason for undertaking the measurements:

1. General check measurement of a sectioned isolated object.

The images chosen for analysis should be representative of the whole section and should be obtained by completely random positioning. The number of images to be prepared should be at least four, which can be intensively analysed so that in total, at least 200 grains are measured.

2. Determination of homogeneity of grain size

In this case a systematic set of images from defined locations within the sectioned are to be obtained and intensively analysed so that at least 200 grains are measured from each location. This will allow for example, trends in grain size greater than the likely error of measurement at each position (fractional error is proportional to $1/\sqrt{N}$ where N is the number of grains at each location) to be determined.

3. Inhomogeneous materials

In cases where the microstructure is inhomogeneous from one field of view to the next it is probably good practice to increase the number of images evaluated, but to evaluate them less intensively, while still achieving a total feature count of > 200.

The magnification of the image obtained should be such that there are between 10 and 15 WC grains across the field of view permitting individual intercepts to be measured to better than 10% accuracy. This will usually allow 3 or 4 linear intercept lines to be drawn across the image without intercepting any individual WC grain more than once. Most hardmetals have little or no anisotropy of structure, so it is unimportant if more or less parallel lines are used. If anisotropy is suspected, then it is better to orientate the lines randomly and permit their intersection [19]. Thus from each

image about 50 linear grain size intercepts may be obtained. **This Measurement Good Practice Guide recommends that at least 200 intercepts are measured.** Hence, at least four images are required.

5.6 Measurement errors

5.6.1 Systematic and random errors.

Measurement errors can have several sources:

- Systematic
such as during calibration of the microscope
- Experimental or accidental
such as during data transfer or calculation of actual intercept lengths
- Statistical
such as due to the random nature of the microstructure

A possible cause of a systematic error is that of calibrating the image from which measurements are to be made. In general, a single number is obtained for the magnification of an optical microscope. But, if the calibration is over different lengths or by different operators, the results will vary, producing a mean magnification and associated standard deviation. Errors are likely to be larger when using an SEM owing to magnifications not being fixed steps.

Accidental or personal errors will occur when measuring individual linear intercepts of WC grains. Different operators measuring along the same intercept line will not choose exactly the same intercept positions or may not detect all boundaries and this will lead to an uncertainty in the measurement. Accidental or personal errors are more difficult to quantify than systematic errors.

Statistical errors can arise if microstructures are inadequately sampled, e.g. too few micrographs are used, or too few grains are measured. A useful test of the adequacy of the statistics is to perform a running average test. As measurements are made, the mean linear intercept size or other parameters are continually re-computed to give running averages which are plotted against the total number of measurements made. The mean result will be seen to fluctuate but to converge towards the true mean for the microstructure with increasing numbers of measurements. Measurements can be halted when the residual fluctuations in the mean are adequately small.

5.6.2 Smallest measurable intercept

At present there are no Standards available relating to the smallest intercept size that can be measured by either optical or scanning electron microscopy. As a guide, the resolution of the instrument used can be used to determine the smallest intercept which can be measured. For a particular resolution, the lower limit to which linear intercepts can be measured are detailed in Table 2. These figures represent the highest resolution which can be obtained under optimum conditions. In practice poorer resolution may be obtained particularly when it is difficult to obtain high resolution images because of problems with surface preparation. Thus the length of the smallest intercept which may be sensibly measured will increase. In practice, the smallest intercept measurable is twice the resolution of the instrument and the uncertainty of the measurement is twice the resolution.

Table 2 - Guide to feasible measurements

INSTRUMENT	MAXIMUM RESOLUTION	MINIMUM VISIBLE INTERCEPT LENGTH
Optical Microscope	230 nm [*] 350 nm ^{**}	500 nm [*] 700 nm ^{**}
Scanning Electron Microscope	20 nm [*] 200 nm ^{**}	40 nm 200 nm
Field Emission Scanning Electron Microscope	1.5 nm [*] 10 nm ^{**}	3 nm 20 nm

* Theoretical resolution on a calibration sample.

** Practical resolution on typical hardmetal image.

Smaller intercept lengths than those recommended may be measured, but, the error in these measurement will increase rapidly. As a guide, the error of measuring the start and finish of an intercept line is twice the resolution, thus to obtain an error less than 10%, the intercept line should be at least twenty times the theoretical resolution. Thus, for an optical microscope working at the highest numerical aperture, only intercept distances greater than about 5 µm can be measured with an error of less than 10%. If the microstructure has a large proportion of WC grains whose linear intercepts are less than 5 µm, the error in measuring these could effect the measured mean linear intercept and distort the grain size distribution. In this case, scanning electron microscopes should be used.

6 Reporting

Objectives

- to provide confidence in the measurement method
- to report the results accurately
- to satisfy the needs of a quality system

When reporting the results of grain size measurement, all relevant information should be given to ensure traceability in those measurements. A single unannotated number such as the mean grain size does not instil confidence compared to when the detail of the measurement procedure is appended. A typical checklist should for example contain the following information:-

- Sample identification
- Etchant and etching time
- Traceability, calibration graticule number and calibration certificate
- Imaging technique :- Optical SEM or FESEM
- Magnifications used:- one or more
- No of fields of view measured
- Total number of intercepts
- Arithmetic mean linear intercept size
- Size distribution; as recommended in this guide. If other, then state method
- Additional comments

Additional information may also be necessary to fit in with a quality system. These might involve the identification of the image or photo micrograph(s) if archived, as well as information about the source of the material and the customer requesting the measurement to be made.

A typical report proforma is shown in appendix B.

It is also useful to consider the additional points

- Largest intercept measured
- Smallest intercept measured
- Largest grains
- Numerical aperture of objective for optical microscopy
- Accelerating voltage, working distance, illuminating aperture for SEMs.

7 Standards and References

- [1] BS EN 23878 : 1993, ISO 3878 : 1983. Hardmetals - Vickers hardness test.
- [2] BS5600 : Part 4 : Section 4.13: 1980, ISO 4499 - 1978 Powder metallurgical materials and products Part 4. Methods of testing and chemical analysis of hardmetals, Section 4.13 Metallographic determination of microstructure[ISO title : Hardmetals - Metallographic determination of microstructure]
- [3] George F Vander Voort, Metallography, principles and practices. McGraw-Hill, pp 229, 706, 1984.
- [4] L E Samuals, Metallographic Polishing by Mechanical Methods, 3rd edition. American Society for Metals, pp 320
- [5] S. Bradbury, An Introduction to the Optical Microscope, Royal Microscopical Society, Oxford Science Publications, p 29.
- [6] B Roebuck, E G Bennett and M G Gee, Grain Size Measurement Methods for WC/Co Hardmetals, 13 International Plansee Seminar, May 24-28 1993, Reutte, Austria, V2, 273-292.
- [7] B Roebuck and E G Bennett, Phase Size Distribution in WC/Co Hardmetals, Metallography, 1986, 19, No 1, 27-47.
- [8] J Wasén and R Warren, A Catalogue of Stereological Characteristics of Selected Solid Bodies, Volume 1: Polyhedrons, Department of Engineering Metals Publication (1990), Chalmers University of Technology, S-412 Göteborg, Sweden, pp 14-20.
- [9] J Wasén and R Warren, Mater. Sci. and Technol., 1989 (5), 222-226.
- [10] B Roebuck and M G Gee, Modelling the Effects of Structure Size Distribution on the Strength and Toughness of Hardmetals. 14th Int. Plansee Seminar, May 1997, Reutte, Austria, V2, 366-380.
- [11] J-H Han and D-Y Kim, Determination of 3-D Grain Size Distribution by Linear Intercepts, Acta. Material., 1998, 2021-2028.
- [12] B Roebuck and M G Gee, Modelling the Effects of Structure Size Distribution on the Strength and Toughness of Hardmetals. 14th Int. Plansee Seminar, May 1997, Reutte, Austria, V2, 366-380.
- [13] N J McCormick and B Roebuck, NPL CMMT(A)10, July 1996. A Technique for the Simulation of Hardmetal Microstructures.

- [14] B Roebuck, N McCormick, A Day and E G Bennett, NPL CMMT(A)141, January 1999. Measurement of WC Grain Size Distribution.
- [15] H E Exner, Powder Metall., 13 (26), 1970, 429-448.
- [16] K H Friedrich, H E Exner and H Tullhoff, Quantitative determination of discontinuous grain growth in WC/Co hardmetals, Proc. 10th Plansee Seminar 2: 792-810 (1981).
- [17] J Topping, Errors of Observation and Their Treatment, Science Paperbacks, Chapman and Hall, pp62, 1979.
- [18] BS EN 24489 : 1993, ISO 4489 : 1978. Sintered hardmetals - Sampling and Testing (which now supersedes BS5600 : Part 4 Section 4.11 Sampling and testing of sintered hardmetals, which has been withdrawn.)
- [19] BS DD ENV 623 -3 1993. Advanced technical ceramics - General textural properties, Part 3. Determination of grain size.

Appendix A: Measurement Case Study

Manual Analysis

Measurement of WC grain size and size distribution using the linear intercept technique

A1 Arithmetic mean linear intercept

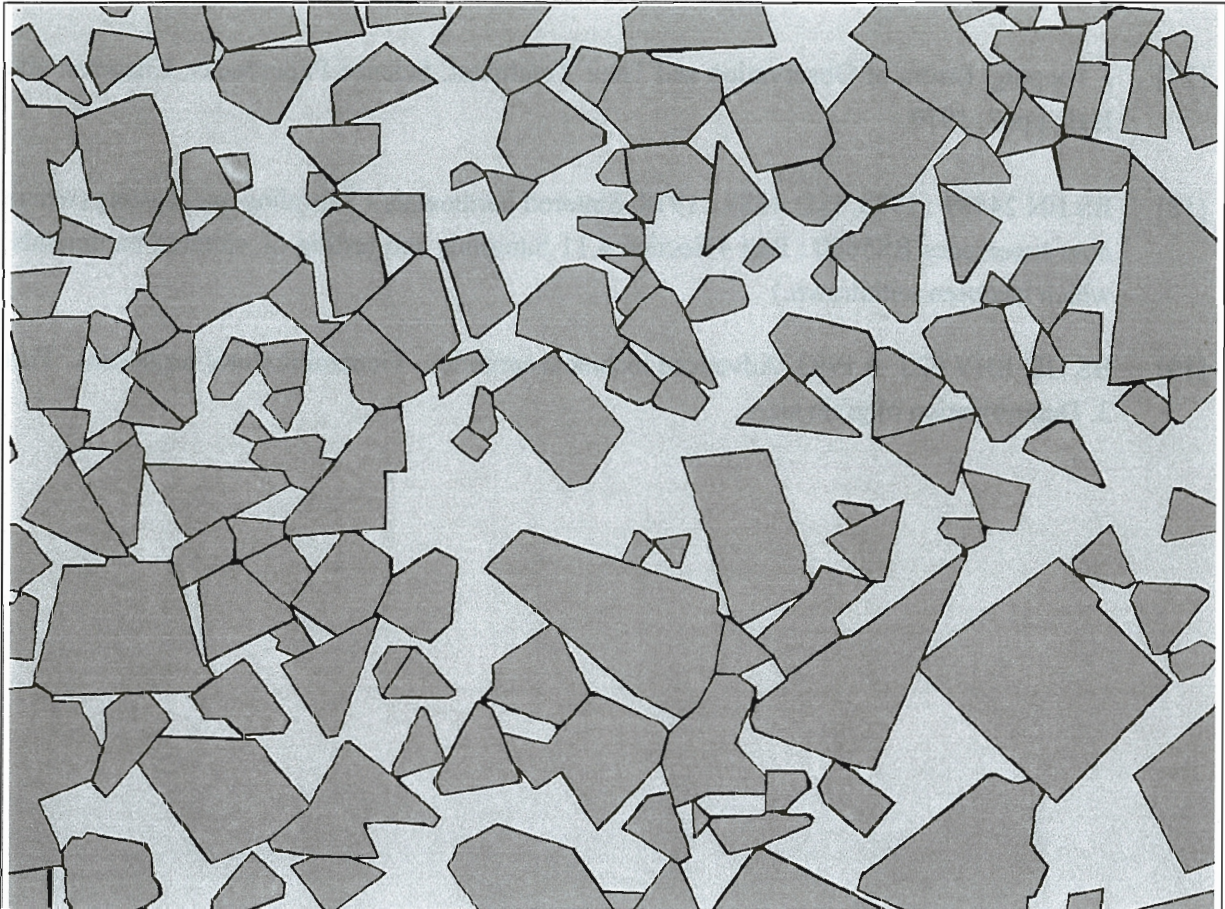


Figure. A1 - Idealised WC/Co hardmetal structure based on Fig.1. The image was chosen for clarity in describing the method for measuring grain size and size distribution using the linear intercept technique. Smaller grains have been removed from the image so as not to confuse the technique. In practice all grain intercepts should be measured.

STEP 1

Obtain an image of the microstructure, this should be representative of the material and free from polishing artefacts. The image may be obtained from an SEM or optical microscope. The choice of magnification will depend upon the grain size, but typically should contain about 15 to 20 grains across the field of view, as shown above.

STEP 2

Obtain an image of a scale or stage micrometer traceable to National Standards. This should be at the same magnification and conditions as used to obtain the image of the hardmetal microstructure as in STEP 1.

STEP 3

From the calibration image obtained in STEP 2, determine the magnification of the image using a Steel Rule (traceable to National Standards), measure the distance between set features on the image of the calibration stage micrometer, to the nearest 0.5 mm. Calculate the distance between the set features on the stage micrometer. In the case of the graticule shown in Fig. 2, the distance between lines is 10 μm , so if the distance between the centres of line 1 and 81 is measured, the actual size measured is 800 μm . The magnification obtained will depend upon the subsequent technique used to print the image.

$$\text{Magnification} = \text{Measured Size} / \text{Actual Size}$$

An estimate of the error of magnification may be made by measuring over different lengths of the calibration graticule and obtaining a mean and standard deviation of the magnification. Alternatively, a maximum and minimum error of the magnification may be obtained by assuming that the visual error of measurement is $\pm 0.5 \text{ mm}$.

$$\text{Maximum Magnification} = (\text{Measured Size} + 0.5 \text{ mm}) / \text{Actual Size}$$

$$\text{Minimum Magnification} = (\text{Measured Size} - 0.5 \text{ mm}) / \text{Actual Size}$$

For this particular example, Fig. A2 was reproduced and enlarged. The image of the calibration graticule was also enlarged by the same amount and the final mean magnification was calculated as x5750.

STEP 4

A series of parallel lines are drawn across the image of the hardmetal microstructure as shown in Fig. A2. These lines should be placed a sufficient distance apart such that only one line can intercept any particular grain. The number of lines placed on an image therefore depends upon the grain size.

STEP 5

Measure the length of line overlaying each carbide grain. These are the linear intercept lengths. The linear intercept lengths are shown in the image measurement mask Fig. A3. Grains which touch the border of the image should not be measured as the intercepts lengths are incomplete. The measured intercept lengths are entered into a table as shown in Table A1. The use of a spreadsheet is recommended.

STEP 6

For each of the measured intercept lengths, the true intercept length is obtained by dividing by the mean magnification. From these, the mean intercept length and standard deviation can be calculated as shown in Table A1. At least 200 intercepts should be measured, see section 5.4.

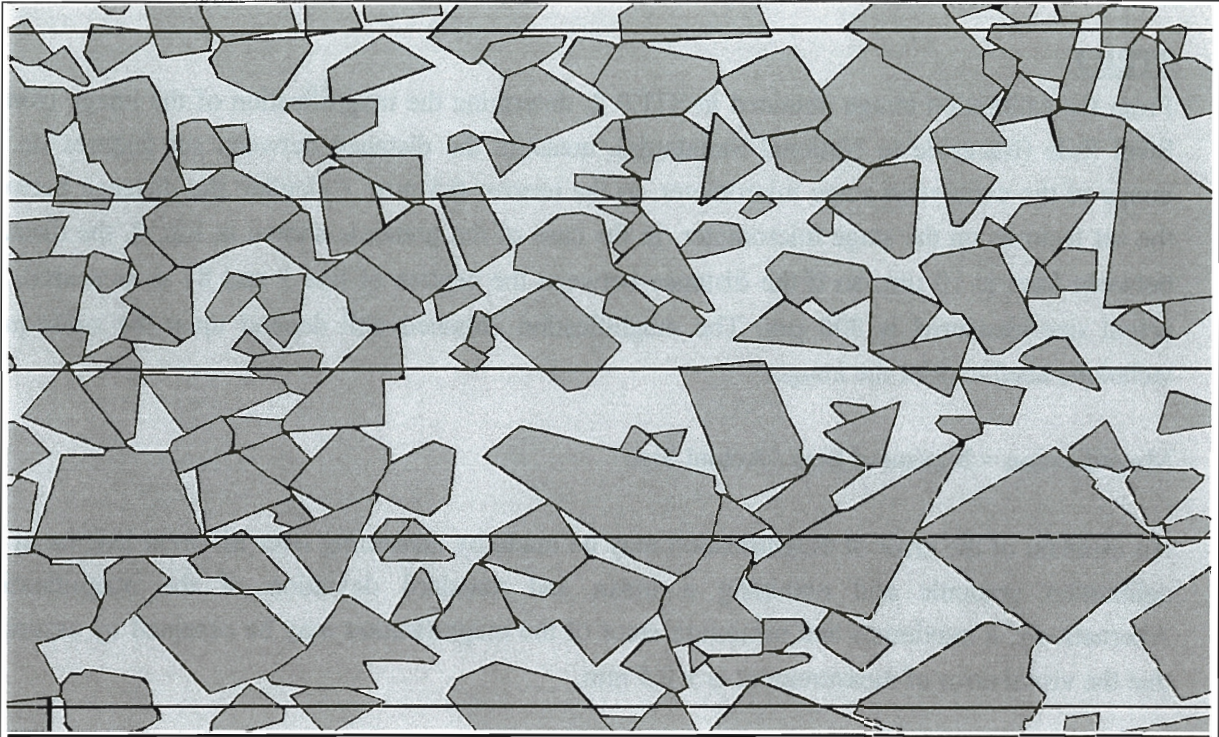


Figure A2 - Linear intercept lines drawn across Fig. A1. These have been placed far enough apart such that no carbide grain is intercepted by more than one line. More or fewer lines may be drawn on the image depending upon the grain size.

It can be useful to plot the running average mean intercept against the number of intercepts measured as a guide to how many intercepts need to be measured. In the example shown in Fig. A4 the mean value converges after about 250 measurements.



Figure A3 - Linear intercepts for measurement from Fig. A2. Intercepts touching the edge of the image should not be measured.

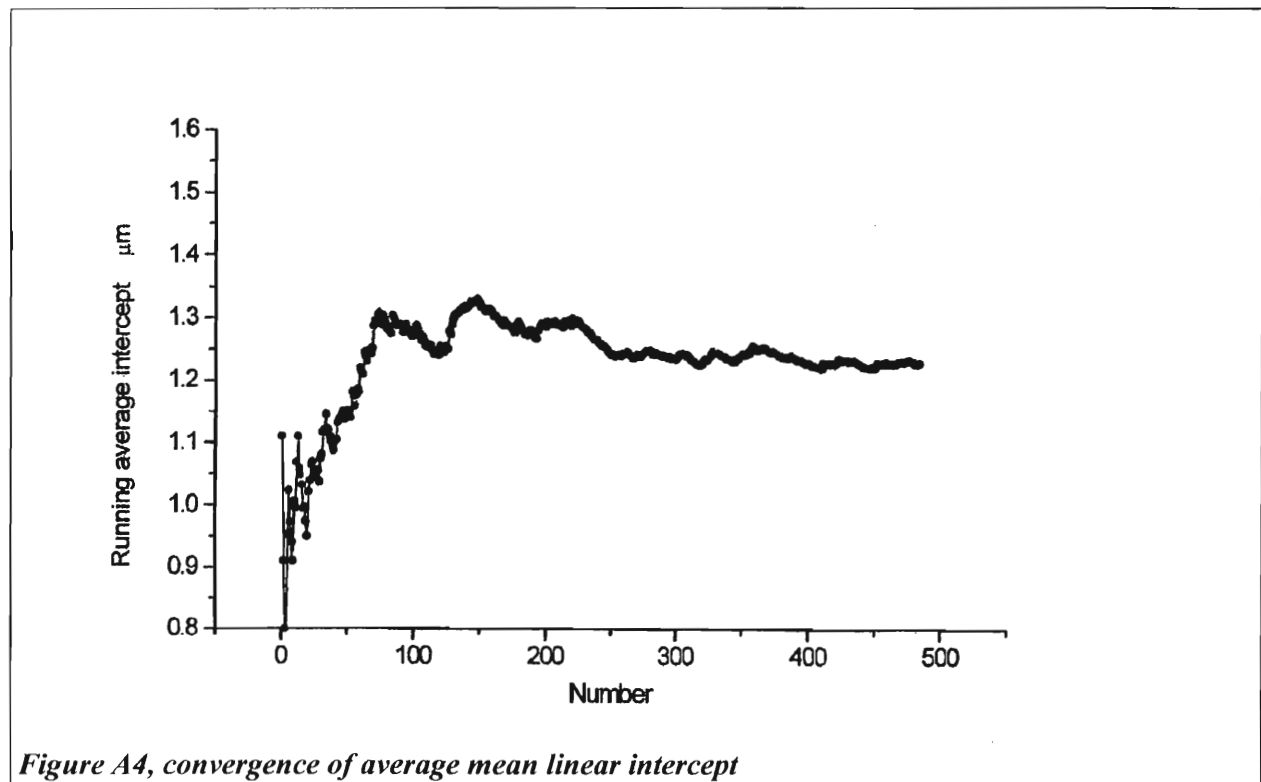


Table A1

Results of measurements made on image shown in Figure A1.

	Measured Intercept Length, mm	Calculated Intercept Length, μm		Measured Intercept Length, mm	Calculated Intercept Length, μm
Line 1	10.0	1.74	Line 4	34.0	5.91
	12.0	2.09		4.0	0.70
	13.0	2.26		15.5	2.70
	6.5	1.13		5.5	0.96
	18.0	3.13		7.0	1.22
	30.0	5.22		17.5	3.04
	23.5	4.09		23.0	4.00
	18.0	3.13		7.0	1.22
	8.5	1.48		2.5	0.43
	5.0	0.87		24.0	4.17
Line 2	11.5	2.00		49.0	8.52
	5.0	0.87		7.0	1.22
	24.5	4.26	Line 5	17.5	3.04
	11.0	1.91		10.0	1.74
	4.0	0.70		14.5	2.52
	9.5	1.65		27.5	4.78
	5.0	0.87		6.5	1.13
	2.0	0.35		18.0	3.13
	4.0	0.70		37.0	6.43
	18.5	3.22	Mean Intercept Length 2.33 μm No of Intercepts 50		
	7.0	1.22			
	6.0	1.04			
Line 3	2.0	0.35			
	8.0	1.39			
	14.5	2.52			
	13.5	2.35			
	1.0	0.17			
	12.0	2.09			
	17.5	3.04			
	12.5	2.17			
	10.0	1.74			

A2 WC Grain size (intercept) distribution

Follow the same steps as in the worked example for arithmetic mean size measurement to obtain a data set of intercepts. It is then necessary to follow the procedure given in Section 5.3.1. This can be done with the aid of a spreadsheet similar to the example given in Table A2 where the columns represent:

• The number of the measurement	i , with values 1 to N
• The intercept values	In measured sequence
• The intercept values sorted	In ascending order from smallest to largest
• The cumulative sum of intercept lengths	Each intercept is added to the previous cumulative total.
• Size (length) probability	Cumulative intercept length divided by the total intercept length (expressed as % or fraction)
• Number probability	Cumulative number divided by the total number of intercept lengths (expressed as %)
• Intercept lengths squared	To give an estimate of area
• The cumulative sum of estimated areas (intercepts squared)	Each value of estimated area is added to the previous cumulative total
• Size (area) probability	Cumulative estimated area divided by total estimated area (expressed as %)
• Normalised intercept length	Sorted intercept length value divided by arithmetic mean linear intercept length

The columns in the spreadsheet can be used to generate the appropriate graphs. Fig. A5 shows the data from the worked example plotted as number and estimated area probabilities versus log (intercept lengths, μm) on probability axes. Figure A6 shows the estimated area probability plotted against normalised intercept and compared with the model prediction taken from Fig.6.

Table A2

The spreadsheet contains the first 29 measurements from a total of 500 linear intercept measurements

Number	Intercept	Sorted Intercept	Cumulative Intercept	Size Probability	Number Probability	Int^2	Cumulative Int^2	Area Probability	Normalised Intercept
1	1.11	0.13	0.13	0.02	0.21	0.02	0.02	0.00	0.11
2	0.71	0.22	0.35	0.06	0.41	0.05	0.07	0.01	0.18
3	0.58	0.27	0.62	0.10	0.62	0.07	0.14	0.01	0.22
4	0.49	0.31	0.93	0.16	0.83	0.10	0.23	0.02	0.25
5	1.87	0.31	1.24	0.21	1.03	0.10	0.33	0.03	0.25
6	1.38	0.31	1.55	0.26	1.24	0.10	0.43	0.04	0.25
7	0.67	0.31	1.86	0.31	1.45	0.10	0.52	0.05	0.25
8	0.71	0.36	2.22	0.37	1.65	0.13	0.65	0.07	0.29
9	0.67	0.36	2.58	0.43	1.86	0.13	0.78	0.08	0.29
10	1.87	0.36	2.94	0.50	2.07	0.13	0.91	0.09	0.29
11	0.89	0.36	3.30	0.56	2.27	0.13	1.04	0.10	0.29
12	1.87	0.36	3.66	0.62	2.48	0.13	1.17	0.12	0.29
13	1.60	0.36	4.02	0.68	2.69	0.13	1.30	0.13	0.29
14	0.40	0.36	4.38	0.74	2.89	0.13	1.43	0.14	0.29
15	0.89	0.36	4.74	0.80	3.10	0.13	1.56	0.16	0.29
16	0.80	0.40	5.14	0.87	3.31	0.16	1.72	0.17	0.33
17	0.40	0.40	5.54	0.93	3.51	0.16	1.88	0.19	0.33
18	1.02	0.40	5.94	1.00	3.72	0.16	2.04	0.21	0.33
19	0.58	0.40	6.34	1.07	3.93	0.16	2.20	0.22	0.33
20	0.49	0.40	6.74	1.13	4.13	0.16	2.36	0.24	0.33
21	2.44	0.40	7.14	1.20	4.34	0.16	2.52	0.25	0.33
22	1.42	0.40	7.54	1.27	4.55	0.16	2.68	0.27	0.33
23	1.64	0.40	7.94	1.34	4.75	0.16	2.84	0.29	0.33
24	1.16	0.40	8.34	1.40	4.96	0.16	3.00	0.30	0.33
25	0.45	0.40	8.74	1.47	5.17	0.16	3.16	0.32	0.33
26	1.07	0.40	9.14	1.54	5.37	0.16	3.32	0.33	0.33
27	1.20	0.40	9.54	1.61	5.58	0.16	3.48	0.35	0.33
28	1.16	0.40	9.94	1.67	5.79	0.16	3.64	0.37	0.33
29	0.53	0.44	10.38	1.75	5.99	0.19	3.83	0.39	0.36

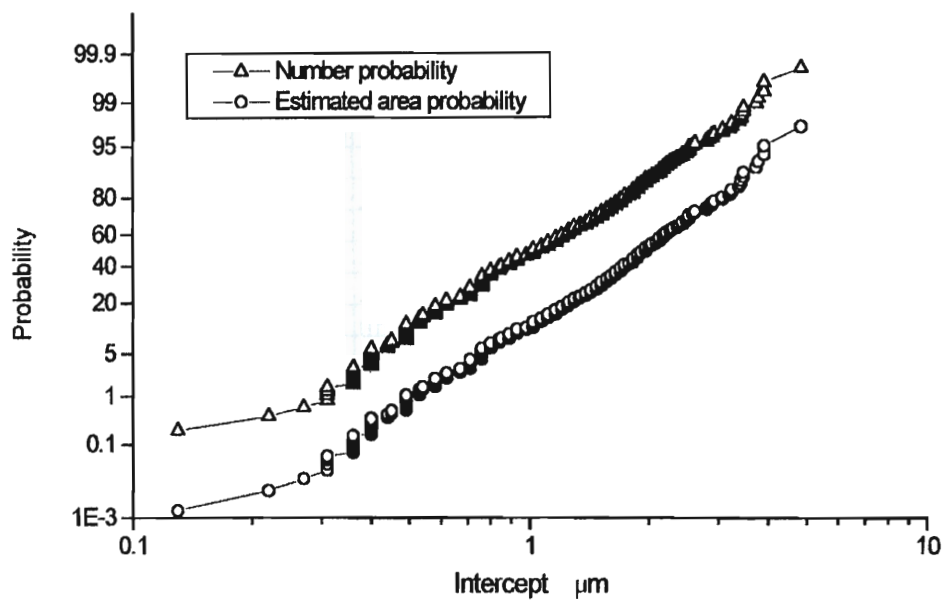


Figure A5, number and estimated area probability plotted against log intercept.

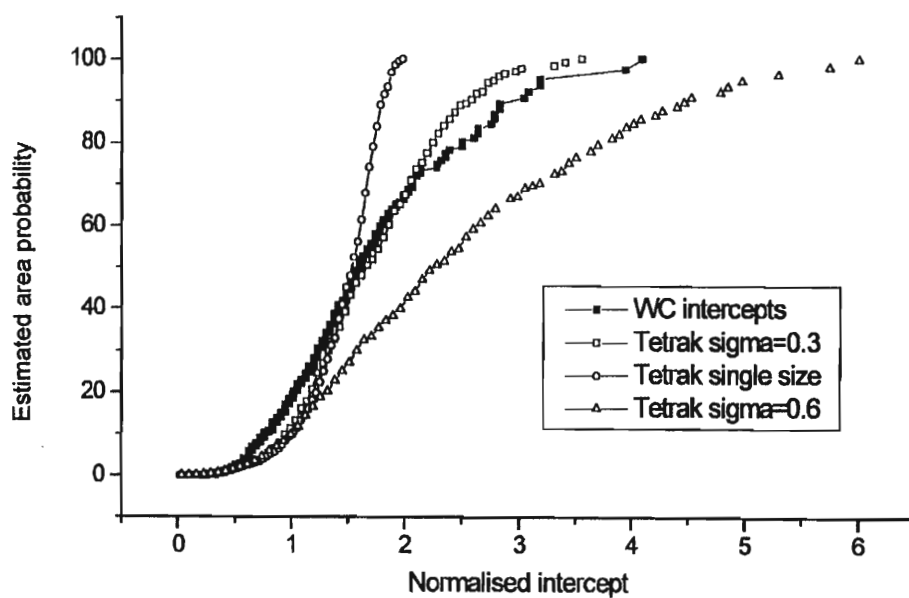


Figure A6 - Estimated area probability plotted against normalised intercept.

Appendix B: Report Proforma

GRAIN SIZE MEASUREMENT REPORT			
REPORT NUMBER		DATE	/ /
CUSTOMER			
ADDRESS			
MATERIAL IDENTIFICATION			
SAMPLE PREPARATION			
ETCHANT AND TIME			
IMAGE IDENTIFICATION		NO OF IMAGES USED	
ARCHIVED	YES / NO		
MAGNIFICATION		OBJECTIVE N. A.	
CALIBRATION CERTIFICATE			
RESULTS			
NO OF INTERCEPTS		MEAN LINEAR INTERCEPT	
OPERATOR		SIGNATURE	

Report proforma with results from measurements detailed in Table A1

GRAIN SIZE MEASUREMENT REPORT			
REPORT NUMBER	CMMT/000/000		10 / 04 / 1999
CUSTOMER	National Physical Laboratory		
ADDRESS	Queens Road, Teddington		
	Middlesex, TW11 0LW		
MATERIAL IDENTIFICATION	CWC25C, Materials Index Code WCX/04/01		
SAMPLE PREPARATION	Prepamatic polishing machine, procedure QPCMMT/B/136. Grinding stages, 120, 65 and 20 μm diamond. Lapping 6 μm Petrodisc M, Polishing 6, 3, and 1 μm diamond on DP Pan cloth.		
ETCHANT AND TIME	Murakami's reagent, 10 g KOH in, 10 gms $\text{K}_3\text{Fe}(\text{CN})_6$ in 200 ml water Etched 6 minutes at room temperature.		
IMAGE IDENTIFICATION	CWC25C.jpg	NO OF IMAGES USED	1
ARCHIVED	YES		
MAGNIFICATION	x1600	OBJECTIVE N.A.	1.4
CALIBRATION CERTIFICATE			
RESULTS			
NO OF INTERCEPTS	50		2.33 μm
OPERATOR	E G Bennett		<i>E G Bennett</i>

Appendix C: Polishing Routines

The following examples of polishing sintered hardmetals were provided by the EC HAMMER Thematic Network participants.

METHOD 1

Semi – automatic polishing machine techniques.

- Cutting and / or grinding
- Baking into Resin 5 standard bakelite
- Grinding on grinding machine type Struers Abraplan. Bakelite bonded abrasive disk with 100 μm diamond, or self adhesive grinding disks of 103 – 105 μm diamond abrasive.
- Rough polishing for 15 minutes on Struers Abrapol - 2 machine. In - house polishing medium consisting of 0.7 g of diamond powder (Dupont MSY 8 – 12 μm) in 2 decilitres of Mobile Velocite Oil No 3, or Struers 9 μm DP suspension. A paper board polishing cloth is used to prevent rounding of edges.
- Ultrasonic cleaning. Do not use hot water, cobalt binder phase materials will be affected.
- Fine polishing for 15 minutes on Struers Abrapol - 2 machine. In-house polishing medium consisting of 0.7 g of diamond powder (Dupont MSY 0 – 1 μm) in 2 decilitres of Mobile Velocite Oil No 3, or Struers 0.25 μm DP suspension. A paperboard polishing cloth is used to prevent rounding of edges.
- Occasionally a light polishing is made on a soft cloth to eliminate scratches.

METHOD 2

Manual hand polishing technique:

- Fine mechanical grinding with diamond wheel
- Coarse polishing with Texmet 2000 lap and 15 μm diamond suspension
- Medium polishing with Texmet 2000 lap and 6 μm diamond suspension
- Fine polishing with Lamplan 410 lap and 3 μm diamond suspension
- Fine polishing with Lamplan 410 lap and 1 μm diamond suspension
- Sample cleaned between polishing stages with alcohol

METHOD 3

Manual hand polishing technique:

- Sectioning using diamond cut off wheel
- Grinding until plane use bakelite bonded diamond, 120 μm
- Grinding for as long as the previous stage to remove surface damage, 65 μm
- Grinding for as long as previous stage to remove surface damage, 20 μm .
- Lapping on Struers Petrodisc M, visual examination to ensure all surface damage has been removed, Struers DP suspension, 6 μm and Struers “Blue” lubricant.*
- Pre - polishing on Struers DP Pan cloth or Buehler Texmet cloth for 5 minutes. Marcon 6 μm diamond abrasive and lapping fluid.*
- Pre - polishing on Struers DP Pan cloth or Buehler Texmet cloth for 5 minutes. Marcon 3 μm diamond abrasive and lapping fluid.*
- Pre - polishing on Struers DP Pan cloth or Buehler Texmet cloth for 5 minutes. Marcon 1 μm diamond abrasive and lapping fluid.*
- Polishing on Struers DP Nap cloth or Buehler Microcloth for 5 minutes. Marcon 1 μm diamond abrasive and lapping fluid.*
- An additional final polishing stage using Struers DP Nap or Buehler Microcloth for 5 minutes, 0.25 μm diamond abrasive and lapping fluid is used for samples being examined in a SEM.*

* Specimen washed in warm water with a detergent which does not effect binder phase, rinsed in alcohol and dried using compressed air. For specimens to be examined in a SEM, additional ultrasonic cleaning in acetone, alcohol wash and dried using compressed air.

METHOD 4

Automatic polishing machine (Struers Prepamatic) technique:

- Sectioning using diamond cut off wheel
- Grinding until plane use bakelite bonded diamond, 120 μm
- Hot mounting into 40 mm bakelite mounts.
- Grinding on Prepamatic polishing machine, bakelite bonded diamond, 65 μm , removal of 100 μm of surface material.*
- Lapping on Struers Petrodisc M, Struers DP suspension, 6 μm and Struers “Blue” lubricant, removal of 50 μm of surface material.*
- Pre polishing on Struers DP Pan cloth for 5 minutes. Struers DP suspension, 6 μm and Struers “Blue” lubricant.*
- Pre - polishing on Struers DP Pan cloth for 5 minutes. Struers DP suspension, 3 μm and Struers “Blue” lubricant.*

- Pre - polishing on Struers DP Pan cloth for 5 minutes. Struers DP suspension, 1 µm and Struers “Blue” lubricant.*
- Polishing on Struers DP Nap cloth for 1 minutes, Struers DP suspension, 1 µm and Struers “Blue” lubricant.*
- An additional final polishing stage using Struers DP Nap for 5 minutes Struers DP suspension, 0.25 µm and Struers “Blue” lubricant is used for samples being examined in a SEM.*

* The polishing machine has its own washing stage with a detergent which does not effect the binder phase, followed by an alcohol spray and compressed air drying. For specimens to be examined in a SEM, additional ultrasonic cleaning in acetone, alcohol wash and dried using compressed air is recommended after polishing or etching.

Conclusion

- As can be seen from the polishing routines, there are many different ways to produce a well polished surface of a hardmetal sample. Automatic polishing machines have the advantage stage.
- Each of the polishing stages must remove the surface damage produced by the previous stage from the whole of the specimen surface.
- The specimen (and holders for automatic polishing machines) must be thoroughly cleaned after each stage of preparation.

Appendix D: Names and Addresses of Suppliers

The following list of suppliers does not contain all companies which may exist within those countries. The inclusion of a company as a supplier of metallographic preparation equipment or consumables is not an endorsement of their products.

AUSTRIA

Wirtz Buehler GmbH
Leoben
Telefon (43) (3842) 46676

Struers
Geschäftsbereich der Radiometer GmbH
Alpenstrasse 96
A - 5020 Salzburg
Telefon (06 62) 62 57 11

DENMARK

Struers A/S
Valhøjs Allé 176
DK - 2610 Rødovre
Copenhagen
Denmark
Telephone +45 36 70 35 00

FRANCE

Kratkramer France Ltd
Limonest
Téléphone (33) (4) 72 179220

Struers Division Radiometer S.A.
8, rue Edmond Michelet
Z.A. La Fontaine du Vaisseau
F-93360 Neuilly-Plaisance
Téléphone 1 49 44 35 50

GERMANY

Wirtz Buehler GmbH
Düsseldorf
Telefon (49) (211) 974100

Struers
Geschäftsbereich der Radiometer GmbH
Linsellesstraße 142
47877 Willich-Schiefbahn
Telefon (02154) 818-0

HOLLAND

Struers Division Radiometer Nederland B.V.
Chroomstraat 6 -8
2718 RR Zoetermeer
Telefoon 079 - 361 45 93

ITALY

Giciesse S.R.L.
Milano
(39) (2)6620-1078

UNITED KINGDOM

MetPrep Ltd
Littleheath Industrial Estate
Old Church Road
Coventry
CV6 7ND
Telephone +44 (0)1203 638857

Struers Ltd
Erskine Ferry Road
Old Kilpatrick
Glasgow
G60 5EU
Telephone 01389 877222

Buehler Krautkramer
Millburn Hill Road
University of Warwick Science Park
Coventry
CV4 7HS
Telephone +44(0)1203 692242

Appendix E: Definitions and Symbols

Following the International Standard, ISO 4490 - 1978, the phases within the hardmetal have been designated as follows:-

α	Tungsten carbide.
β	Binder phase; cobalt, nickel or iron.
γ	Cubic carbide such as MC where M is any or a mixture of Ta, Nb, Ti and W.
η	Mixed carbide of W, C and binder phase.

AIA Automatic Image Analysis. Measurements are obtained from a digital image of the microstructure automatically by a computer based system. Usually by discrimination of the “grey levels” that define the feature of interest (grains).

IA Image Analysis. Measurement of some structure or feature of an image. For instance, volume fraction (area %) of a phase, grain size, shape or intercept length.

SAIA Semi-automatic Image Analysis. Measurements are obtained from a digitised image or an image on a digitising tablet. The operator marks off the regions or features of interest interactively which are then converted to the required measurement by a computer based system.

PIXELS Picture elements. The method by which a digital image is stored and displayed on image analysis systems.

SEM Scanning Electron Microscope. The term is usually used to describe thermionic emission instruments. These have a lower resolution and depth of field than a FESEM due to the larger spot size of the electron beam.

FESEM Field Emission Scanning Electron Microscope. High resolution scanning electron microscope with small spot size and high depth of field. The electron beam is produced with a high current intensity by field emission from a W filament.

N.A. Numerical aperture of the objective.

ENERGY

