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Ultrafine Grained Hardmetals
Grain Size and Distribution

The trend to ever smaller grained WC/Co hardmetals poses a severe challenge to the measurement of the mean size and distribution of the WC grains in the sintered structures of ultrafine grained materials.

The British Hardmetal Association Research Group provided NPL with a set of baseline hardmetals to support research into this measurement issue. This Measurement Note provides a summary of data on grain size and appropriate measurement procedures. Also included in the summary are magnetic and analytical data provided by industry together with graphs of the WC size distributions. Different methods of testpiece preparation suitable for satisfactory imaging of the structure of ultrafine grained materials are evaluated.

It is recommended that a high resolution field emission scanning electron microscope is used to image these extremely refined structures.

The terminology for the description of grain size is not standardised. A proposed scheme is discussed that includes the following

Range, μm	Description
<0.2	Nano
0.2-0.5	Ultrafine
0.5-0.8	Submicron
0.8-1.3	Fine
1.3-2.5	Medium
2.5-6.0	Coarse
>6.0	Extra Coarse

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Terminology

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 and sintered products.

A more intransigent problem is that of a definition for the size and/or distribution of the WC, either as a powder or in the hardmetal. There is as yet no standard available and a terminology scheme must take this into account. For example, powders are available with mean sizes expressed as particle diameters in 3-D; furthermore the mean value is given as the mean of the mass distribution of the 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. For example, an intercept distribution measured on an as-received powder might give an arithmetic mean linear intercept of about 0.6 μm from a powder sold with a mean particle diameter of 1.0 μm on a mass basis, assuming no substantive change in diameter occurs in the sintering process.

The appropriate definitions for size could, until acceptable standards are developed, be the arithmetic mean linear intercept obtained from 2-D polished cross-sections in sintered products and mean particle diameter (by mass) for powders. It should be clearly understood from this that ultrafine powders will not necessarily sinter to produce ultrafine hardmetals.

A Classification Scheme

A proposed scheme in current discussion by worldwide hardmetal communities is based on the following:

Size range μm	Terminology
< 0.2	Nano
0.2-0.5	Ultrafine
0.5-0.8	Submicron
0.8-1.3	Fine
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where the size range refers to the arithmetic mean WC intercept value in the sintered structure.

Rationale and Materials

The objective of this work was to establish a measurement procedure that could reliably be applied to the measurement of grain size distribution of these finer grained materials. The material with the finest grain size was eventually found to have an arithmetic mean linear intercept of 0.15 μm.

Sixteen WC based hardmetals were supplied by the Research Group of the British Hardmetals Association. Seven of these were subsequently found to have mean grain sizes, defined as the arithmetic mean linear intercept, less than about 0.5 μm, thus falling within the ultrafine to nano categories. Some of the materials contained binder-phases other than Co (Table 1).

Surface Preparation

The difficulties in resolving individual WC grains in the ultrafine materials can be seen in Fig. 1 where an optical micrograph at x1600 is shown. All that can be seen is that the structure is extremely fine.

Preparing the structure for grain size measurement in these fine grained materials is the key to obtaining useful data [2]. Various methods were explored, including the examination of fractured as well as polished and etched surfaces. This exercise demonstrated that both fractography, Fig. 2, and electropolishing, Fig. 3, show good potential in this respect but there were insufficient resources to obtain size distribution data using all the different preparation methods. However, these observations could underpin additional work in this area.

Grain size distribution data were based on a diamond grinding and polishing method down to 0.25 μm on a napless cloth to obtain a scratch free, flat surface that could be observed at magnifications up to x50k, without the presence of artefacts that might obscure the measurement process. The samples were then etched in a dilute (10% solution) alkali mixture of potassium hydroxide and potassium ferricyanide to reveal WC/WC boundaries followed by an etch for 30s in dilute nitric acid to remove the cobalt binder-phase, Fig 4.

Table 1 - WC based hardmetals

Material Code	Source	Coercivity, kAm^{-1}	Magnetic moment, $\mu T\ m^3\ kg^{-1}$	Composition wt%		HV30	Arithmetic mean linear intercept μm
				Co	Ni		
cw3	CW Carbides	28.1	0.44	3.0	0.0	1918	0.4
cwn8	CW Carbides	0.0	0.04	0.5	7.6	1301	0.85
ma6	Marshalls	12.6	0.87	5.9	0.0	1518	1.03
ma11	Marshalls	3.9	1.64	11.7	0.0	955	5.16
ma14	Marshalls	8.9	1.88	14.0	0.0	1206	0.91
macn9	Marshalls	29.2	0.83	6.0	3.0	1683	0.23
n15	Neepsend	14.7	1.9-2.0	14.5	0.0	1248	0.49
t25	Teco	6.8	3.0	24.2	0.0	980	0.77
h10	Hoybide	18.2	1.48	10.1	0.0	1367	0.41
shm3	Sandvik HM	32.0	0.45	3.3	0.0	2071	0.31
shmcn5	Sandvik HM	27.4	0.45	3.3	1.1	1953	0.37
shm9	Sandvik HM		-	9.0	0.0	2000	0.15
d10	Dymet	9.8	1.32-1.4	10.0	0.0	1336	1.05
uc9	Hydra	4.1	1.38-1.41	9.8	0.0	996	4.97
t	Hydra	8.4	0.95-0.99	9.1	0.0	1344	1.68
b9	Boart	11.6	1.13	8.3	0.0	1438	0.82

Figure 1: Optical micrograph of ultrafine grained hardmetal.

Figure 2: SEM image of fracture surface of ultrafine grained hardmetal.

Figure 3: High resolution SEM image of electropolished and etched surface of ultrafine grained hardmetal.

Figure 4: High resolution SEM image of alkali/acid etched ultrafine grained hardmetal.

Measurements

The polished and etched surfaces were examined in a high resolution field emission scanning electron microscope and images were obtained at magnifications high enough to resolve individual WC grains, usually greater than x20k for the ultrafine grained materials. About 10 images were obtained for subsequent measurement using image analysis equipment. Each image was targeted to encompass about 8-10 grains from side to side across which a line was drawn for measurement using the line intercept method [2]. The collected data were analysed using the running average method [2] to ensure that the arithmetic linear mean was representative. It was found, using the principle of running average [2], that at least 200 grains needed to be counted, Fig. 5.

Results

Cumulative number distribution data are plotted for all the sixteen materials in Fig. 6. It can be seen that the plots from individual hardmetals cover a wide range of WC grain sizes from coarse to ultrafine.

The results from the ultrafine grained hardmetals are shown in Fig. 7 where the data show good discrimination between the materials supplied and it can be seen that the measurement procedure allowed intercepts as small as 0.02-0.03 μm to be measured. This was thought to be adequate for measuring the size distribution of the materials supplied. However, if materials with mean grain sizes less than 0.1 μm are subsequently developed this procedure will probably require some modification since the smallest intercepts will be below the resolution limit of 0.02-0.03 μm.

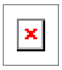

Figure 5: Running average intercept.

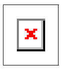

Figure 6: Grain size distribution in WC based hardmetals.

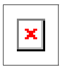

Figure 7: Grain size distribution in ultrafine grained hardmetals.

Summary

A method has been developed to satisfactorily measure the WC grain size distribution in several ultrafine grain hardmetals. A field emission scanning electron microscope provided micrographs of sufficiently high resolution to measure individual WC grains, even below 0.1 μm in size.

Sixteen WC based hardmetals were provided for study by the Research Group of the British Hardmetal Association. The smallest grained material had an arithmetic mean linear intercept of 0.15 μm.

References

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