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Hardmetals — Metallographic determination of microstructure —

Part 3: Measurement of microstructural features in Ti (C, N) and WC/cubic carbide based hardmetals

Métaux-durs — Détermination métallographique de la microstructure —

Partie 3: Mesure des caractéristiques des microstructures des métaux-durs à base de carbures Ti (C, N) et WC/cubiques

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 119, *Powder metallurgy*, Subcommittee SC 4, *Sampling and testing methods for hardmetals*.

ISO 4499 consists of the following parts, under the general title *Hardmetals — Metallographic determination of microstructure*:

— *Part 1: Photomicrographs and description*

— *Part 2: Measurement of WC grain size*

— *Part 3: Measurement of microstructural features in Ti(C,N) and WC/cubic carbide based hardmetals*

— *Part 4: Characterisation of porosity, carbon defects and eta-phase content*

Introduction

This part of ISO 4499 essentially covers the following topics:

— materials types and phases to be measured including the following:

  — Ti(C, N) cermets;

  — WC/Cubic carbide hardmetals;

— preparation methods to highlight differences between conventional WC/Co hardmetals and materials containing cubic phases;

— linear analysis techniques to acquire sufficient statistically meaningful data for phase quantification;

— analysis method to calculate representative average values;

— reporting to comply with modern quality requirements.

Hardmetals — Metallographic determination of microstructure —

Part 3: Measurement of microstructural features in Ti (C, N) and WC/cubic carbide based hardmetals

1 Scope

This part of ISO 4499 gives guidelines for the measurement of microstructural features in Ti(C,N) based hardmetals and WC/Co hardmetals that contain additional cubic carbides by metallographic techniques only using optical or electron microscopy. It is intended for sintered hardmetals (also called cemented carbides or cermets) containing primarily inorganic carbides and nitrides as the hard phase. It is also intended for measuring the phase size and distribution by the linear intercept technique.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4499–1:2008, *Hardmetals — Metallographic determination of microstructure — Part 1: Photomicrographs and description*

ISO 4499–2:2008, *Hardmetals — Metallographic determination of microstructure — Part 2: Measurement of WC grain size*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
nano
with carbonitride or cubic carbide phase size <0,2 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.2
ultrafine
with carbonitride or cubic carbide phase size 0,2 µm to 0,5 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.3
submicron
with carbonitride or cubic carbide phase size 0,5 µm to 0,8 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.4
fine
with carbonitride or cubic carbide phase size 0,8 µm to 1,3 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.5
medium
with carbonitride or cubic carbide phase size 1,3 µm to 2,5 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.6
coarse
with carbonitride or cubic carbide phase size 2,5 µm to 6,0 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.7
extra coarse
with carbonitride or cubic carbide phase size >6,0 µm, respectively

Note 1 to entry: Measured by the mean-linear-intercept method described in ISO 4499-2.

3.8
Ti(C, N) cermets
TiCN-based cermet contains 3 to 30 weight % of a binder phase mainly composed of Co and/or Ni, but may also include Mo

Note 1 to entry: The balance being substantially a hard phase and a few minor impurities.

Note 2 to entry: The hard phase is mainly composed of titanium carbide, nitride and/or carbonitride, but may also include carbonitrides of (Ti,Ta), (Ti,W) or (Ti,Ta, W).

Note 3 to entry: These materials typically contain hard phases that can have grains with a core/rim structure.

3.9
WC/Cubic carbide hardmetals
hexagonal WC-based hardmetals containing substantial amounts of a carbide having a cubic lattice, such as, for example TiC or TaC, and which can contain W in solid solution

Note 1 to entry: These materials typically contain hard phases that may have grains with a core/rim structure.

Note 2 to entry: See Table 1.

3.10
phase region
single constituent of the hardmetal like WC, cubic carbide or binder

4 Symbols and units

A	area, in square millimetres (mm^2)
ECD	Equivalent Circle Diameter of a specified phase, in micrometres (µm)
L	total line length in a specified phase, in millimetres (mm)
l_i	measured length of individual intercepts in a specified phase, in micrometres (µm)
$\sum l_i$	sum of the measured length of each individual intercept

l_x arithmetic mean linear intercept in phase x, in micrometres (µm)

N number of grain boundaries traversed in or between specified phases

n number of WC, carbonitride or cubic carbide grains intercepted

m magnification

m_{max} maximum magnification

m_{min} minimum magnification

5 Principle

This part of ISO 4499 addresses the issue of good practice for the measurement of a mean value for the hard phase and binder phase size in hardmetals other than straight WC/Co. It recommends the use of a linear intercept technique for obtaining data on feature sizes. The measurements are to be made using good practice for the preparation of suitable microstructures for examination outlined in ISO 4499-1.

Methods of metallographic preparation and etching techniques are as important as the phase size measurement method (see also ASTM B 657, ASTM B 665, Reference [1] and Reference [2]). Basic methods are described in ISO 4499-1. Further relevant information is given in Clause 8. The principal types of hardmetal considered are those that contain cubic carbides as well as WC and those that are based on TiC or Ti(C,N).[3][4][5] A cubic carbide phase is defined as a carbide having a cubic lattice, such as, for example, TiC or TaC, and which usually also contains W in solid solution after sintering. These materials typically contain hard phases that have grains with a core/rim structure. Guidelines to measure these internal details are included in ISO 4499–2:2008, Annex A.

The most direct way to measure the phase 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 feature size, either by area counting or by linear intercept techniques.

The following are three ways by which the mean size by number of the various phases can be defined:

— by length (of a line across a 2D section of a phase);

— by area (of 2D sections of phase regions);

— by volume (of individual phase regions).

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.

The values for phase size most used to date have been based on a length parameter. This can be obtained in the following several ways, for example:

— by parallel lines or circles as described in ASTM E112;

— by linear intercept, called the Heyn method, from a straight line drawn across the structure;

— by equivalent circle diameter (see ISO 4499-2), this is obtained by measuring hard phase grain areas and then taking the diameter of a circle of equivalent area.

6 Apparatus

6.1 Metallographic optical microscope, or other suitable equipment permitting observations and measurements on a screen up to the required magnification.

6.2 Scanning electron microscope, permitting observations and measurements of features too small to be resolved with an optical microscope.

6.3 Equipment for preparation of test-piece sections.

Phase size measurements are obtained from images of the microstructure. ISO 4499-1, ASTM B 657 and ASTM B 665 should be consulted for best practice in the preparation of surfaces for imaging.

Structural images are usually generated by either optical microscopy or Scanning Electron Microscopy (SEM). For accurate measurements, it is better to use scanning electron microscopic images. Even in coarse grained materials, the imaged surface cuts through a substantial number of the corners of grains giving a proportion of small intercepts that can only be measured accurately using the scanning electron microscope.

Measurements of intercept lengths from the acquired images can be obtained manually or semi-automatically using image analysis. Automatic image analysis can be used in some circumstances when the images are fairly coarse and good contrast can be obtained but for many materials, especially those with very fine grain sizes, good images are difficult to acquire and are generally not amenable to automatic analysis.

For the ultrafine and nano structural materials, good images are particularly difficult to acquire using conventional scanning electron microscopes with tungsten filament electron sources. It is recommended for these materials that a field emission SEM is used. These systems give significantly higher resolution images, sufficient to measure materials with mean intercept sizes of about 0,1 µm to 0,2 µm. For materials with ever smaller grain sizes, it can be necessary to use Transmission Electron Microscopy (TEM). However, the problems of sampling and specimen preparation are particularly severe. Careful specimen preparation for good images is vital for these materials and often a combination of etching methods is helpful (see ISO 4499-1).

7 Calibration

To give reliable quantitative measurements, images shall be calibrated against a stage micrometer or scale traceable to a National Reference Standard.

For images obtained from an optical microscope, an image of the calibration graticule shall also be obtained using the same objectives (and internal magnification step changers or zoom position) and illuminating technique. The microscope shall be set up for Köhler illumination to obtain the maximum resolution (see Reference [6]).

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.

8 Preparation of test samples

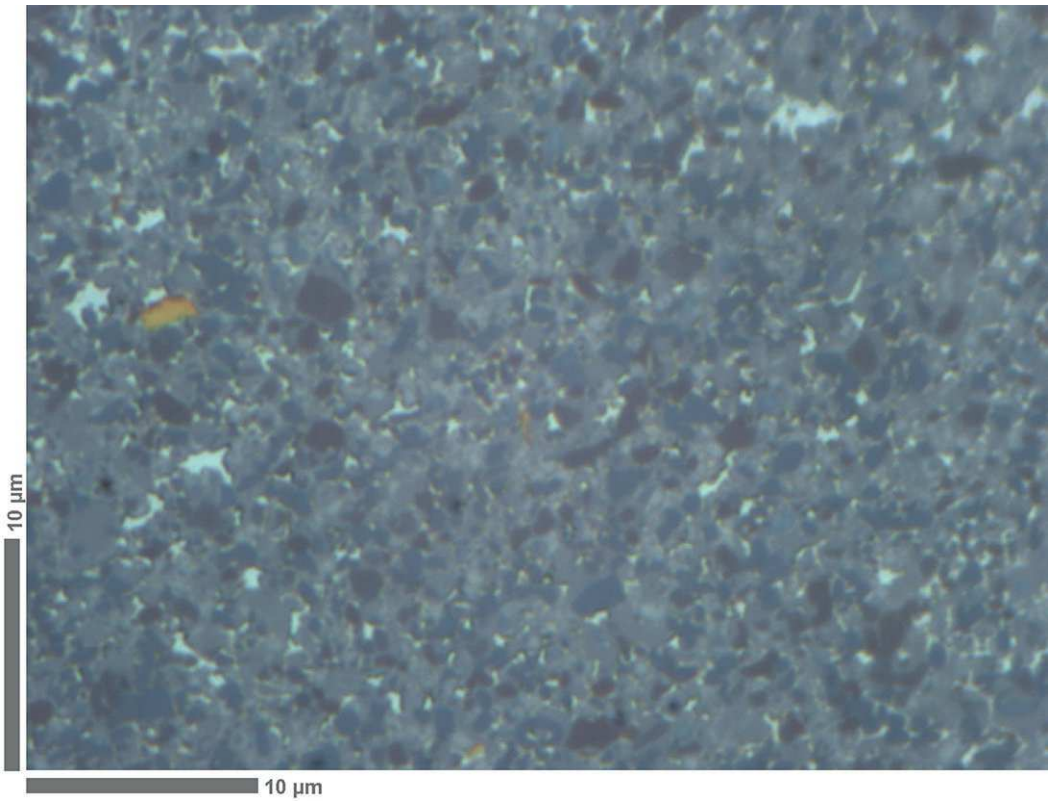
8.1 Metallographic preparation

The basic steps for good metallographic sections of hard materials are given in detail in ISO 4499-1:2008, 6.1 for sectioning, mounting, grinding, lapping, polishing and cleaning, except for the final polishing stage for these materials, which was performed using colloidal suspension of silica (at 40 nm particle size) on a napless silk cloth. Appropriate etching methods for cermets and hardmetals containing cubic carbides are outlined in 8.2 and 8.3, respectively.

8.2 Ti(C, N) based hardmetals – cermets

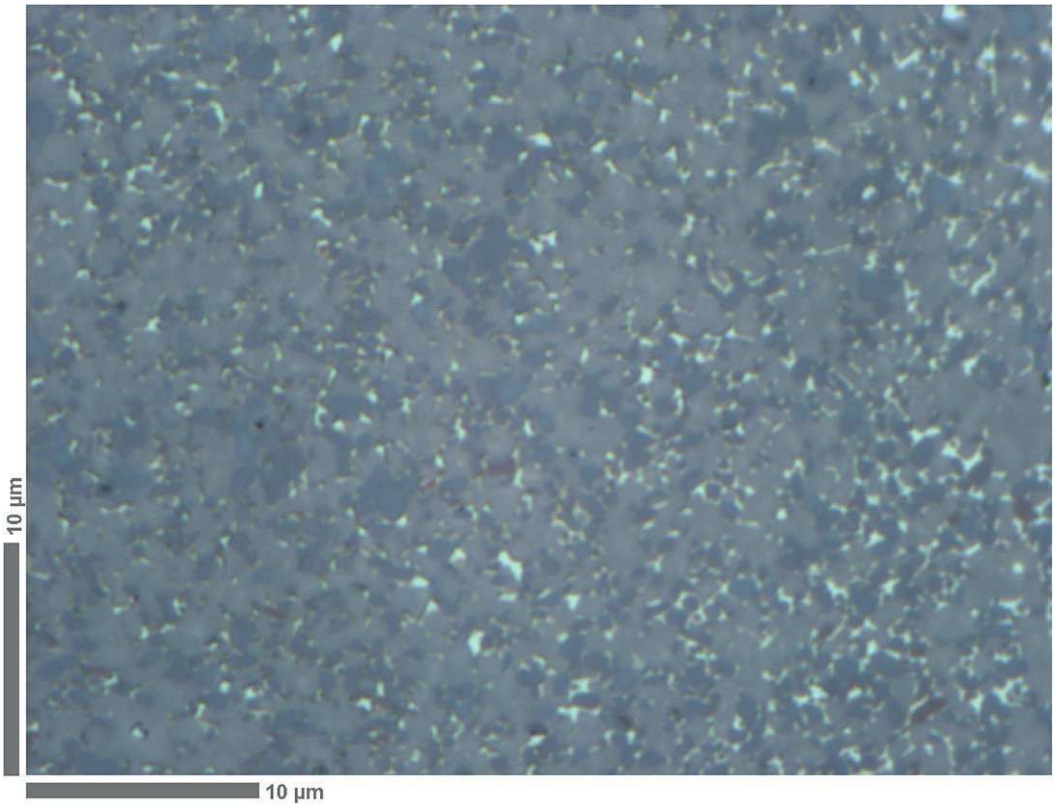
The preparation of the test samples is recommended to be according to ISO 4499-1:2008, 6.2.1 by using etching technique 1. The conditions of etching in mixture A should be changed to approximately 20 °C

for 30 s to 60 s. Representative images of typical cermets are shown in Figure 1 to Figure 5 for both optical and electron microscopical techniques. The SEM images show that many of the hard phase particle have a core/rim structure, where the dark "cores" are undissolved Ti(C,N) from the original powder mix and the grey "mass" are (Ti,W,X)(C,N) structures, of the same orientation as the "core" formed during liquid phase sintering at high temperature.



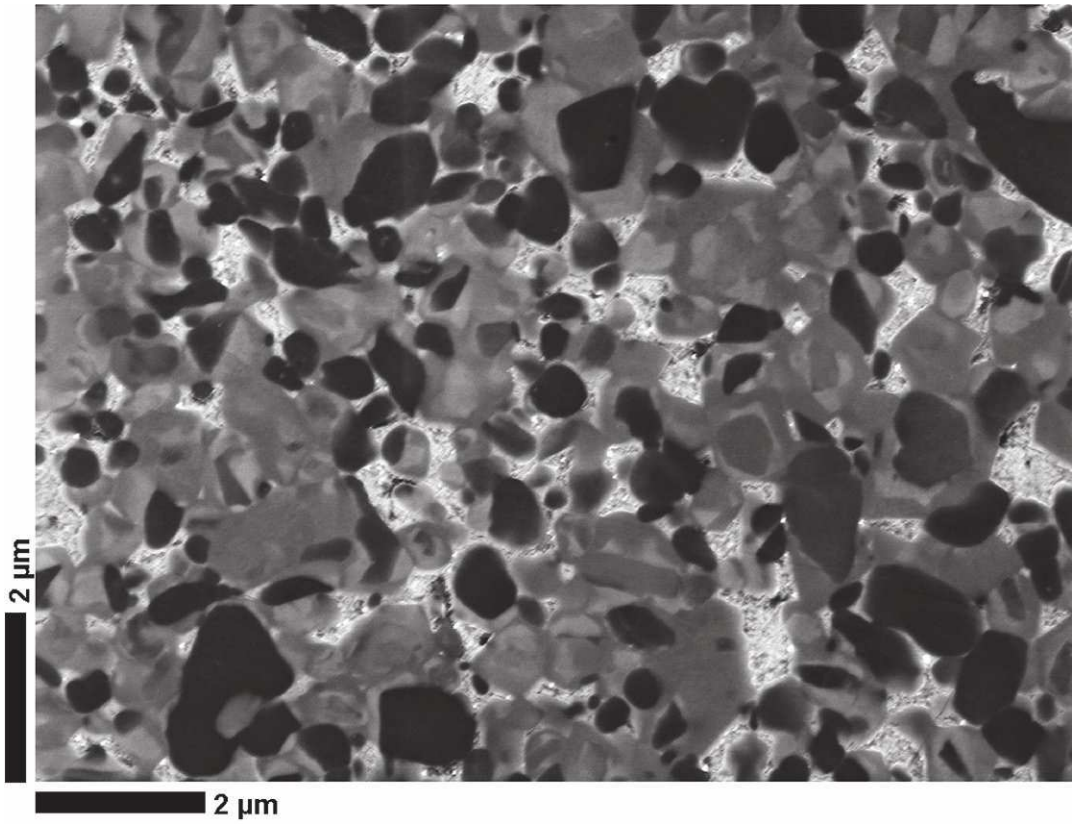
NOTE When using an optical microscope, major phases appear as binder phase (light blue), undissolved Ti(C,N) from original powder (dark blue-grey), (Ti,W,X)(C,N) (grey) and TiN impurity (gold).

Figure 1 — Low binder phase content (6 wt %) commercial cermet, optical micrograph using oil immersion objective, original magnification ×1 600



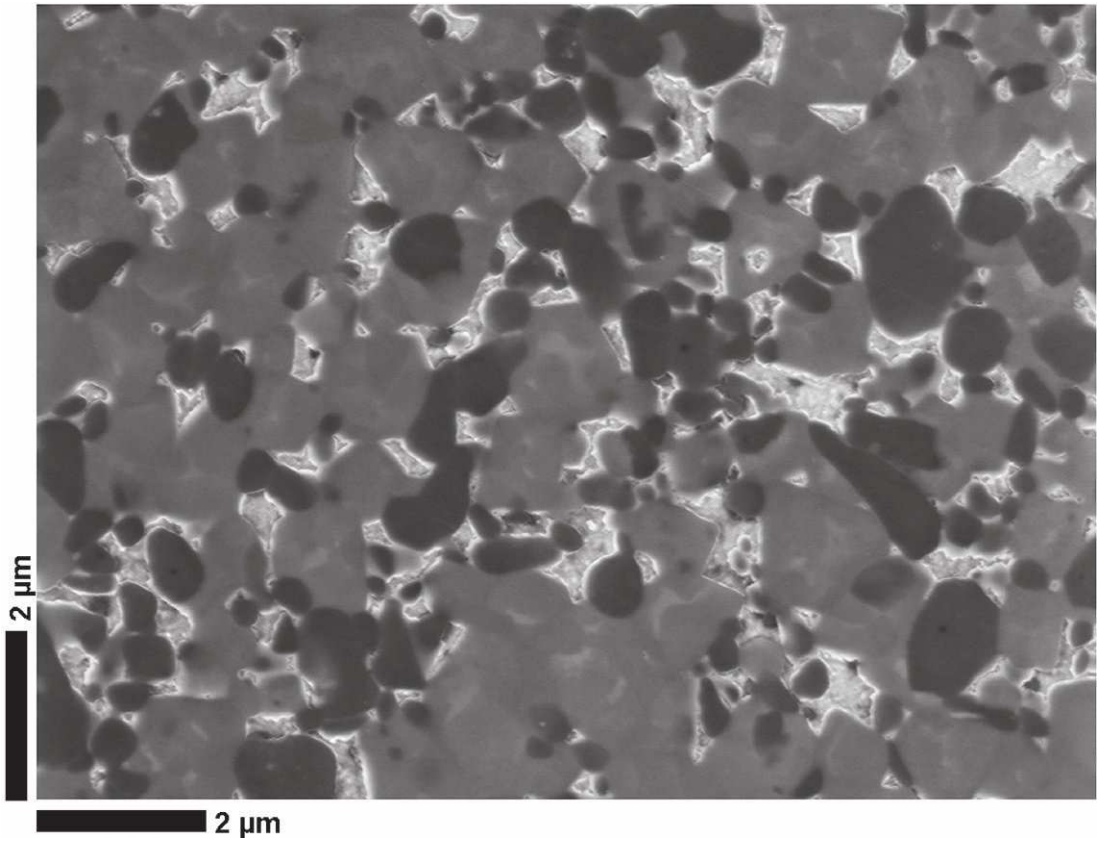
NOTE When using an optical microscope, major phases appear as binder phase (light blue), undissolved Ti(C,N) from original powder (dark blue-grey), and (Ti,W,X)(C,N) (grey).

Figure 2 — Medium binder phase content (11 wt %) commercial cermet, optical micrograph using oil immersion objective. Original magnification ×1 600



NOTE Major phases are binder phase (light), undissolved Ti(C,N) from original powder (dark grey) and (Ti,W,X)(C,N) of variable composition (pale grey).

Figure 3 — Low binder phase content (6 wt %) commercial cermet, scanning electron microscope secondary electron image, original magnification ×30 000



NOTE Major phases are binder phase (light), undissolved Ti(C,N) from original powder (dark grey) and (Ti,W,X)(C,N) of variable composition (pale grey).

Figure 4 — Medium binder phase content (11 wt %) commercial cermet, scanning electron microscope secondary electron image, original magnification ×30 000

8.3 WC/Cubic carbide based hardmetals

In the former hardmetal microstructural standard ISO 4499, this type of material was illustrated with three examples of mixed WC/cubic carbide materials where the hard phase is given the Greek letter, γ, as identifier. It is recommended in this update to the International Standard that the γ name is retained but that the size is defined more precisely by linear intercept measurements. Preparation of samples in the use of etching technique 2 is as described in ISO 4499-1:2008, 6.2.1, i.e. etch in Murakami's reagent (mixture A) for about 3 min; followed by etch in concentrated HCl (mixture B) for 10 s; followed by wash in water then alcohol and a final etch in mixture A for 20 s.

Four different grades of cubic carbide hardmetals are illustrated in the standard with compositions as shown in Table 1.

Table 1 — Composition of WC/Cubic carbide based hardmetals

	Cobalt %	Tantalum %	Titanium %	Niobium %
Material 1	5,7	1,9	Trace	Trace
Material 2	6,3	3,5	2,0	1,5
Material 3	11,5	1,9	Trace	0,4
Material 4	9,5	5,5	6,0	2,5

Representative images are shown in Figure 5 to Figure 12 (optical) and Figure 13 to Figure 20 (SEM).

The optical images were obtained using an ×100 oil immersion objective with a numerical aperture of 1,3 at nominal magnifications of ×1 000 and ×1 600. When using an optical microscope, major phases appear as binder phase (white), tungsten carbide (blue/grey) and cubic carbide (pale orange).

The SEM images were taken under the same operating conditions, 9 kV accelerating voltage, 15 mm working distance, secondary electron mode. The SEM images show the major phases binder phase (black), tungsten carbide (light grey) and cubic carbide (medium grey).

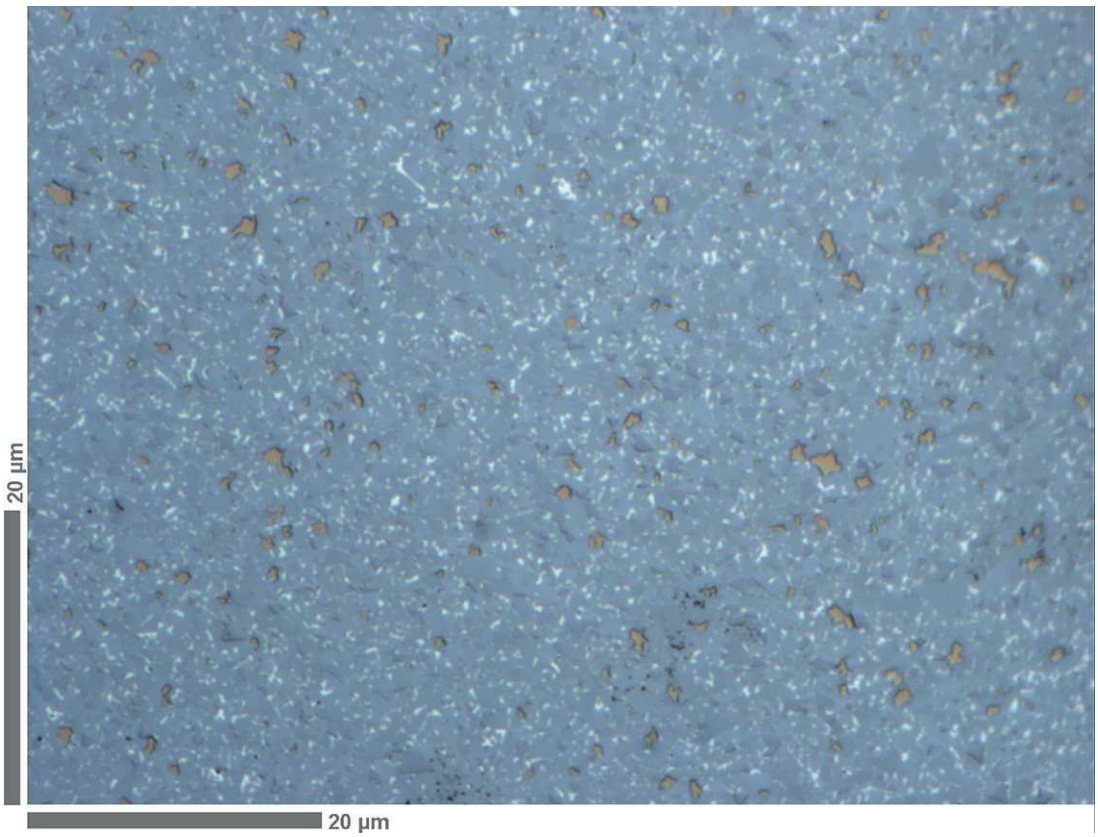


Figure 5 — Material 1, optical micrograph, original magnification ×1 000

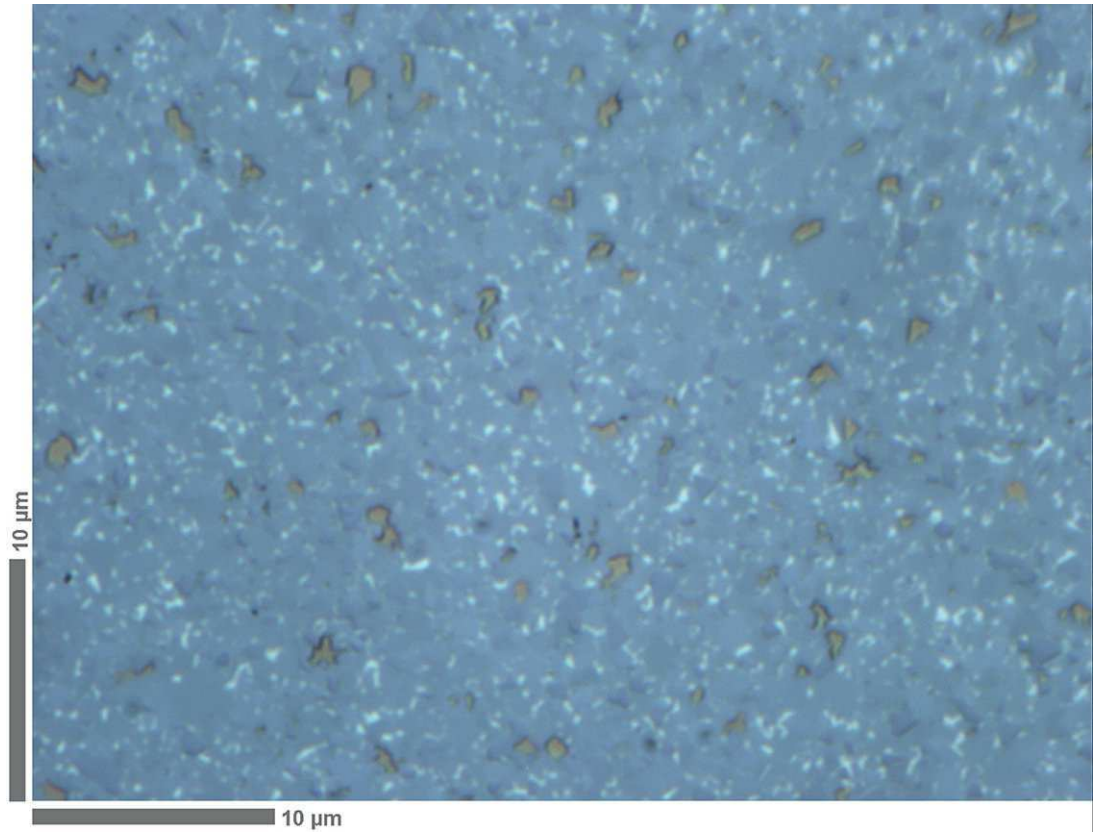


Figure 6 — Material 1, optical micrograph, original magnification ×1 600

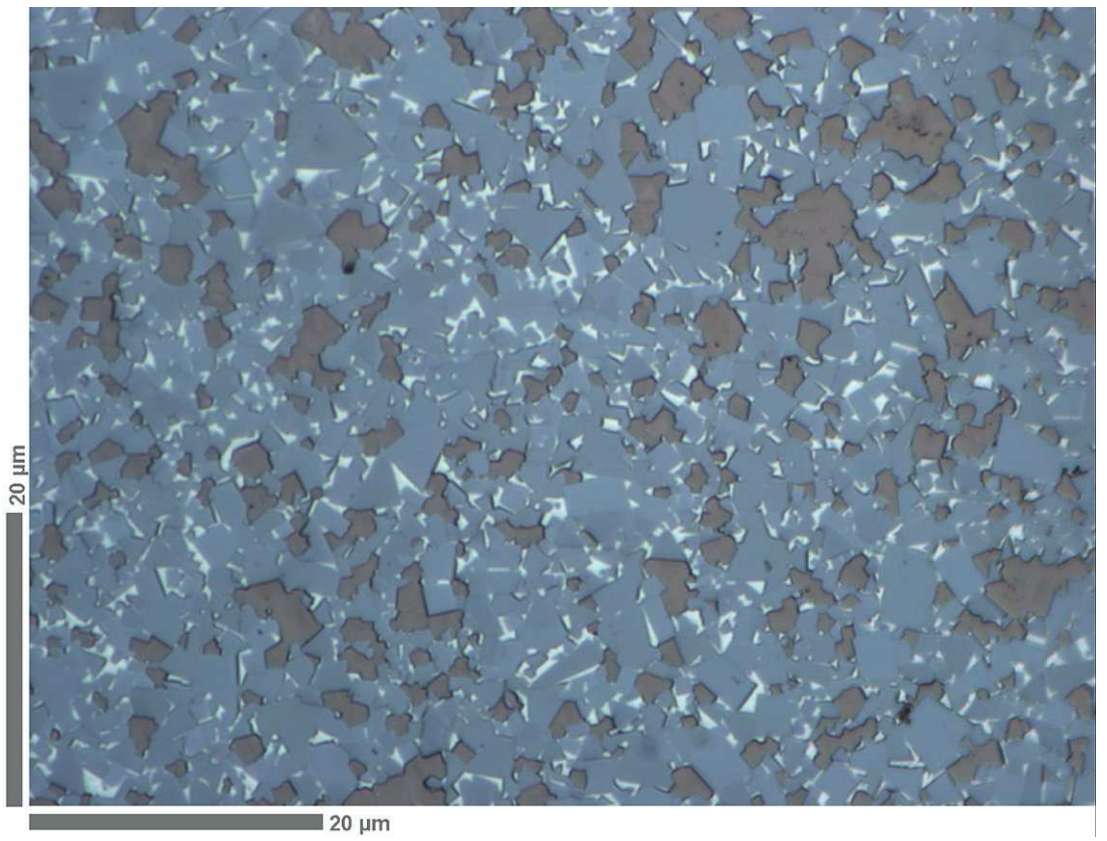


Figure 7 — Material 2, optical micrograph, original magnification ×1 000

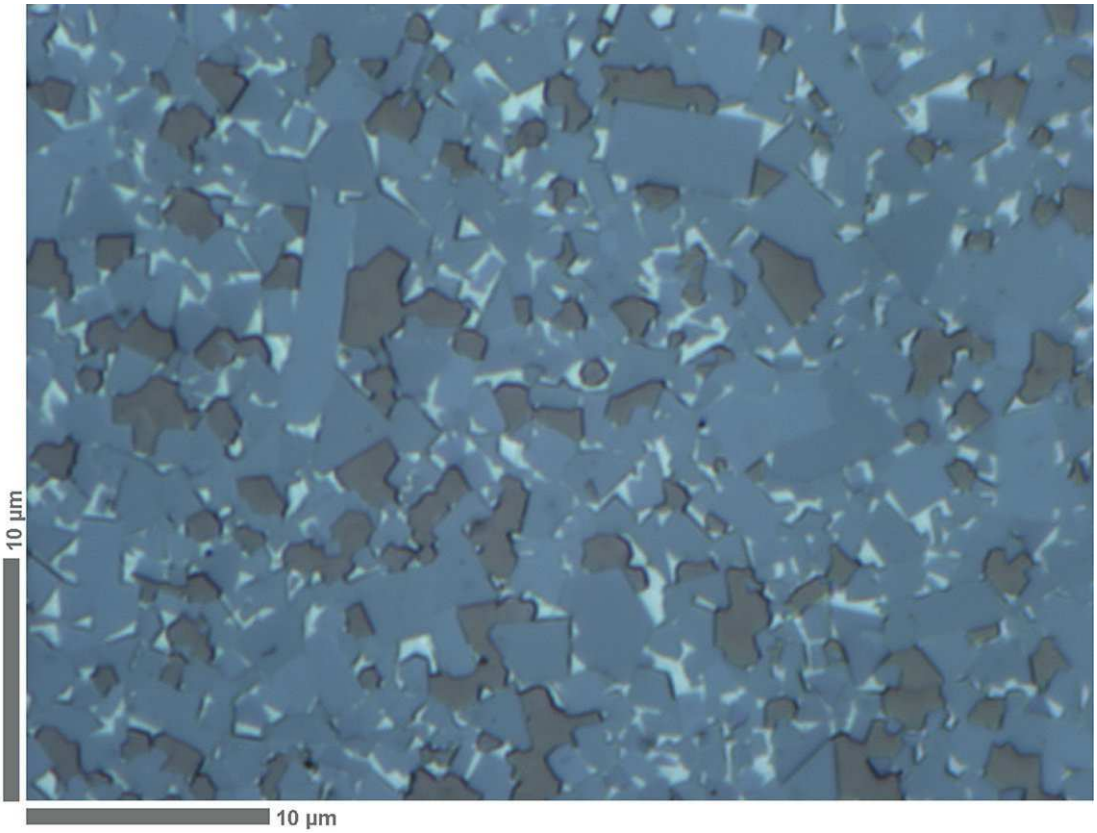


Figure 8 — Material 2, optical micrograph, original magnification ×1 600

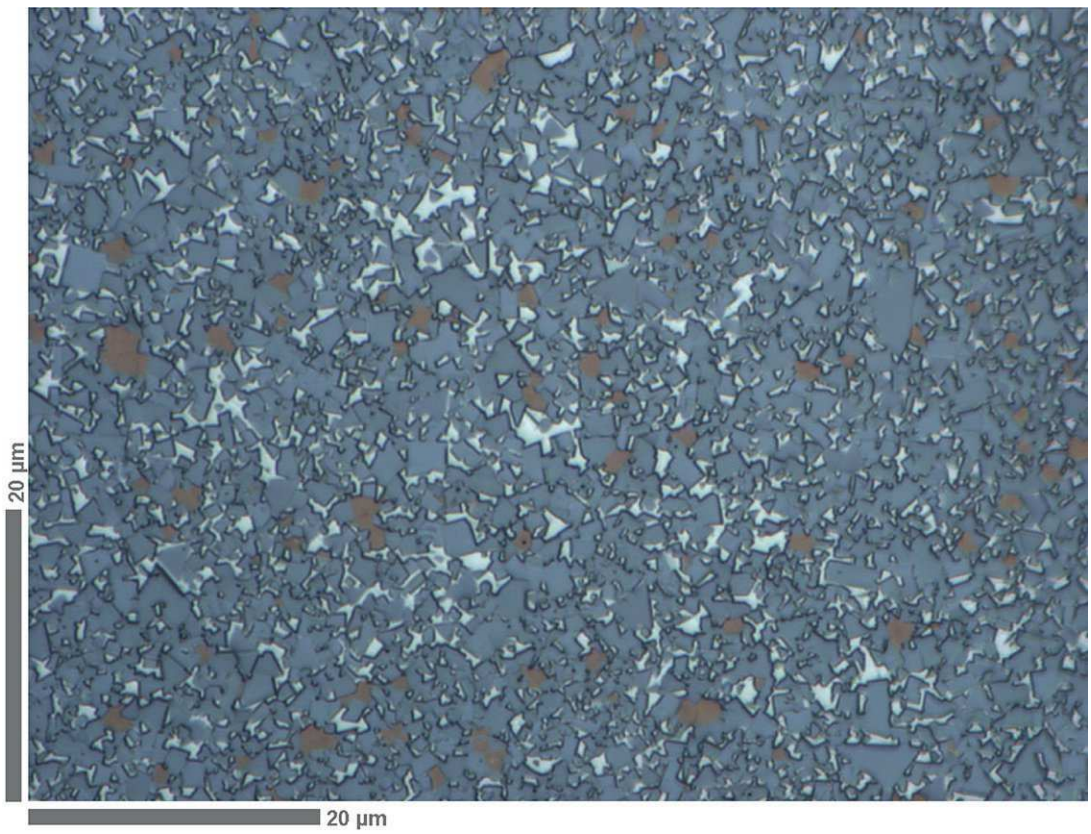


Figure 9 — Material 3, optical micrograph, original magnification ×1 000

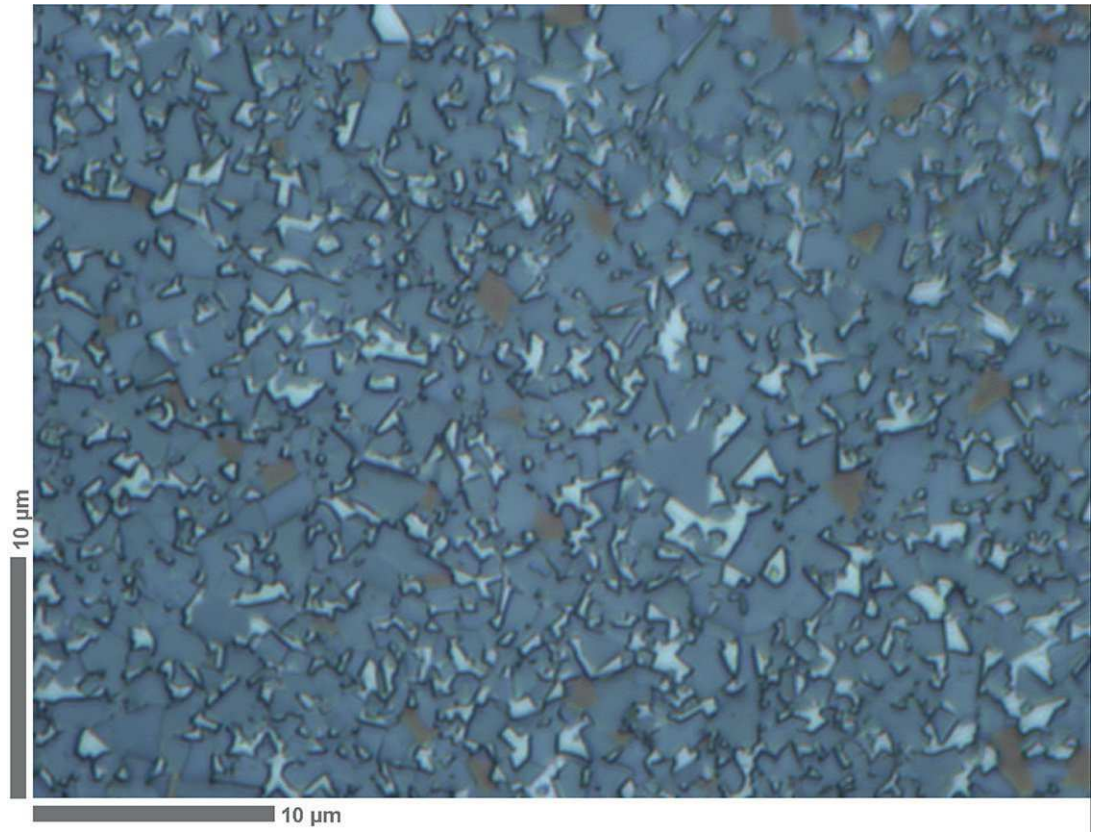


Figure 10 — Material 3, optical micrograph, original magnification ×1 600

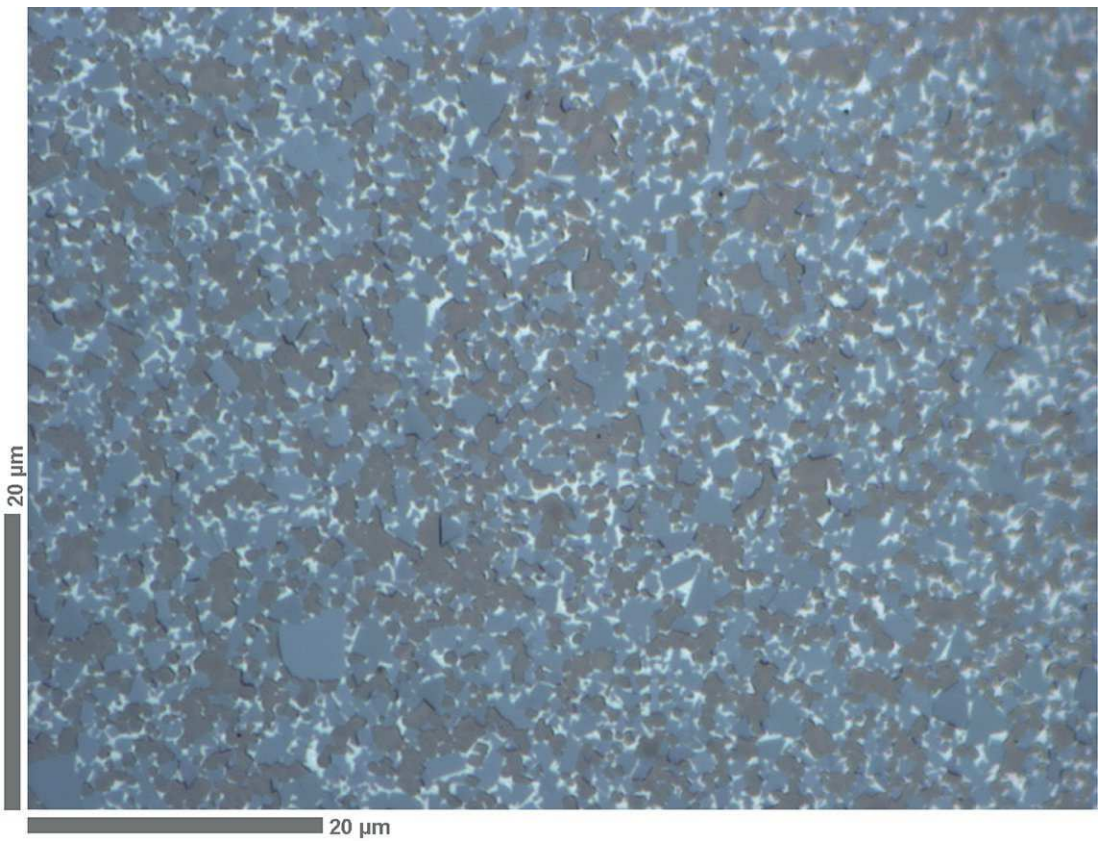


Figure 11 — Material 4, optical micrograph, original magnification ×1 000

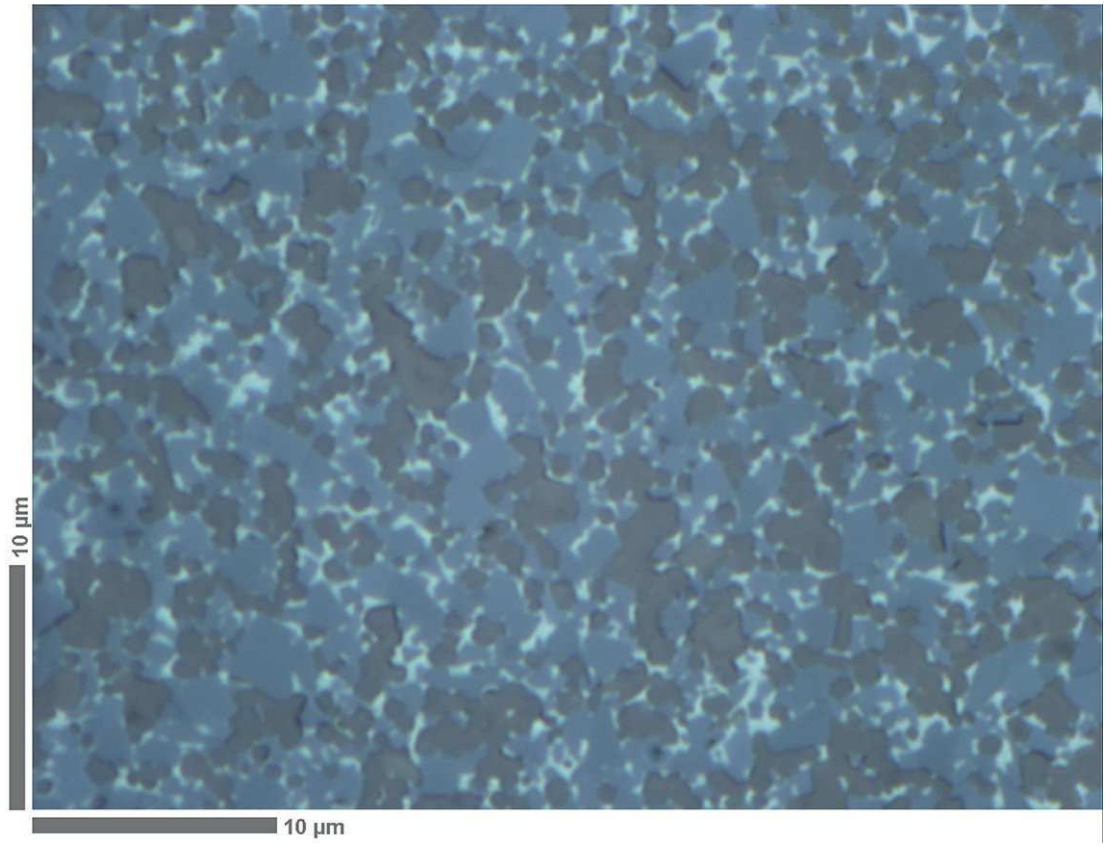


Figure 12 — Material 4, optical micrograph, original magnification ×1 600

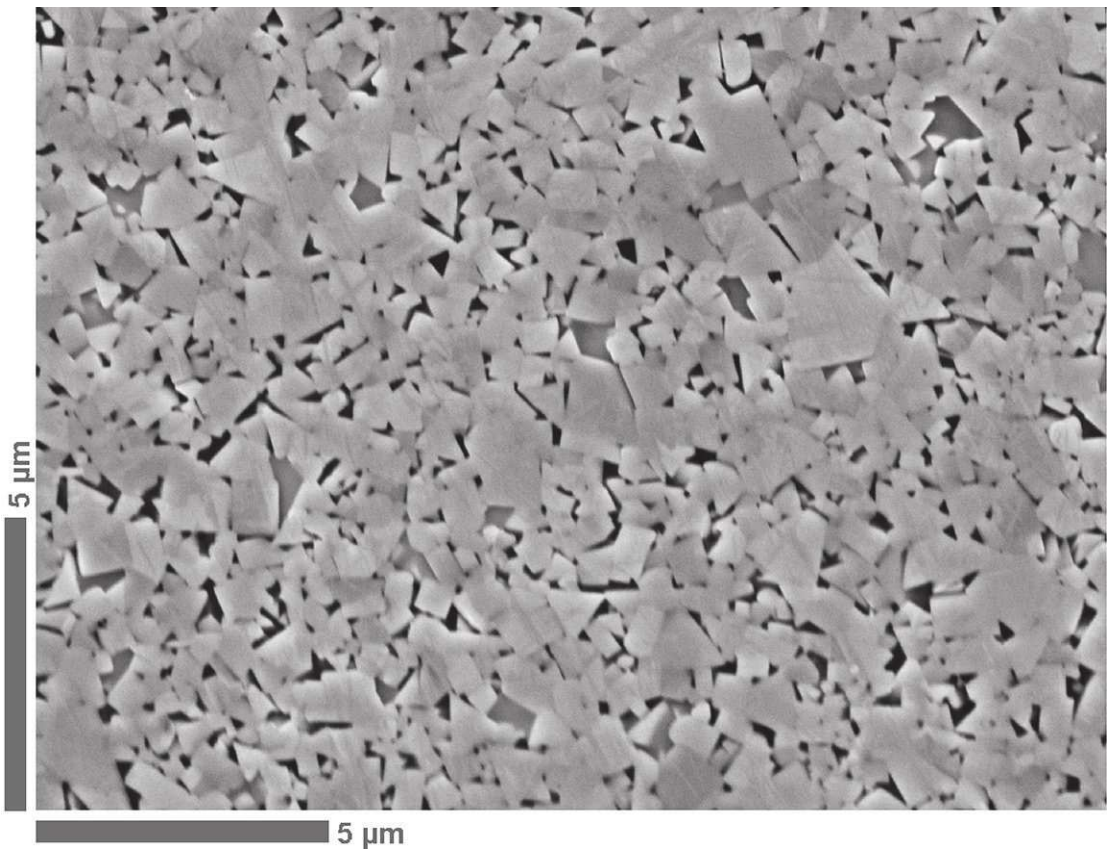


Figure 13 — Material 1, SEM micrograph, original magnification ×20 000

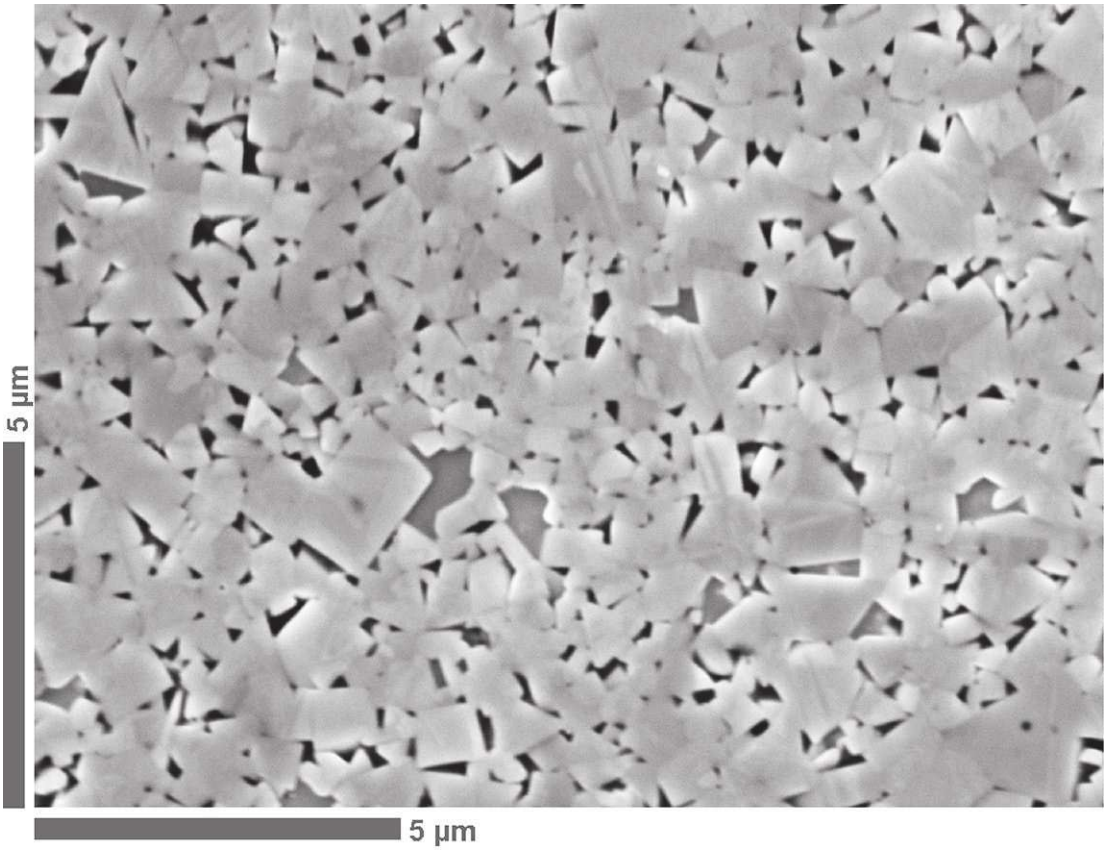


Figure 14 — Material 1, SEM micrograph, original magnification ×25 000

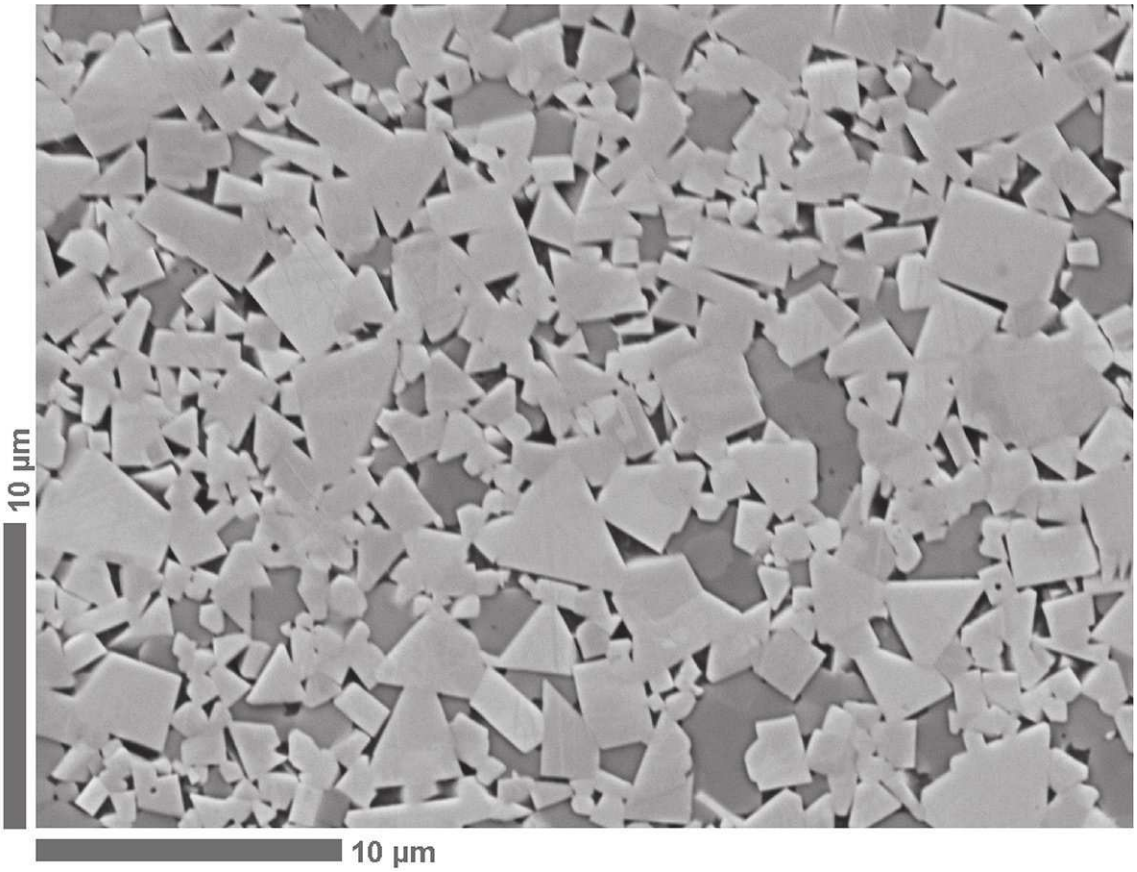


Figure 15 — Material 2, SEM micrograph, original magnification ×10 000

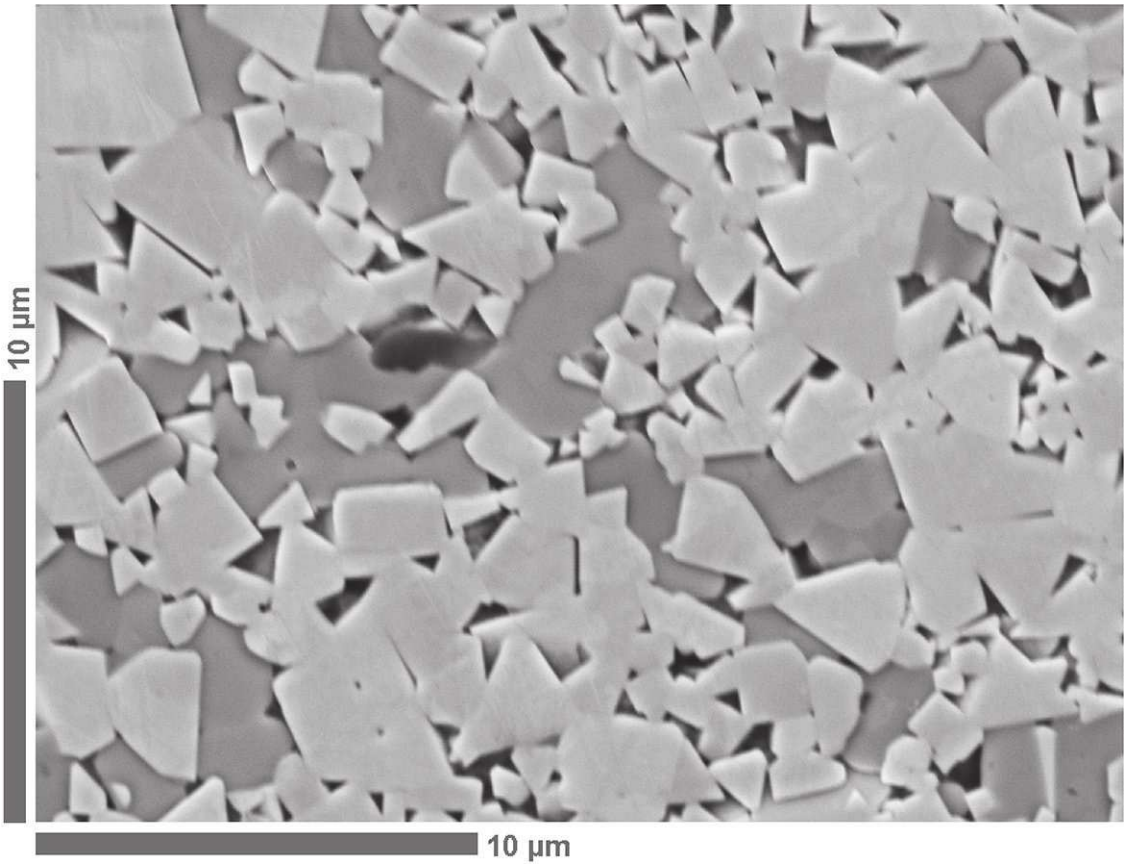


Figure 16 — Material 2, SEM micrograph, original magnification ×15 000

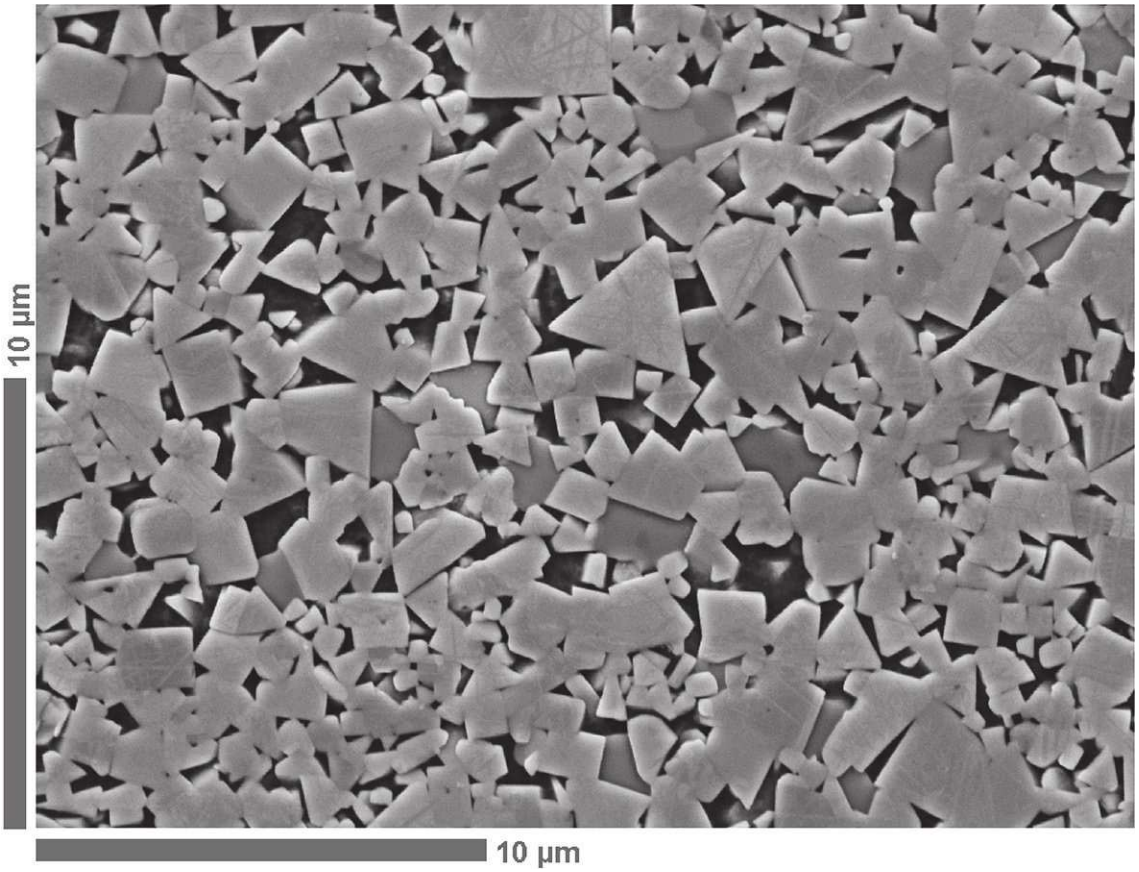


Figure 17 — Material 3, SEM micrograph, original magnification ×15 000

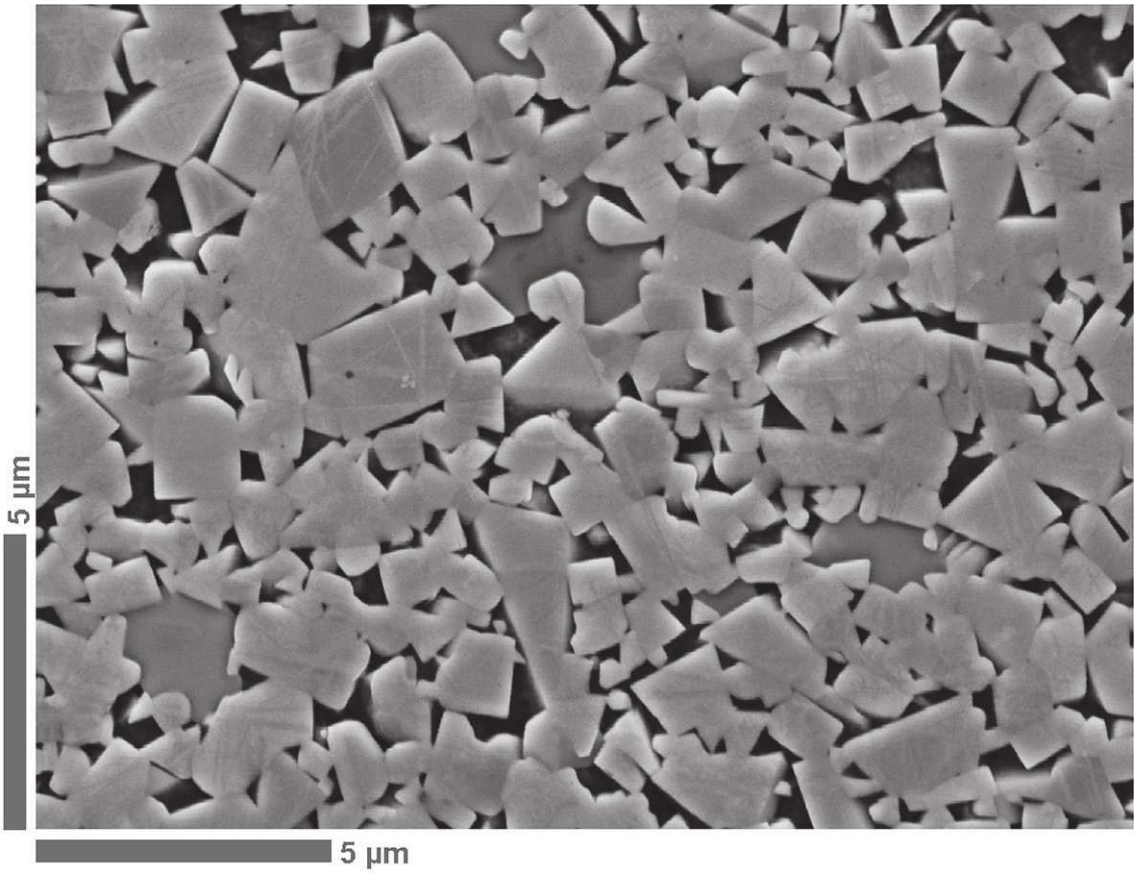


Figure 18 — Material 3, SEM micrograph, original magnification ×20 000

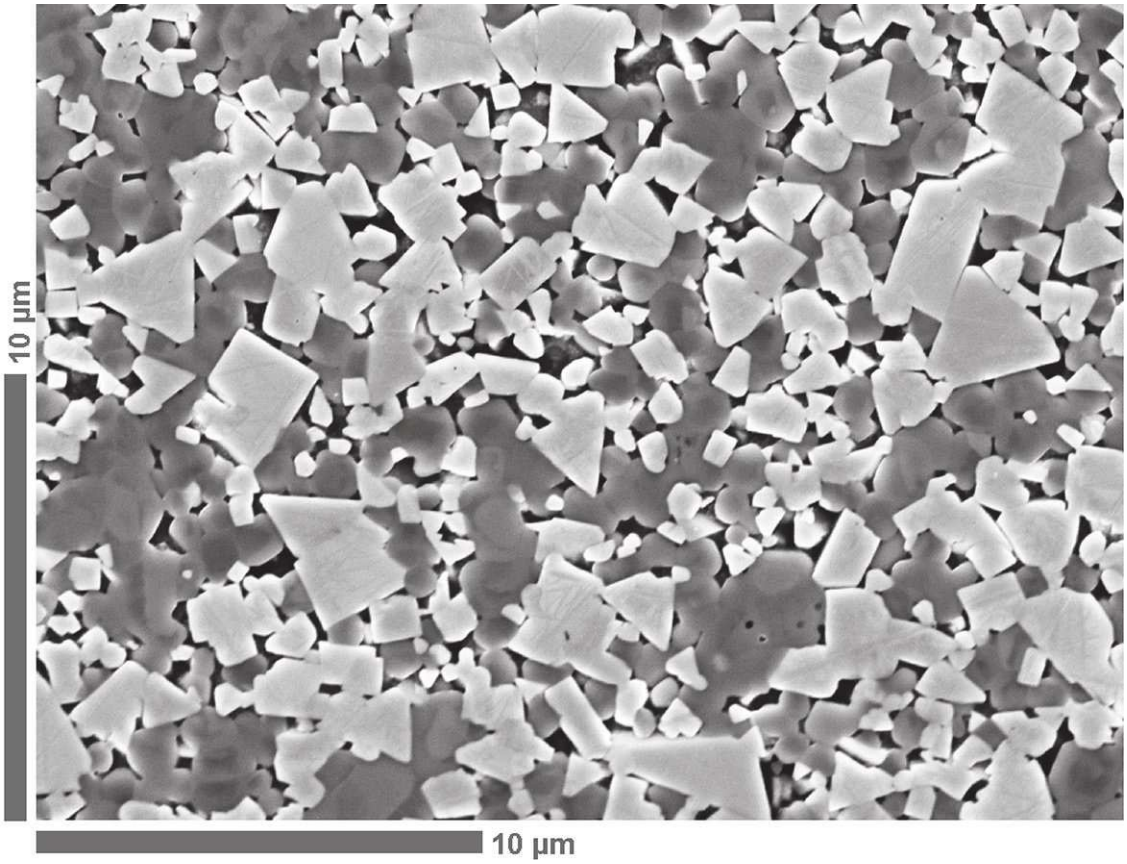


Figure 19 — Material 4, SEM micrograph, original magnification ×15 000

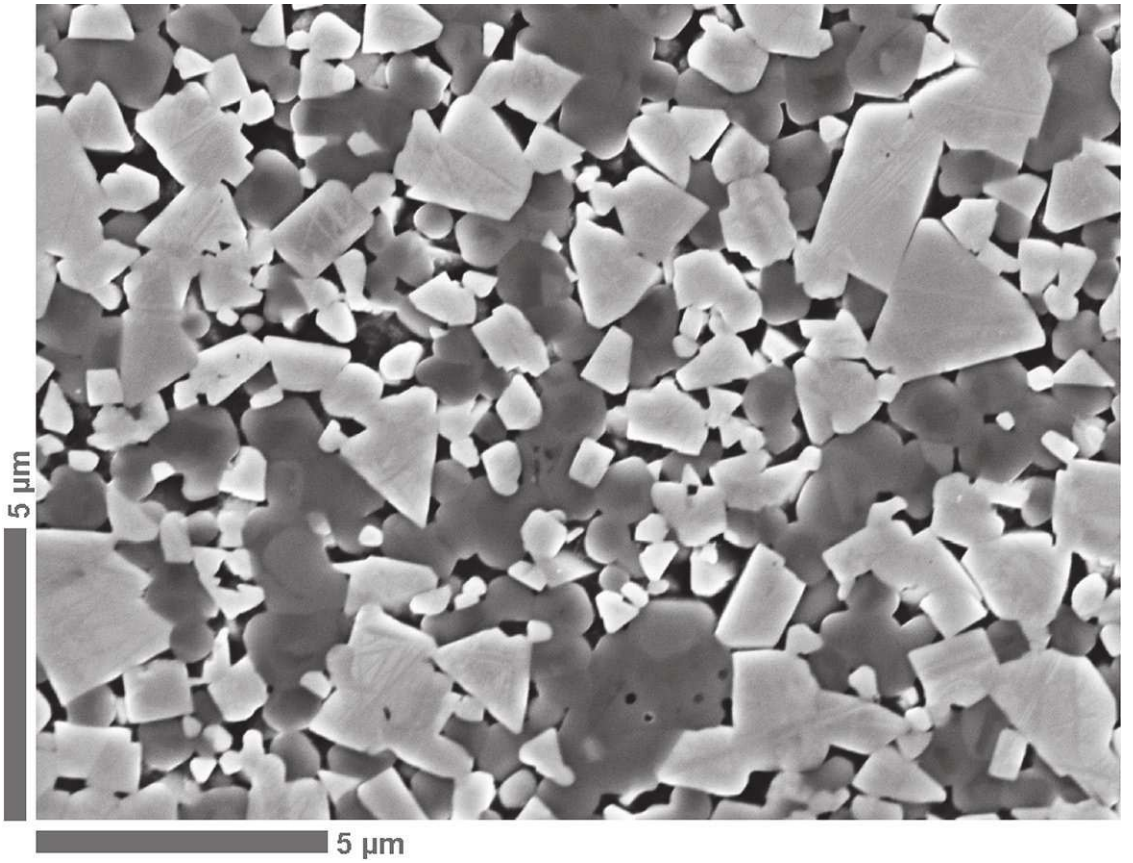


Figure 20 — Material 4, SEM micrograph, original magnification ×20 000

9 Procedure for characterisation of structures

9.1 Sampling of images of structure

9.1.1 General

Sampling for microstructural purposes has to be carefully considered depending on the reason for undertaking the measurements. Attention should be paid to the explanation in 9.1.2 to 9.1.4.

9.1.2 Representative selection

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

9.1.3 Determination of homogeneity of hard phase sizes

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 phase regions are measured from each location. This will allow for example, trends in phase 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 phase regions in each location) to be determined.

9.1.4 Inhomogeneous materials

In cases where the microstructure is inhomogeneous from one field of view to the next, it is 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 20 phase regions across the field of view permitting individual intercepts to be measured to better than 10 % accuracy. This will usually allow three or four linear intercept lines to be drawn across the image without intercepting any individual phase regions 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. Thus, from each image, about 50 linear phase size intercepts can be obtained.

9.2 Phase size measurement

9.2.1 General

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

For a two, three or four phase material such as can be present in Ti(C,N) or mixed WC/cubic carbide hardmetals, the linear intercept technique is less straightforward because each phase has to be measured independently. However, it can also provide information on phase size distribution.

A line is drawn across a calibrated image of the microstructure of a hardmetal sample. Where this line intercepts a hard phase or region of binder, the length of the line (l_i) is measured using a calibrated rule (where i = 1, 2, 3,... n for the 1st, 2nd, 3rd ...nth grain). It is advisable to count at least 100 lengths, preferably at least 200, in order to reduce the uncertainty in the mean value of size (phase or grain) to below 10%.

The mean linear intercept phase or binder phase size is defined as given in Formula (1):

$$d_x = \sum l_i / n \tag{1}$$

Hardmetal phase sizes generally fall in the range 0,01 µm to 10 µm. Because of the uncertainties of measurement, it is good practice to report the mean linear intercept size to one decimal place for values >1,0 µm and to two decimal places for values <1,0 µm. Thus, the results are reported to two significant figures, such as 3,4 µm or 0,18 µm.

9.2.2 Phase measurement by intercepts

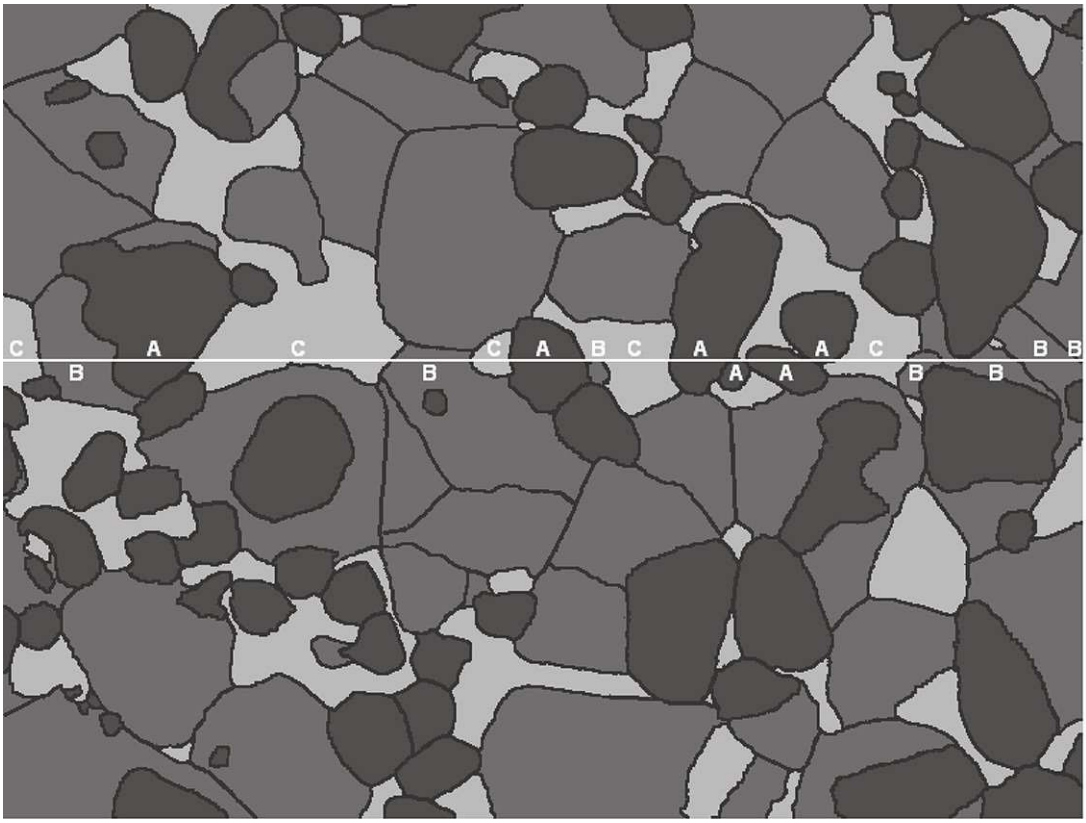
A schematic representation of a typical WC/CC/Co structure is shown in Figure 21 where the white crystals are WC, the black is the Co binder phase and the cubic phase is represented as crystals with a dark grey "core" and an outer light grey "rim". Size and volume fraction of all these constituents are measured in a quite straightforward way by using the intercept method. A typical line across the structure is shown in Figure 21 with the WC, Co, core and rim constituents identified as such. Preferably, 200 intercepts should be measured for each constituent, as described in 9.2.1, within a specified total line length. All intercepts that intersect the edge of the image should be ignored. Note that in some materials, there might also be a thin "inner rim" present, typically of lighter contrast (and higher atomic number) than the "outer rim". If this is present, the intercept method should also be used to measure its size and volume fraction.

For cermets, a similar approach can be used though often there is no WC present in the structure just Ti(C,N) "cores" and (Ti,W,X)(C,N) "rims" (see Figure 22). Inner "rims" of light contrast (i.e. high in atomic number) can also be seen in these materials, as well as in cubic carbide hardmetals.

Key

A WC
B Co binder
C cubic core
D cubic rim

Figure 21 — Schematic diagram of typical cubic carbide hardmetal showing intercepts through each part of the structure (WC, Co, cubic core, cubic rim)



Key

A Ti-based hard phase core

B (Ti:M) based hard phase rim

C binder phase

Figure 22 — Representative cermet showing intercepts through binder phase, dark grey Ti(C,N) "cores" and light grey (Ti,W,X)(C,N) "rims"

10 Uncertainty of measurement

Systematic and random measurement errors can have several sources as specified in ISO 4499-2:2008, 7.3.1. Systematic and random measurement errors should be minimized.

The measurement uncertainty in mean size is usually less than ±10 % when a population of 200 phase lengths are measured to obtain a mean value of intercept length.

11 Test report

The test report shall include the following information:

a) reference to this part of ISO 4499, i.e. ISO 4499-3;

b) all details necessary for identification of the test sample;

c) etchant and etching time;

d) traceability, calibration graticule number and calibration certificate;

e) imaging technique: optical, SEM or FESEM;

f) magnification used: one or more;

g) number of fields of view measured;

h) total number of intercepts for each relevant phase;

i) arithmetic mean linear intercept size for phase characterisation in micrometres (μm);

j) size distribution as recommended in this part of ISO 4499, if other than statement of used method;

k) all operations not specified in this part of ISO 4499, or regarded as optional;

l) details of any occurrence that may have affected the result.

The test report should additionally include the following information:

— identification number of the image or photo micrographs if archived;

— information about the source of the material and the customer requesting the measurement to be made;

— largest intercept measured;

— smallest intercept measured;

— numerical aperture of objective for optical microscopy;

— acceleration voltage, working distance and illuminating aperture for SEM;

— comment on measurement uncertainty.

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