

BS EN ISO 4499-4:2016



BSI Standards Publication

Hardmetals — Metallographic determination of microstructure

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

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National foreword

This British Standard is the UK implementation of EN ISO 4499-4:2016. It supersedes BS EN 24505:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee ISE/65, Sintered metal components.

A list of organizations represented on this committee can be obtained on request to its secretary.

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English Version

**Hardmetals - Metallographic determination of
microstructure - Part 4: Characterisation of porosity,
carbon defects and eta-phase content (ISO 4499-4:2016)**

Métaux-durs - Détermination métallographique de la
microstructure - Partie 4: Caractérisation de la
porosité, des défauts carbone et de la teneur en phase
êta (ISO 4499-4:2016)

Hartmetalle - Metallographische Bestimmung der
Mikrostruktur - Teil 4: Charakterisierung von
Porosität, Kohlenstofffehlern und Anteil an Eta-Phase
(ISO 4499-4:2016)

This European Standard was approved by CEN on 4 February 2016.

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European foreword

This document (EN ISO 4499-4:2016) has been prepared by Technical Committee ISO/TC 119 "Powder metallurgy".

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2016, and conflicting national standards shall be withdrawn at the latest by September 2016.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

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Endorsement notice

The text of ISO 4499-4:2016 has been approved by CEN as EN ISO 4499-4:2016 without any modification.

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

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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*.

This first edition of ISO 4499-4 cancels and replaces ISO 4505:1978, which has been technically revised.

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

In standard WC/Co hardmetals, the chemistry, magnetic properties and density are generally controlled so that only two phases WC and Co are present.^{[1][2][3]} The Co phase is an alloy and contains some W and C in solid solution. The WC phase is stoichiometric. If the composition is either high or low in total carbon content, then it is possible to see a third phase in the structure. For high C, this is graphite; for low C, it is eta phase (η); typically, an M_6C or $M_{12}C$ carbide where M is (Co_xW_y) . This part of ISO 4499 is concerned with the detection and measurement of these microstructural features together with the measurement of porosity levels. Porosity is important since these materials are manufactured by a powder metallurgical route and although the technique of liquid phase sintering is used to consolidate the multiphase structure, low levels of porosity can arise in some instances and affect properties such as density and strength.

Hardmetals — Metallographic determination of microstructure —

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

1 Scope

This part of ISO 4499 specifies methods for the metallographic determination of the presence, type, and distribution of porosity, uncombined carbon and eta-phase in hardmetals.

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 4499-2:2008, *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

carbon defects

macroscopic precipitates of carbon (graphite) which can be in the form of large angular rosettes or small flakes

3.2

eta-phase

η -phase

cubic carbide based on M₆C or M₁₂C structure where M is a mixture of Co and W usually in equal proportions; and which can be present as large (up to 100 μm diameter) rosettes or small micrometre-sized particles

4 Symbols and Units

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 eta-phase particles intercepted
m	magnification
$m_{\max}$	maximum magnification
$m_{\min}$	minimum magnification

5 Principle

This part of ISO 4499 handles the following key issues:

- description of methods for sample preparation;
- description of how to identify and measure the relevant feature.

In some cases, the approach adopted in ISO 4499-2 and ISO 4499-3 can be useful, whereby the intercept method is used on microphotographs of the structure for relevant quantification of feature size, such as eta-phase or graphite rosettes.

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 (SEM), permitting observations and measurements of features too small to be resolved with an optical microscope.

6.3 Equipment for preparation of test-piece sections.

7 Calibration of measurement apparatus

For reliable quantitative measurements, images shall be calibrated against a stage micrometre or scale traceable to a National Reference Standard. The most commonly used stage micrometres for SEMs are the SIRA grids. These are ruled lines which form a grid and are available with 19,7 lines/mm and 2 160 lines/mm. However, these shall 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 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 [4].

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 Methods of preparation

There are several methods for the preparation of hardmetal surfaces for metallographic examination. For example, a detailed description is given in ISO 4499-1. Firstly, careful coarse grinding is carried out to remove sufficient material to ensure that the true structure is revealed. After grinding with fine diamond grit wheels, polishing is effected by using diamond paste or diamond powders of progressively finer grain size down to 1 µm on rigidly supported laps of, for example, thin plastic, thin felt or paper.

8.2 Characterisation of porosity and carbon (graphite) defects

For porosity and carbon defects, the test-piece section shall be prepared as for metallographic examination and the surface to be examined shall be free from grinding and polishing marks. Care shall be taken to avoid tearing out of particles, which can lead to a misleading evaluation of porosity.

8.3 Characterisation of eta-phase

Etching is necessary to reveal eta-phase particles (see 9.4). Eta-phase is metal carbide (usually M_6C or $M_{12}C$, where M is a combination of Co and W, for example, Co_3W_3C), that forms when the overall carbon content of the hardmetal is relatively low. Generally, it can grow in one of two morphologies, either as large rosettes or as small particles of a similar size to the other hard phases (WC or cubic carbides) present in the hardmetal (see 9.4). The presence of the eta-phase is usually determined after light etching in 10 % Murakami's reagent for a few seconds with immediate water flush following etching (see ISO 4499-1), which works well for identifying large eta-phase rosettes. When the eta-phase is present as smaller particles (see Figure 6), it is recommended to use a 5 % Murakami's solution for 20 min followed by washing the sample with water. In both cases, the surface should be dried carefully with acetone or alcohol without wiping.

9 Procedure

9.1 General

If the porosity or uncombined carbon is not uniform over the area of the test piece section being examined, the locations on the section to which the evaluation refers shall be identified, for example, as top, bottom, edge, rim (case), core, etc.

It should be noted that the figures given in this Clause are only representing approximately $\frac{1}{7}$ of the field of view in the microscope.

9.2 Determination of porosity

Pore size is defined as the maximum dimension of the pore in the section. Special reference shall be made to the presence of cracks or slits.

9.2.1 Pores up to 10 μm shall be assessed by scanning the surface of the test-piece section at a magnification of either $\times 100$ or $\times 200$. An area fully representative of the test-piece section shall be examined and compared with the range of photomicrographs shown in Figure 1 or Figure 2, according to the chosen magnification. The porosity level shall be reported by reference to the appropriate photomicrograph and designated as A02, A04, A06 or A08. If the level of A-type pores is less than 50 % of that shown in Figure 1 (A02) or Figure 2 (A02), it shall be designated as A00.

9.2.2 Pores within the range 10 μm to 25 μm shall be assessed by scanning the surface of the test-piece section at a magnification of $\times 100$. An area fully representative of the test-piece section shall be examined and shall be compared with the range of photomicrographs shown in Figure 3. The porosity level shall be reported by reference to the appropriate photomicrograph and designated as B02, B04, B06 or B08.

If the number of B-pores appears to be less than or equal to that represented by B02, the number of B-pores in the representative area ($\geq 0,25 \text{ cm}^2$) shall be counted. This number shall be divided by the area examined to obtain the number of B-pores/ cm^2 .

If this number is less than 70 pores/ cm^2 , it shall be designated as B00 - #, where # is the number of B-pores/ cm^2 so obtained. If the number is greater than or equal to 70 pores/ cm^2 , it shall be designated as B02.

9.2.3 If it is necessary to inspect for pores larger than 25 μm , they shall be examined at a suitable magnification up to $\times 100$ and shall be counted and reported as the number of pores per unit area. The size ranges shall be chosen as follows: 25 μm to 75 μm , 75 μm to 125 μm , over 125 μm .

9.3 Determination of carbon defects

9.3.1 Uncombined carbon shall be assessed by scanning the surface of the test-piece section at a magnification of $\times 100$. An area fully representative of the test-piece section shall be examined and shall be compared with the range of photomicrographs shown in [Figure 4](#). The level of uncombined carbon shall be reported by reference to the appropriate photomicrographs and designated as C02, C04, C06 or C08.

9.3.2 If A-type or B-type porosity or C-type uncombined carbon is not detected, it shall be reported as A00, B00 or C00, as applicable.

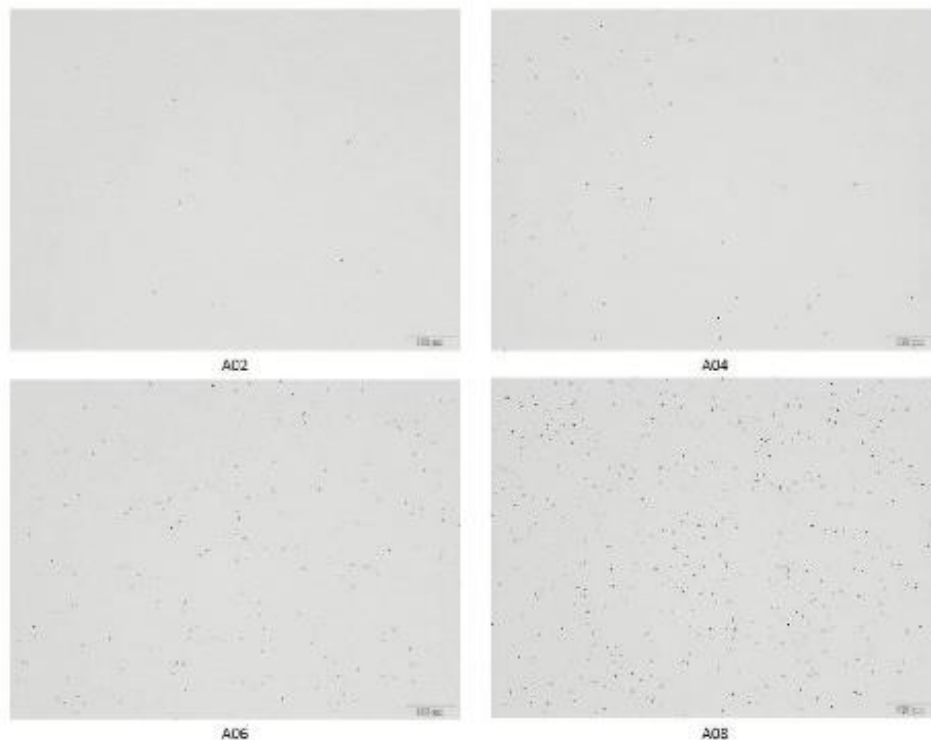


Figure 1 — A-type porosity classes at $\times 100$ magnification (optical)

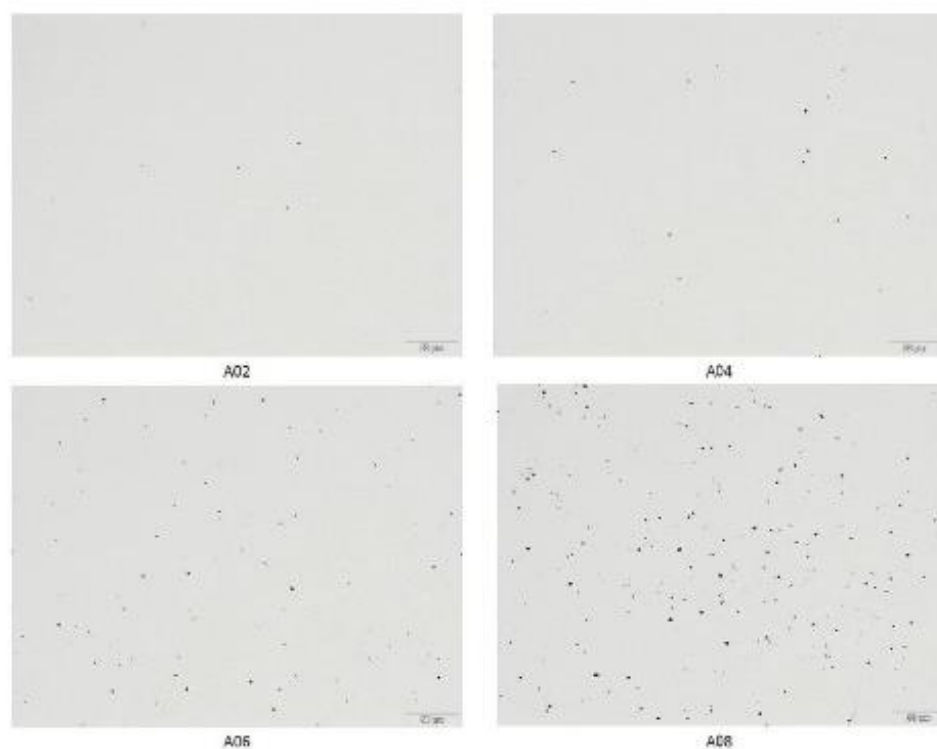


Figure 2 — A-type porosity classes at $\times 200$ magnification (optical)

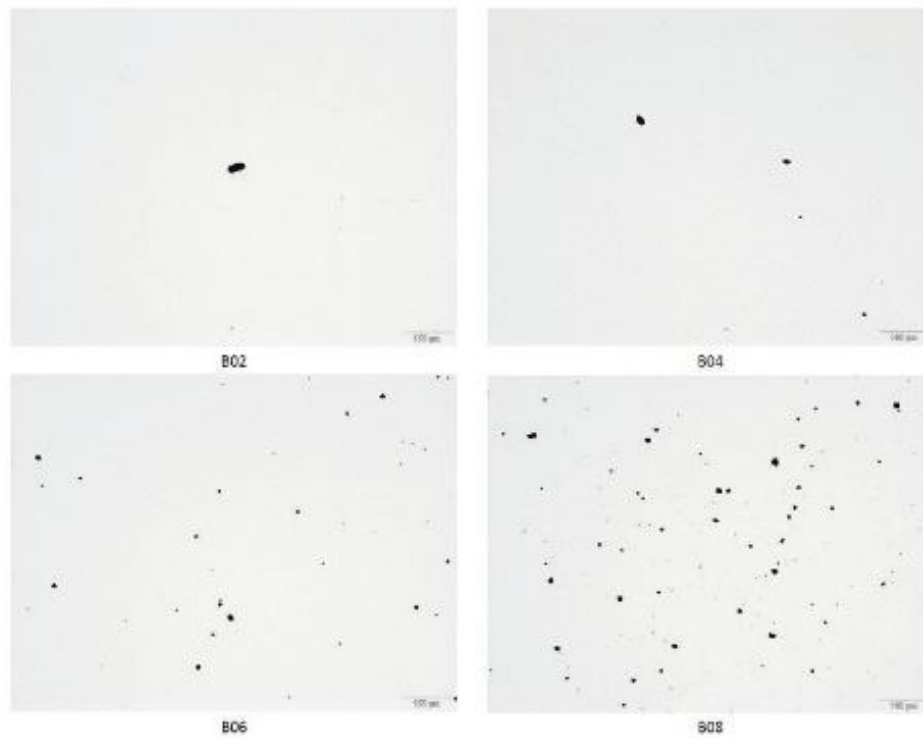


Figure 3 — B-type porosity classes at $\times 100$ magnification (optical); A-pores ($< 10 \mu\text{m}$) are included

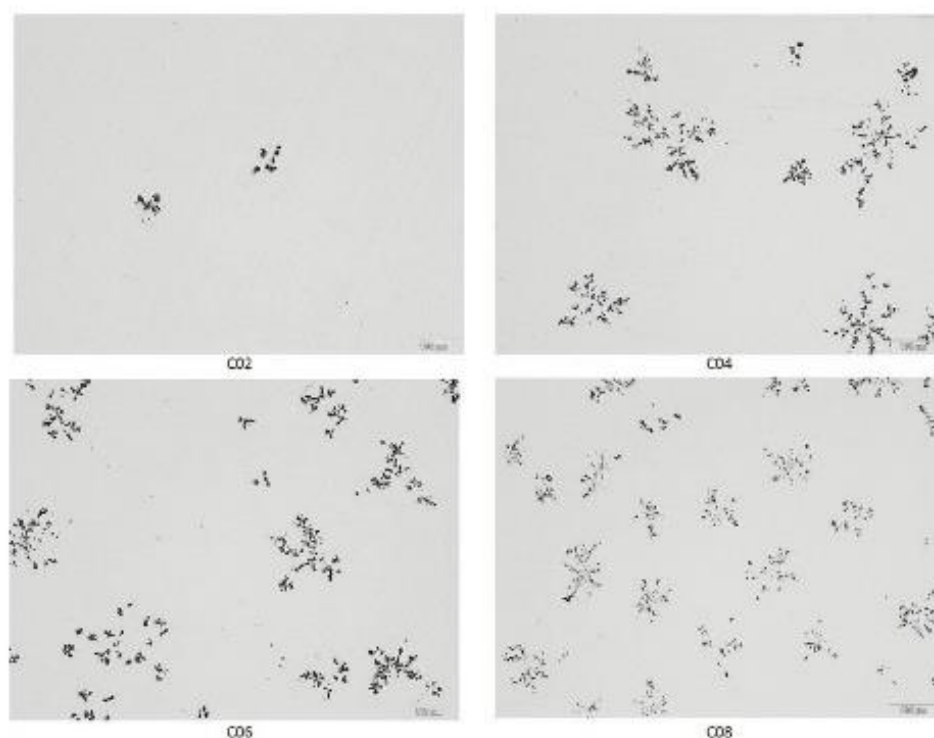


Figure 4 — Carbon porosity at $\times 100$ magnification (optical)

9.4 Determination of the η -phase (eta-phase)

The eta-phase is a metal carbide (usually M_6C or $M_{12}C$, where M is a combination of Co and W, for example, Co_3W_3C), that forms when the overall carbon content of the hardmetal is relatively low. Generally, it can grow in one of two morphologies, either as large rosettes (see [Figure 5](#)) or as small particles of a similar size to the other hard phases (WC or cubic carbides) present in the hardmetal (see [Figure 6](#)). Phase of the eta-type appear orange to brown when observed by optical microscopy after light etching in 10 % Murakami's reagent. Examine the whole surface at low magnification to reveal large rosettes (see [Figure 5](#)) and then at progressively higher magnifications to observe smaller particles or grains. When the eta-phase is present as smaller particles, it is recommended to use a 5 % Murakami's solution and the eta-phase is revealed as small white particles that contrast with the grey WC grains (see [Figure 6](#)). A typical micrograph showing these smaller eta-phase particles is given in [Figure 6](#). The commonly used etching methods are listed in [8.3](#). However, smaller particles cannot be identified easily using this method. SEM techniques such as atomic number contrast or Orientation Imaging Microscopy (OIM) using Electron Back Scatter Diffraction techniques (EBSD) are more appropriate.

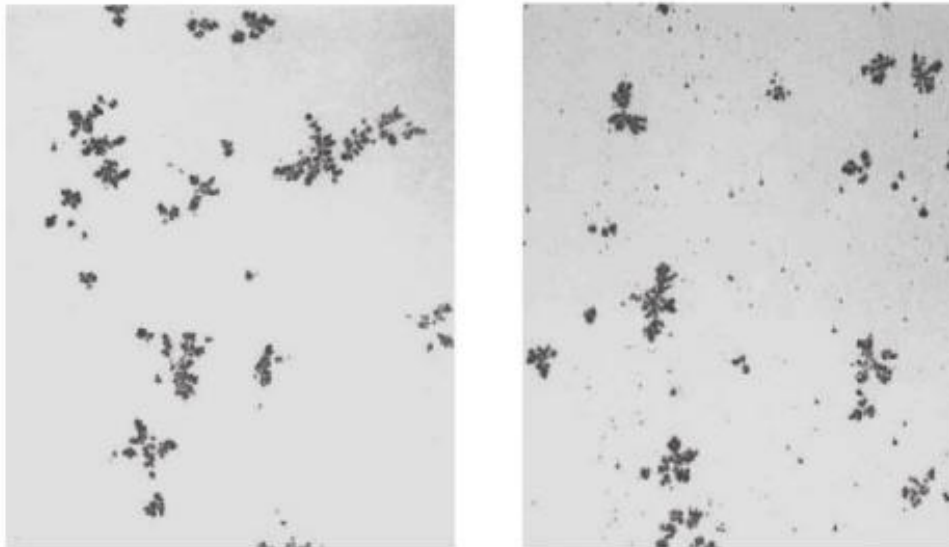


Figure 5 — Large eta-phase rosettes (about 100 μm in diameter)

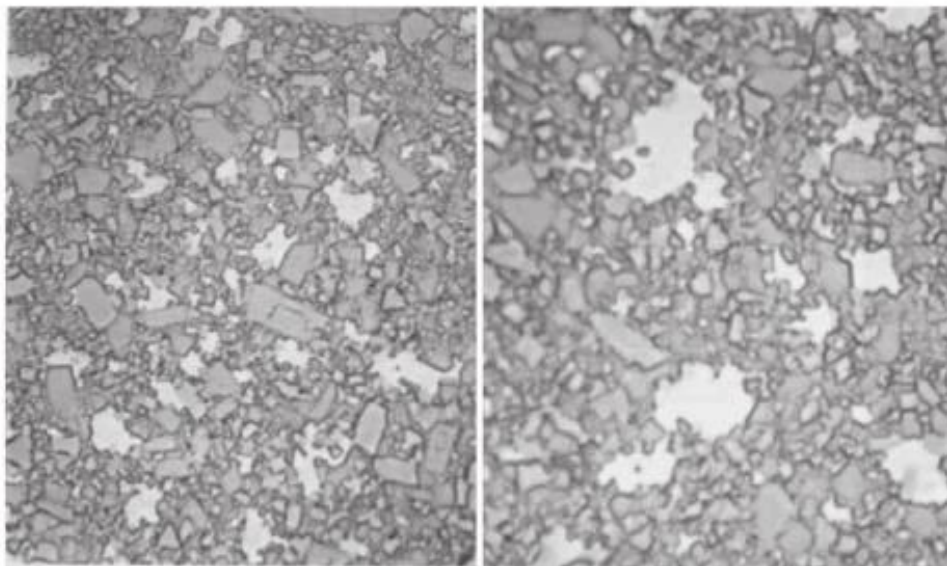


Figure 6 — Small eta-phase particles (light grey, about 5 μm in diameter)

The presence of the eta-phase is usually determined after light etching in 10 % Murakami's reagent for a few seconds with an immediate water flush following etching. The surface should be dried carefully with acetone or alcohol without wiping. Phases of the eta-type appear orange to brown when observed by optical microscopy. Examine the whole surface at low magnification to reveal large rosettes (see [Figure 5](#)) and then at progressively higher magnifications to observe smaller particles or grains. When the eta-phase is present as smaller particles (see [Figure 6](#)), it is recommended to use a 5 % Murakami's solution for 20 min. The eta-phase is revealed as small white particles that contrast with the grey WC grains. A typical micrograph showing these smaller eta-phase particles is given in [Figure 6](#).

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 shall be avoided wherever possible.

11 Test report

The test report shall include the following information:

- a) reference to this part of ISO 4499, i.e. ISO 4499-4;
- b) all details necessary for identification of the test sample;
- c) results obtained;
- d) etchant and etching time;
- e) traceability, calibration graticule number and calibration certificate;
- f) imaging technique: optical or SEM techniques;
- g) magnification used: one or more;
- h) number of fields of view measured;
- i) for eta-phase characterisation, total number of intercepts;
- j) arithmetic mean linear intercept size for eta-phase characterisation in micrometres (μm);
- k) all operations not specified in this part of ISO 4499, or regarded as optional;
- l) details of any occurrence that might 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;
- numerical aperture of objective for optical microscopy;
- acceleration voltage, working distance and illuminating aperture for SEM;
- comment on measurement uncertainty.

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