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Hardmetals — Metallographic determination of microstructure —

Part 1:
Photomicrographs and description

Métaux-durs — Détermination métallographique de la microstructure —

Partie 1: Prises de vue photomicrographiques et description

Reference number
ISO 4499-1:2008(E)

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Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 4499-1 was prepared by Technical Committee ISO/TC 119, *Powder metallurgy*, Subcommittee SC 4, *Sampling and testing methods for hardmetals*.

ISO 4499-1, together with ISO 4499-2, cancels and replaces ISO 4499:1978, which has been technically revised.

In ISO 4499-2, a new section has been added for the quantitative measurement of the WC grain size of hardmetals. ISO 4499-3 and ISO 4499-4 are additional parts that will deal with the microstructures of hardmetals containing cubic carbides and Ti (C, N)-based hardmetals, and miscellaneous microstructural features, such as defects and non-stoichiometric phases (e.g. carbon and eta-phase). ISO 4499-3 and ISO 4499-4 are currently in development.

In standard WC/Co hardmetals the density is generally controlled so that only two phases WC and Co are present. 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 a high C content this is graphite; for a low C content it is eta phase (η), typically an M_6C or $M_{12}C$ carbide where M is (Co_xW_y). Metallographic determination of these phases will be outlined in ISO 4499-3.

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*

Hardmetals — Metallographic determination of microstructure —

Part 1:
Photomicrographs and description

1 Scope

This part of ISO 4499 specifies the methods of metallographic determination of the microstructure of hardmetals using photomicrographs.

2 Normative references

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

ISO 3878:1983, *Hardmetals — Vickers hardness test*

ISO 4499-2, *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
α-phase
tungsten carbide

3.2
β-phase
binder phase (for example, based on Co, Ni, Fe)

3.3
γ-phase
carbide having a cubic lattice (for example, TiC, Tac) which may contain other carbides (for example WC) in solid solution

4 Apparatus

4.1 Metallographic microscope, permitting observations at magnifications up to 1 500 ×.

4.2 Scanning electron microscope for magnification over 1 500 ×.

4.3 Equipment for preparation of testpiece sections.

5 Preparation of testpiece section

The testpiece 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 may lead to a wrong evaluation of microstructure.

NOTE There are several methods for preparation of hardmetal surfaces for metallographic examination. 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. A Good Practice Guide[1] has been written by the UK National Physical Laboratory that gives detailed guidelines on microstructural preparation. Key points from the Good Practice Guide are included in 6.1. ASTM has also prepared a thorough standard on sample preparation that merits study (ASTM B665)[2].

6 Procedure

6.1 Metallographic preparation

6.1.1 General

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 affect any subsequent measurement.

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.

6.1.2 Sectioning

In many cases, the hardmetal sample may have to be sectioned into smaller samples for metallographic preparation. 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.

6.1.3 Mounting

Mounting of the sample into a resin has several advantages: it is more suitable for automatic preparation, the sample is easier to handle, and 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 in 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 is 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 shall 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.

6.1.4 Grinding

Whichever method is used to obtain a section of a hardmetal sample, it will have considerable surface and subsurface damage that shall 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. Typically, for homogenous microstructures, at least 200 µm of material (see ISO 3878:1983) should be removed during the grinding process to obtain a section representative of the bulk microstructure. For materials with gradient structures, more care may be needed in controlling the amount removed.

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.

6.1.5 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 following:

- the production of a plane surface;
- an intermediate step between grinding and polishing;
- the removal of surface damage without imparting substantial further subsurface 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.

6.1.6 Polishing

The polishing stages are normally carried out on a short nap or napless cloth1) 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.

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1) Texmet and DP Pan are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

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.

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 cut into the WC grains and high temperatures are probably 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) shall be thoroughly cleaned.

6.1.7 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 be carried out in an ultrasonic bath using a suitable detergent in warm water which is known not to affect the Co binder, or alternatively, if the specimen is not mounted in plastic, to rinse it in acetone. If specimens for optical examination are mounted in plastic then acetone should be avoided. In this case, it is better to use warm water and ethanol. Cleaning specimens ultrasonically in acetone prior to examination in an electron microscope is especially recommended.

6.2 Etching

6.2.1 General

The primary etchant recommended 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 ferricyanide and (nascent) oxygen which attacks the carbide grains and grain boundaries whilst the binder phase is generally unaffected. 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 the times required for effective etching are extended unacceptably.

The preferred etchant is a freshly prepared solution of equal quantities of 10 % to 20 % (mass fraction) aqueous solutions of potassium hexacyanoferrate(III) [potassium ferricyanide] and potassium or sodium hydroxide (10 g to 20 g in 100 ml of water). The etching time at 20 °C is advised to be in the range 0,5 min to 6 min, dependent on the WC grain size. For coarse-grained structures, longer etching times are required.

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. 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 be 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 affects 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 that are 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.

The microstructure is examined by the gradual development of phases by etching. There are several methods for etching hardmetal surfaces for metallographic examination, and it is worthwhile examining ASTM B657[3] for additional details. Examples of suitable etching techniques are given in Table 1. Care shall be taken to ensure that the true microstructure is revealed.

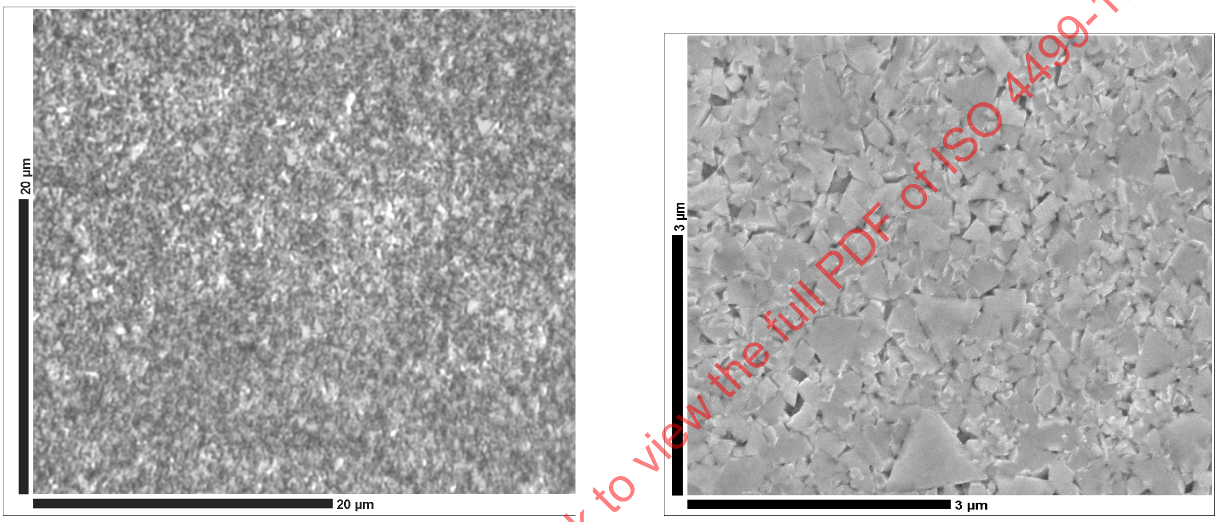
Table 1 — Examples of suitable etching techniques

Etching technique	Composition of etchants		Conditions of etching	Application of etching
1	A	Freshly prepared mixture of equal quantities of 10 % to 20 % (mass fraction) aqueous solutions of potassium hexacyanoferrate(III) (potassium ferricyanide) and potassium or sodium hydroxide (Murakami's reagent).	Etch in mixture A at approximately 20 °C for 3 min to 6 min.	Identification of α-phases.
2	B	Etchant A. A mixture of equal volumes of concentrated hydrochloric acid and water.	Etch at approximately 20 °C in mixture A for 3 min to 4 min. Then wash in water and etch in mixture B for approximately 10 s. Next wash in water, then in alcohol, and dry the testpiece section. Finally, etch in mixture A for approximately 20 s.	Identification of γ-phase.
The separate solutions of potassium hexacyanoferrate(III) and potassium or sodium hydroxide can be stored for a long time, but shall be freshly mixed each day when used.				

6.2.2 The existence of α-phase is determined after etching the surface, for example by technique 1 or, in the case of the presence of γ-phase, by technique 2 (see Table 1). The α-phase is noted and recorded. Its size is measured and recorded according to ISO 4499-2 in classes identified as nano, ultrafine, submicron, fine, medium, coarse or extra coarse (see Figures 1, 2 and 3). The magnifications were chosen for comparison of adjacent classes. Optical images for the finer-grained materials clearly do not resolve the grain structure and SEM images that are required for this purpose.

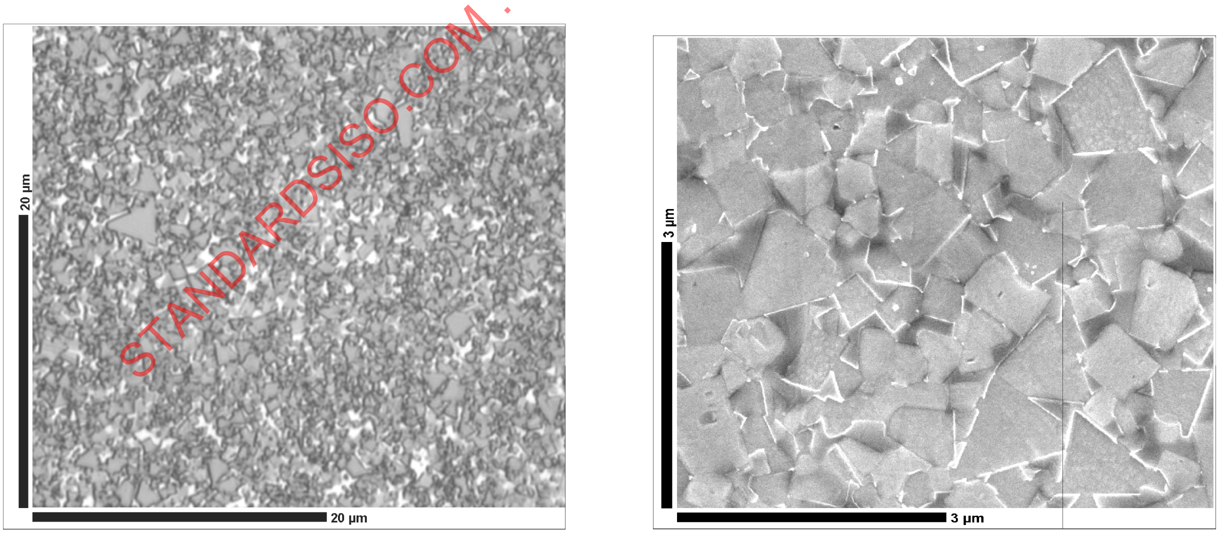
6.2.3 The β-phase is identified after etching the surface, for example by the second part of technique 2 in Table 1 (concentrated HCl). This phase remains white.

6.2.4 The existence of γ-type (gamma) phases is determined after etching the surface, for example by technique 2 (see Table 1). This phase has a light yellowish-brown colour and has a typically rounded shape. The etched section is examined and the existence of the γ-phase is noted and recorded. Its size can be measured by the linear intercept technique outlined in ISO 4499-2.



a) Nano — optical

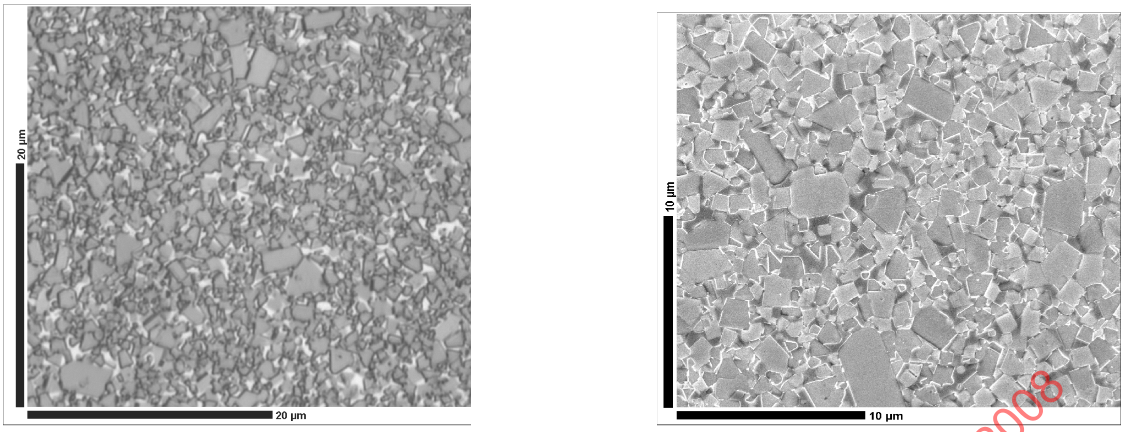
b) Nano — SEM



c) Ultrafine — optical

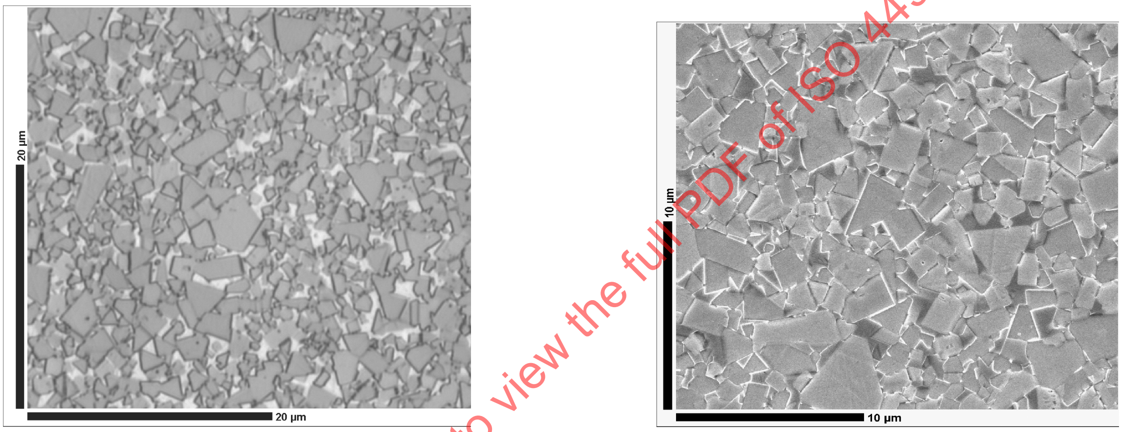
d) Ultrafine — SEM

Figure 1 — α-phase (WC) — Optical and scanning electron microscope (SEM), nano and ultrafine



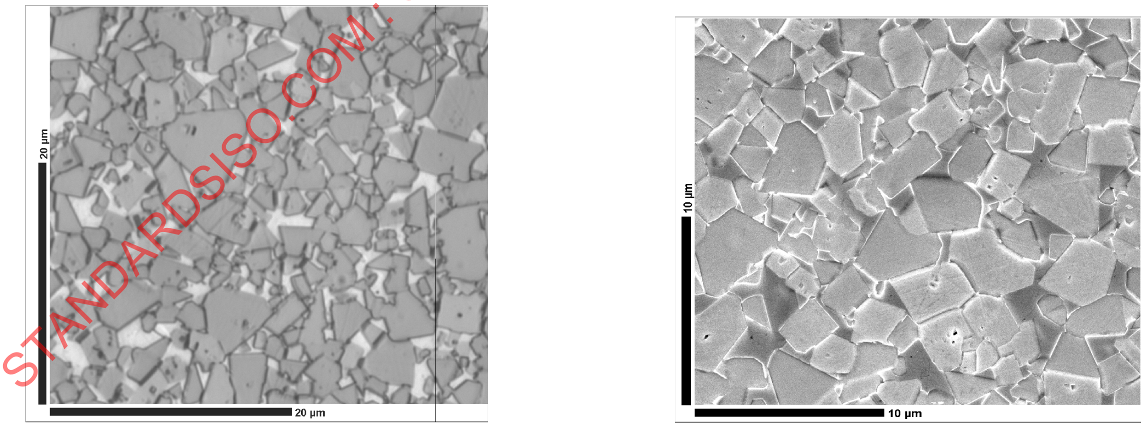
a) **Submicron — optical**

b) **Submicron — SEM**



c) **Fine — optical**

d) **Fine — SEM**



e) **Medium — optical**

f) **Medium — SEM**

Figure 2 — α–phase (WC) — Optical and scanning electron microscope (SEM), submicron, fine and medium