Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2547926 C 2013/08/06

(11)(21) 2 547 926

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2004/12/07
(87) Date publication PCT/PCT Publication Date: 2005/06/23
(45) Date de délivrance/Issue Date: 2013/08/06
(85) Entrée phase nationale/National Entry: 2006/06/01
(86) N° demande PCT/PCT Application No.: SE 2004/001817
(87) N° publication PCT/PCT Publication No.: 2005/056854
(30) Priorités/Priorities: 2003/12/15 (SE0303360-2); 2003/12/22 (SE0303486-5)

(51) Cl.Int./Int.Cl. *C22C 29/08* (2006.01)

(72) Inventeurs/Inventors:
TILLMAN, MATHIAS, GB;
NORGREN, SUSANNE, SE;
COLLIN, MARIANNE, SE

(73) Propriétaire/Owner:
SANDVIK INTELLECTUAL PROPERTY AB, SE

(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : OUTILS EN CARBURE CEMENTE DESTINES A DES APPLICATIONS MINIERES ET A DES APPLICATIONS DE CONSTRUCTION ET LEUR PROCEDE DE FABRICATION

(54) Title: CEMENTED CARBIDE TOOLS FOR MINING AND CONSTRUCTION APPLICATIONS AND METHOD OF MAKING THE SAME

(57) Abrégé/Abstract:
The present invention relates to a cemented carbide cutting tool insert/button for mining and construction comprising hard constituents in a binder phase of Co and/or Ni and at least one surface portion and an interior portion in which surface portion the grain size is smaller than in the interior portion. The surface portion with the fine grain size has a lower binder phase content than the interior portion.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 June 2005 (23.06.2005)

PCT

(10) International Publication Number
WO 2005/056854 A1

(51) International Patent Classification[7]: C22C 29/08

(21) International Application Number:
PCT/SE2004/001817

(22) International Filing Date: 7 December 2004 (07.12.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0303360-2	15 December 2003 (15.12.2003)	SE
0303486-5	22 December 2003 (22.12.2003)	SE

(71) Applicant *(for all designated States except US)*: **SANDVICK AB** [SE/SE]; S-811 81 Sandviken (SE).

(72) Inventors: **TILLMAN, Mathias**; 1 Meadow Rise, berkswell Gate, Balsall Common CV7 7RT (GB). **NORGREN, Susanne**; Norrskogsvägen 17, S-14141 Huddinge (SE). **COLLIN, Marianne**; Kanslersvägen 28, S-128 38 Skarpnäck (SE).

(74) Agent: **TÅQUIST, Lennart**; Sandvik AB, Intellectual Property, S-811 81 Sandviken (SE).

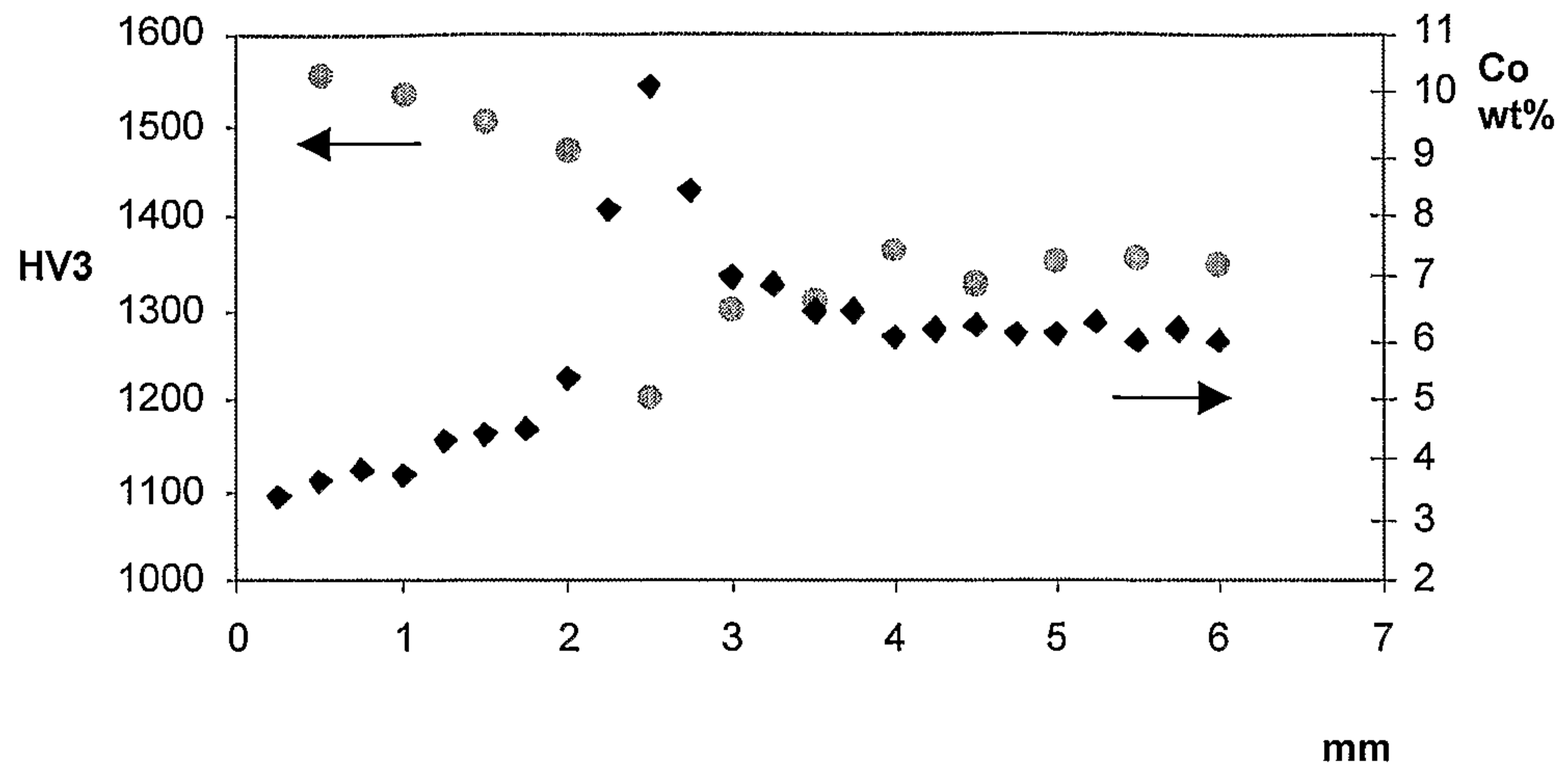
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CEMENTED CARBIDE TOOLS FOR MINING AND CONSTRUCTION APPLICATIONS AND METHOD OF MAKING THE SAME



(57) Abstract: The present invention relates to a cemented carbide cutting tool insert/button for mining and construction comprising hard constituents in a binder phase of Co and/or Ni and at least one surface portion and an interior portion in which surface portion the grain size is smaller than in the interior portion. The surface portion with the fine grain size has a lower binder phase content than the interior portion.

WO 2005/056854 A1

Cemented carbide tools for mining and construction applications and method of making the same

The present invention relates to cemented carbide bodies preferably used in tools for drilling/cutting of rock and mineral. Also cemented carbide tools used for asphalt and concrete are included. More specifically, the invention pertains to cemented carbide tools made via sintering techniques wherein there are two distinct microstructural zones having complementary properties.

In cemented carbides, the grain size, as well as the binder phase (e.g., cobalt) content, each has an influence on the performance of the composite. For example, a smaller/finer grain size of the tungsten carbide results in a more wear resistant material. An increase in cobalt content typically leads to an increase in toughness.

Cemented carbides having a fine grain size are produced through the incorporation of grain refiners in the initial powder blend. Such cemented carbide has a fine grain size throughout its microstructure. Cemented carbide with a coarse grain size is produced via sintering without the incorporation of any grain refiners since the tendency of a cemented carbide like a WC-Co composite is for the WC grains to coarsen during sintering. Such cemented carbide has a coarse grain size throughout its microstructure. As can be appreciated, these hard bodies have a uniform microstructure throughout the cemented carbide body.

Cemented carbide bodies having at least two distinct microstructural zones are known in the art. For example drills having a core of a tough cemented carbide grade and a cover of a more wear resistant grade are disclosed in EP-A-951576.

EP-A-194018 relates to a wire drawing die made from a central layer with coarse grained tungsten carbide particles and a peripheral layer with finer grained tungsten carbide particles. Initially the layers have the same content of cobalt. After sintering the coarse grained layer in the center is reduced in cobalt content.

EP-A-257869 discloses a rock bit button made with a wear resistant tip portion and a tough core. The tip portion is made from a powder with low Co-content and a fine WC grain size and the core portion is made from a powder with high Co content and coarse WC grains. Nothing is disclosed about the Co-content in the two

portions after sintering. However, also in this case the Co-content in the coarse grained portion will be reduced at the expense of the Co-content in the fine grained layer. A similar disclosure is found in US 4,359,335.

An alternative approach is disclosed in US 4,743,515, which discloses cemented carbide bodies, preferably for rock drilling and mineral cutting. The bodies comprise a core of cemented carbide containing eta-phase surrounded by a surface zone of cemented carbide free of eta-phase and having a low content of cobalt in the surface and a higher content of cobalt next to the eta-phase zone. US 4,843,039 is similar, but it relates to cutting tool inserts for metal machining.

US 5,623,723 discloses a method of making a cemented carbide body with a wear resistant surface zone. The method includes the following steps: providing a compact of cemented carbide; placing a powder of grain refiner on at least one portion of the exposed surface of the compact; and heat treating the compact and grain refiner powder so as to diffuse the grain refiner toward the center of the green compact thereby forming a surface zone inwardly from the exposed surface in which the grain refiner was placed, and forming an interior zone. As a result a cemented carbide body is obtained with a surface zone having a grain size that is smaller but with a Co-content that is higher than that of the interior portion of the body. This means that the increased wear resistance that is obtained as a result of the smaller WC grain size is to a certain extent lost by the increase in Co-content.

It is therefore the object of the present invention to provide a cemented carbide body with a surface zone with a low binder phase content and fine WC grain size and thus high wear resistance and a method of making the same.

It is a further object of the present invention to provide a cemented carbide insert/button with compressive stresses in the surface portion which has a positive effect upon the strength and the toughness of the insert/button.

It has now surprisingly been found that it is possible from a single mixture of tungsten carbide and binder to obtain a cemented carbide body with a surface portion with a smaller grain size and a lower cobalt content than those in the interior portion.

Fig 1 is a graph showing hardness (HV3) and cobalt content (WDS-analysis) versus distance from the surface where the grain refiner powder was placed on a button for mining application according to the invention.

Fig 2 is a graph showing chromium content (WDS-analysis) versus distance from the surface where the grain refiner powder was placed on a button according to the invention.

Fig 3a is a micrograph showing the microstructure at a distance of 20 µm from the surface where the grain refiner powder was placed (FEG-SEM, 2000X, BSE mode) on a button according to the invention.

Fig 3b is a micrograph showing the microstructure at a distance of 2.5 mm from the surface where the grain refiner powder was placed (FEG-SEM, 2000X, BSE mode) in a button according to the invention.

Fig 3c is a micrograph showing the microstructure in the interior portion (center) of the button (FEG-SEM, 2000X, BSE mode) according to the invention.

According to the present invention there is provided a cemented carbide tool insert/button for mining and construction applications comprising at least one surface portion, the surface zone poor in binder has a width of 0.05-0.9 of the diameter/width of the cemented carbide body, preferably 0.1-0.5, most preferably 0.15-0.4 and the grain size is smaller than in the interior portion and the Co-content is lower than that in the interior portion resulting in compressive stresses at the surface after sintering. More particularly the Co-content of the surface portion is <1, preferably <0.9, most preferably <0.75 of the Co-content in the interior portion and the WC grain size of the surface zone is <1, preferably <0.9, most preferably <0.8 of the WC grain size in the interior portion. Preferably the surface zone contains Cr such that the ratio between the parameter A=((wt-% Cr/wt-% binder phase)+0.01) in the surface portion and the parameter B=((wt-% Cr/wt-% binder phase)+0.01) taken at the part of the body that is characterized by the lowest Cr content is A/B >1.5, preferably A/B>3.0.

The composition of the cemented carbide is WC+Co with a nominal Co-content of 4-25 wt-%, preferably 5-10 wt-% and a nominal WC grain size, arithmetic mean of intercept, of 1-15 µm, preferably 1.5-5 µm.

In one embodiment the cemented carbide contains η-phase.

In another embodiment there is a maximum in Co-content between the fine grained and the coarse grained portion.

The present invention also relates to a method of making a cemented carbide body with a wear resistant surface zone including the following steps:

- providing a compact of cemented carbide made from a single powder comprising powders forming hard constituents and binder phase of Co and/or Ni;
- possibly grind the compact to desired shape and size;
- placing a powder of grain refiner containing on at least one portion of the exposed surface of the compact by dipping, spraying, painting applying a thin tape or in any other way, preferably being any chromium carbide (Cr_3C_2, $Cr_{23}C_6$ and Cr_7C_3 or mixtures of these) or a mixture of chromium and carbon or other compounds containing chromium and carbon and/or nitrogen;
- sintering the compact and grain refiner powder so as to diffuse the grain refiner away from the surface(s) of grain refiner application thereby forming a gradient zone characterised of low binder phase content, higher chromium content and lower WC grain size compared to the interior portion.
- possibly adding an isostatic gas pressure during the final stage of sintering to obtain a dense body;
- possibly post-HIP-ing at a temperature lower than the sintering temperature and at a pressure of 1-100 MPa;
- possibly grinding to final shape;
- possibly removing undesired carbides and/or graphite from the surface using grinding or any other mechanical method;

Sintering is performed for shortest possible time to obtain a dense body with a surface portion with a smaller grain size and lower cobalt content than those in the interior portion.

The nominal carbon content of the cemented carbide compact shall be determined by consideration of the carbon contribution from the applied grain refiner. Also compacts that would result in a eta-phase containing microstructure can be used. The sintering shall be performed for shortest possible time to obtain the desired structure and a body with closed porosity, preferably a dense body. This time depends on the grain size of WC and the composition of the cemented carbide and can therefore not be closer defined. It is within the purview of the person skilled in

the art to determine whether the requisite structure has been obtained and to modify the sintering conditions in accordance with the present specification. If necessary the body can be post-HIP-ed at a lower HIP-temperature compared to the sintering temperature and at a pressure of 2-100 MPa.

Alternatively, the grain refiner/chromium carbide powder is placed on a pre-sintered body that is subsequently heat treated to obtain the desired structure at a temperature higher than the temperature for pre-sintering.

Example 1

Cemented carbide compacts were made according to the following: Cylindrical green compacts were pressed (diameter 12mm) from a powder with the composition of 94 weight-% WC and 6 weight-% Co. The WC raw material was relative coarse-grained with an average grain size of 3.0 μm (FSSS). All surfaces were covered with a Cr_3C_2 containing thin layer (0.02 g Cr_3C_2/cm^2). Thereafter the compacts were sintered at 1350°C for 30 minutes. During the last 15 minutes of the sintering an isostatic gas pressure of 10 MPa was applied to obtain a dense body. A cross-section of the sintered button was examined. No Cr_3C_2 could be seen on the surface. Figure 1 shows a graph of hardness and cobalt content versus the distance to the previously Cr_3C_2-covered surface. The cobalt content is lowest close to the surface and increases with increasing distance to a max value and then decreases again. The hardness is highest close to the surface and decreases with the distance to a min value and then increases again towards the center. Figure 2 shows a graph of chromium content versus the distance to the previously Cr_3C_2-covered surface. The chromium content is highest close to the surface and decreases with the distance. Figure 3a is a micrograph showing the microstructure at a distance of 20 μm from the previously Cr_3C_2-covered surface (FEG-SEM, 2000X, BSE mode). Figure 3b is a micrograph showing the microstructure at a distance of 2.5 mm from the previously Cr_3C_2-covered surface (FEG-SEM, 2000X, BSE mode). Figure 3c is a micrograph showing the microstructure in the interior portion (6 mm from the previously Cr_3C_2-covered surface) of the button (FEG-SEM, 2000X, BSE mode). The WC-grain sizes measured as arithmetic mean of intercept values are presented in table 1.

Table 1.

Distance from surface	Mean grain size [µm]
20 µm	1.5
2.5 mm	1.8
6.0 mm	1.8

CLAIMS

1. A cemented carbide tool insert/button for mining and construction comprising hard constituents in a binder phase of Co and Ni, or Co and at least one surface portion and an interior portion, wherein in said surface portion the grain size is smaller than in the interior portion wherein the surface portion with the fine grain size has a lower binder phase content than the interior portion,
wherein the surface portion contains Cr such that the ratio between the parameter A=((wt-% Cr/wt-% binder phase)+0.01) in the surface portion and the parameter
B=((wt-% Cr/wt-% binder phase)+0.01) taken at the part of the body that is characterized by the lowest Cr content is
A/B >1.5, and
wherein there is a maximum in Co-content between a fine grained and a coarse grained portion.

2. The cemented carbide insert/button according to claim 1 having a ratio between a binder phase content of the surface portion and a binder phase content of the interior portion, which ratio is < 1.

3. The cemented carbide insert/button according to claim 2 wherein the ratio is <0.9.

4. The cemented carbide insert/button according to claim 2 wherein the ratio is <0.75.

5. The cemented carbide insert/button according to any one of claims 1 to 4 having a ratio between a WC grain size of the surface portion and a WC grain size of the interior portion, which ratio is < 1.

6. The cemented carbide insert/button according to claim 5 wherein the ratio between a WC grain size of the surface portion and a WC grain size of the interior portion is <0.9.

7. The cemented carbide insert/button according to claim 5 wherein the ratio between a WC grain size of the surface portion and a WC grain size of the interior portion is <0.8.

8. The cemented carbide body according to any one of claims 1 to 7 having a ratio between a width of a surface zone poor in binder phase and of the diameter/width of the cemented carbide body, which ratio is 0.05-0.9.

9. The cemented carbide body according to claim 8 wherein the ratio between a width of a surface zone poor in binder phase and of the diameter/width of the cemented carbide body is 0.1-0.5.

10. The cemented carbide body according to claim 8 wherein the ratio between a width of a surface zone poor in binder phase and of the diameter/width of the cemented carbide body is 0.15-0.4.

11. The cemented carbide body according to any one of claims 1 to 10 wherein the composition of the cemented carbide is WC+binder with a nominal binder phase content of 4-25 wt-% and a nominal as sintered WC grain size, arithmetic mean intercept, of 1-15 µm.

12. The cemented carbide body of claim 11 wherein the nominal binder phase content is 5-10 wt-% and the nominal grain size is 1.5-5 µm.

13. Cemented carbide body according to any one of claims 1 to 12 comprising η-phase.

14. A method of making a cemented carbide body with a wear resistant surface zone including the following steps:

- providing a compact of cemented carbide from a single powder;
- placing a powder of grain refiner containing carbon and/or nitrogen on at least one portion of an exposed surface of the compact/presintered blank, containing Cr;
- sintering the compact/presintered blank and grain refiner powder so as to diffuse the grain refiner toward the center of the body thereby forming a surface zone inwardly from the exposed surface on which the grain refiner was placed, and forming an interior zone;

wherein said sintering is performed for a time such to obtain a dense body with a surface portion with a smaller grain size and lower cobalt content than those in the interior portion,

wherein the surface portion contains Cr such that the ratio between the parameter A=((wt-% Cr/wt-% binder phase)+0.01) in the surface portion and the parameter B=((wt-% Cr/wt-% binder phase)+0.01) taken at the part of the body that is characterized by the lowest Cr content is A/B >1.5, and

wherein there is a maximum in Co-content between a fine grained and a coarse grained portion.

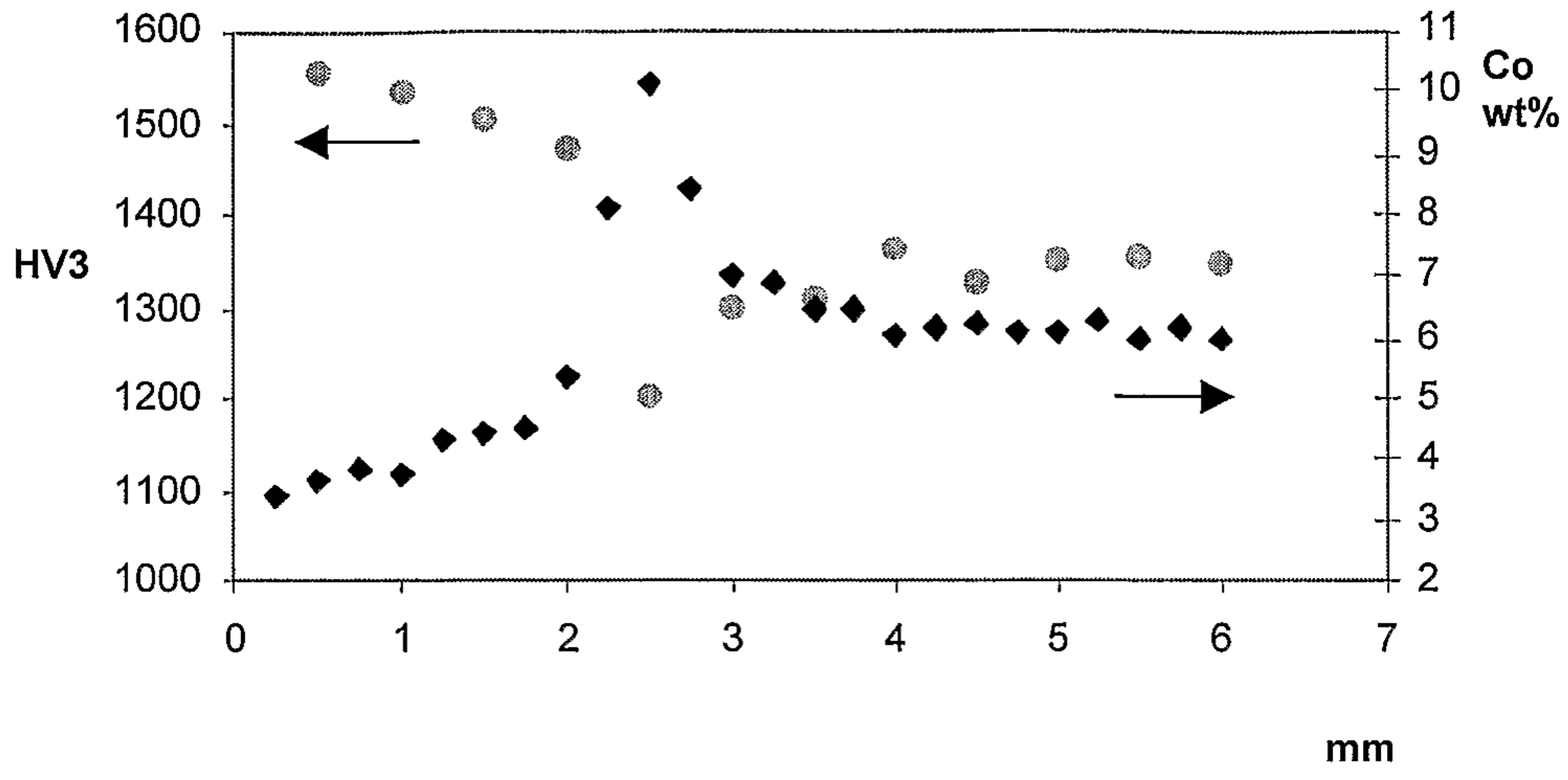

HV3
Co
wt%
mm
1600
1500
1400
1300
1200
1100
1000
11
10
9
8
7
6
5
4
3
2
0
1
2
3
4
5
6
7

Fig. 1

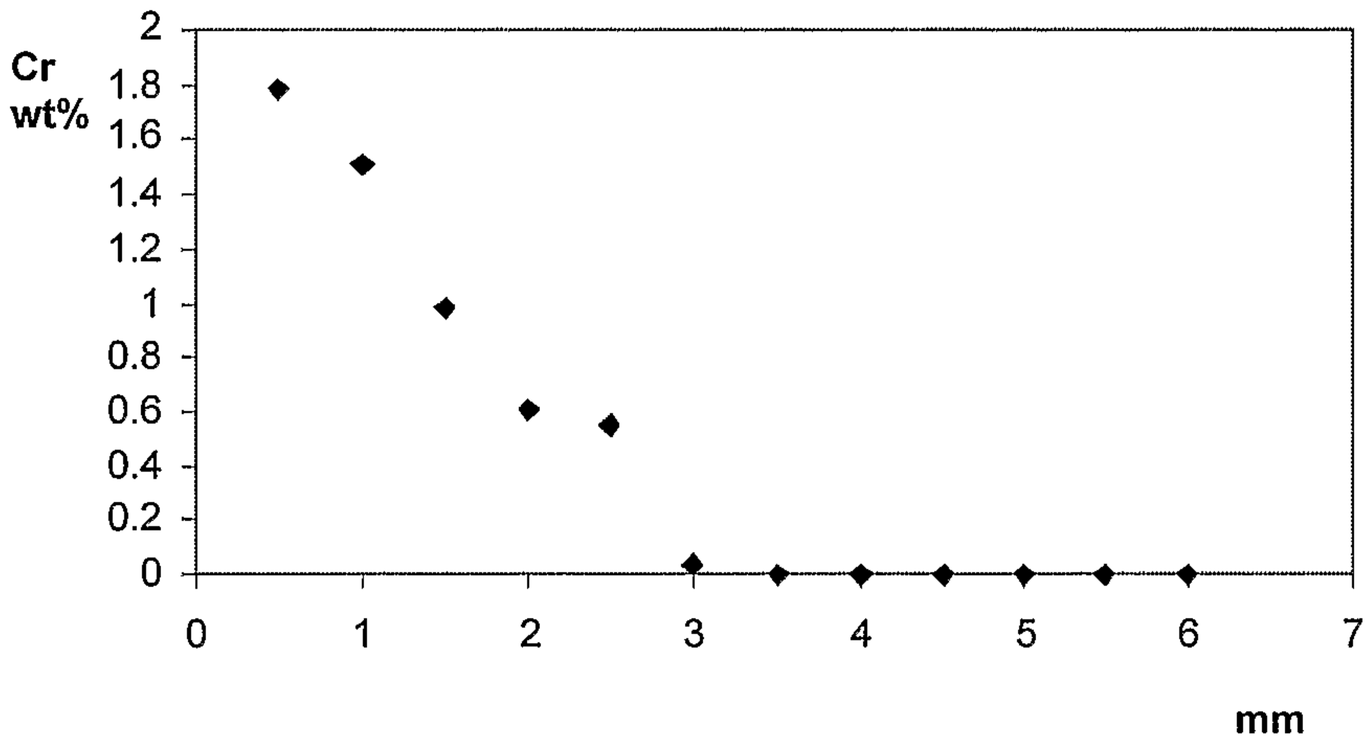

Cr
wt%
mm
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7

Fig 2

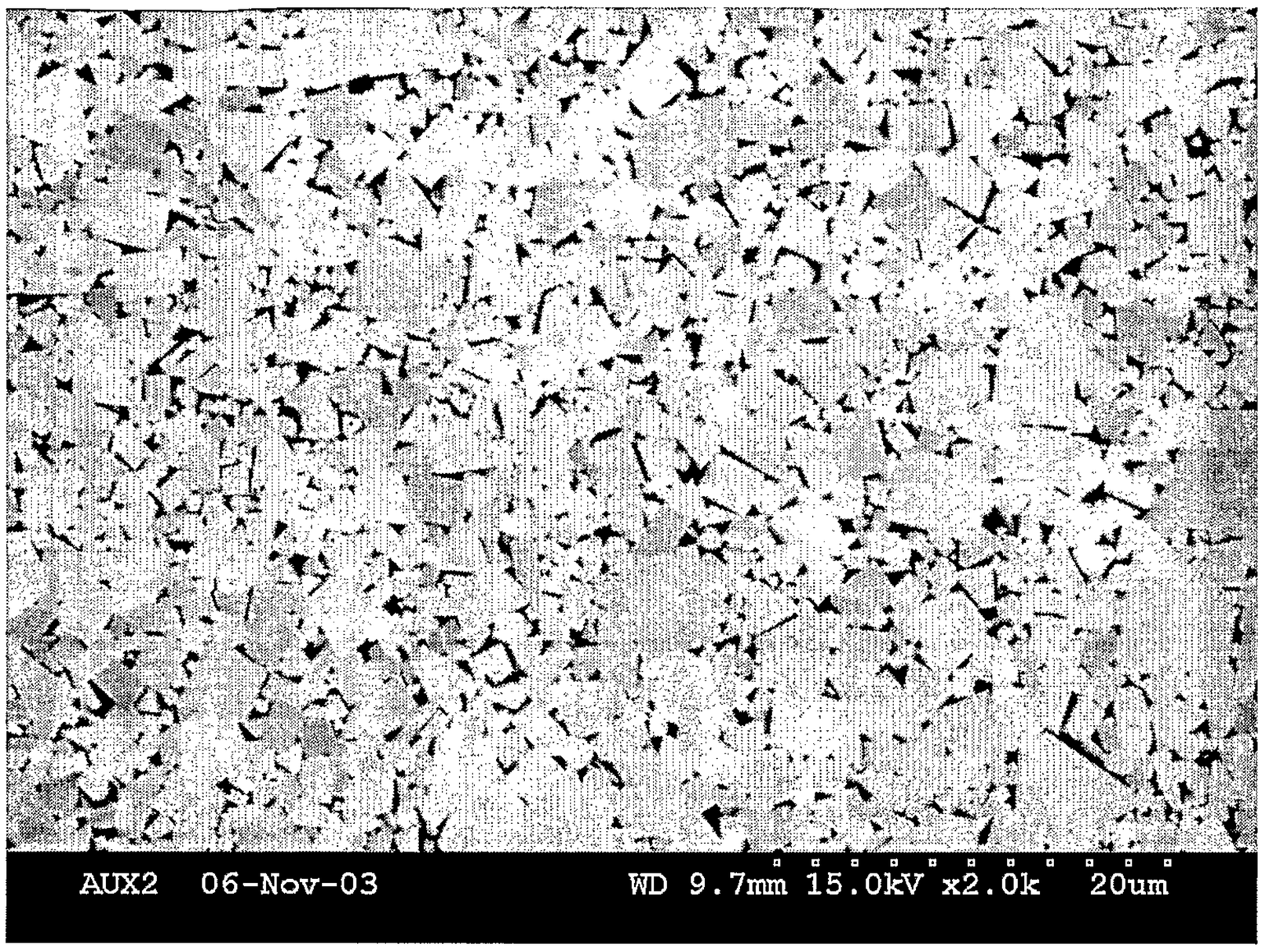

AUX2 06-Nov-03
WD 9.7mm 15.0kV x2.0k 20um

Fig. 3a

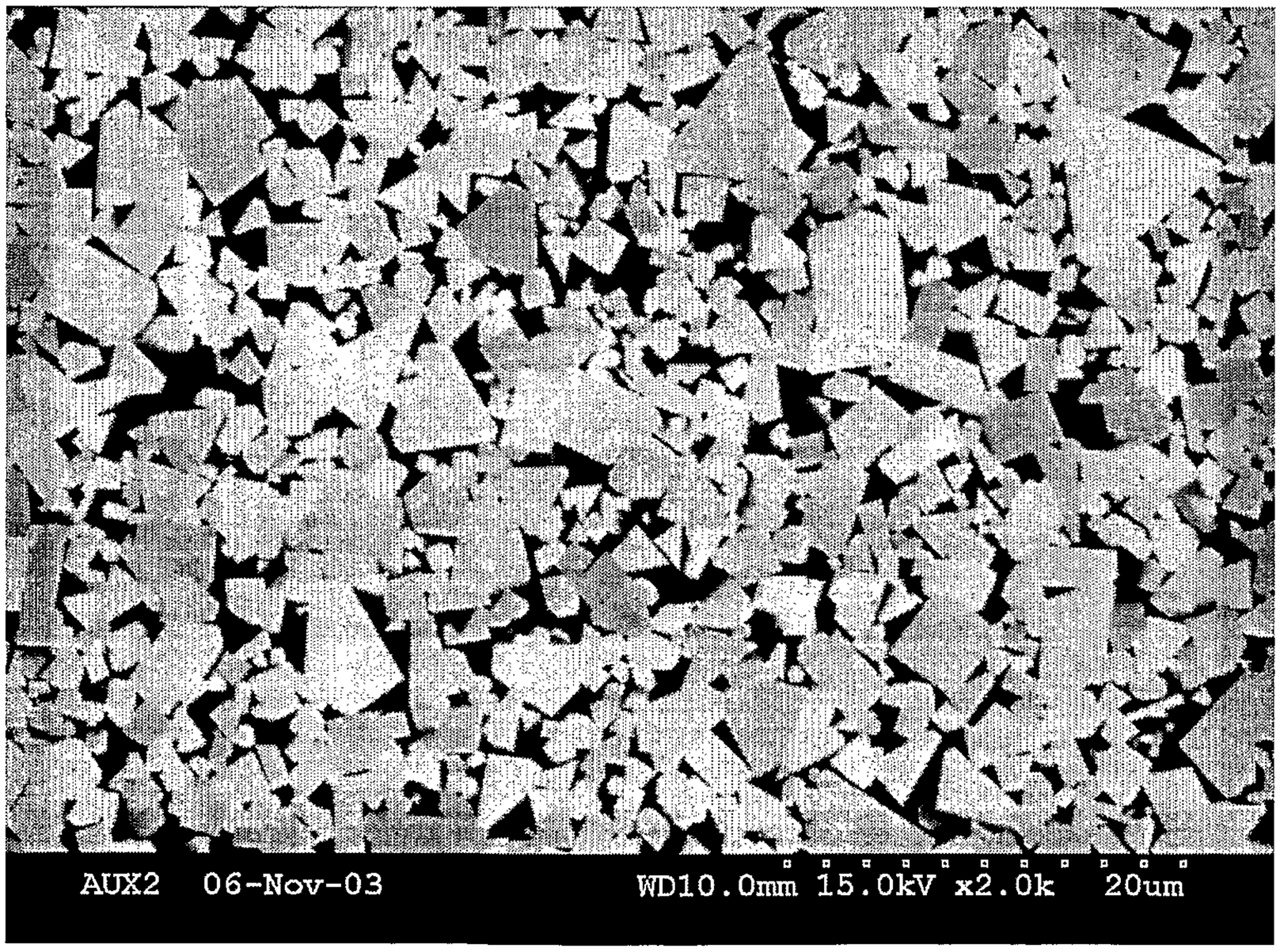

AUX2 06-Nov-03
WD10.0mm 15.0kV x2.0k 20um

Fig. 3b

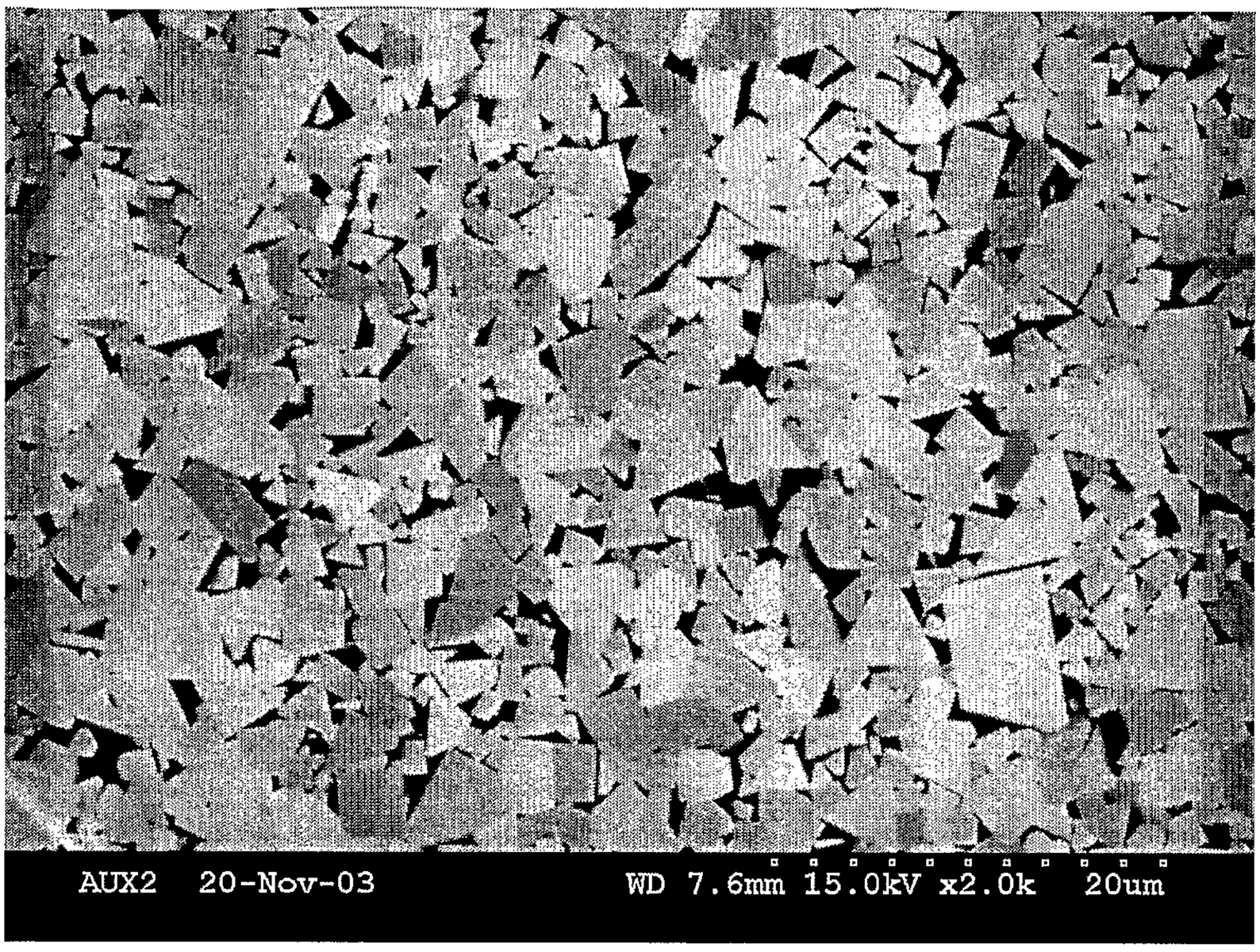


Fig. 3c