

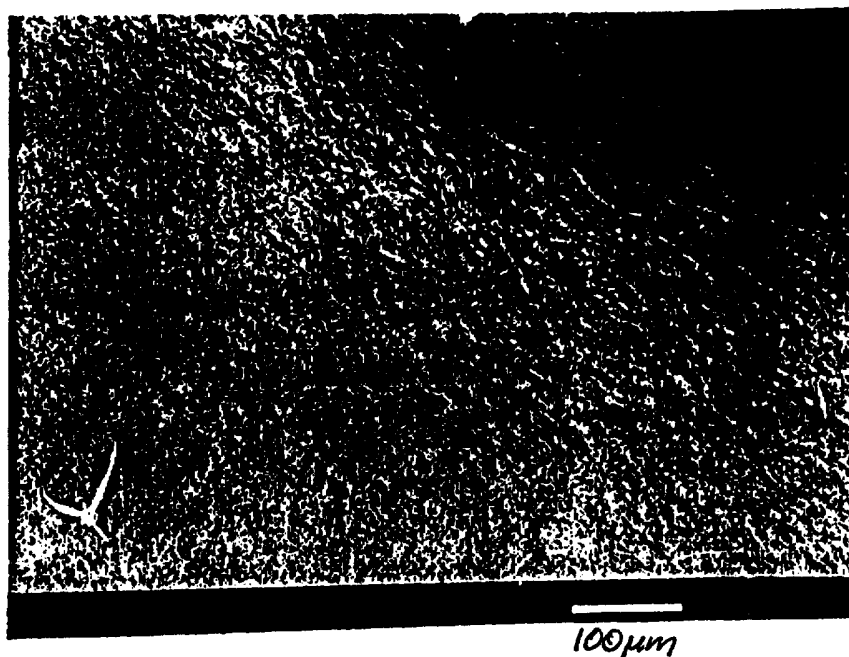
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 18/08, C04B 41/88	A1	(11) International Publication Number: WO 96/21051 (43) International Publication Date: 11 July 1996 (11.07.96)
(21) International Application Number: PCT/SE95/01586 (22) International Filing Date: 27 December 1995 (27.12.95) (30) Priority Data: 9404588-7 30 December 1994 (30.12.94) SE (71) Applicant (for all designated States except US): SANDVIK AB [SE/SE]; S-811 81 Sandviken (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): EDERYD, Stefan [SE/SE]; Galärvägen 14, S-132 47 Saltsjö-Boo (SE). GALLI, Enrico [SE/DK]; Mikkelborg Allé 100, DK-2980 Kokkedal (DK). NYGREN, Mats [SE/SE]; Västerled 181, S-161 42 Bromma (SE). WESTIN, Gunnar [SE/SE]; Storgatan 44, S-114 55 Stockholm (SE). EKSTRAND, Åsa [SE/SE]; Carl Bondes väg 82, S-165 74 Hässelby (SE). (74) Agents: ÖSTLUND, Alf et al.; Sandvik AB, Patent Dept., S- 811 81 Sandviken (SE).		(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: METHOD OF COATING CUTTING TOOL INSERTS**(57) Abstract**

The present invention relates to a method of coating cemented carbide inserts at least partly with a layer of at least one iron group metal. When inserts coated with such a layer are brazed to a holder or similar, a joint with improved strength is obtained. According to the method of the invention one or more metal salts of at least one iron group metal containing organic groups are dissolved and complex bound in at least one polar solvent with at least one complex former comprising functional groups in the form of OH or NR₃, (R=H or alkyl). A soluble carbon source is added to the solution which is subsequently at least partly applied to the cemented carbide inserts by dipping, spraying or painting. The inserts are dried and heat treated in an inert and/or reducing atmosphere. As a result, cemented carbide inserts are obtained at least partly coated with a layer of an iron group metal.



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Method of coating cutting tool inserts

The present invention relates to a method of coating cutting tool inserts with a layer of an iron group metal. Inserts with a coating applied according to the invention are particularly suitable for brazing.

Cemented carbide inserts are generally attached to tool-holders by mechanical means if possible. In case of saw-blades, drills and circular cutters the design does not permit mechanical clamps and/or similar mechanical attachments. In these cases the inserts have to be brazed to the toolholder.

When brazing cemented carbide with a low binder content there are problems with the wetting of the braze and therefore the inserts have to be coated with cobalt prior to the brazing procedure. For coating on industrial scale this cobalt coating is generally made electrolytically. However, such coating generally has poor adherence and in order to improve the adhesion the inserts are heat treated in a subsequent production step. This coating method is rather complex and expensive and the resultant coating adhesion is still not always satisfactory.

It has now surprisingly been found that using a technique related to the SOL-GEL technique cemented carbide inserts can be provided with a cobalt layer with improved bond to the tool.

Fig 1. shows in 150X the surface structure of the coating of cemented carbide insert coated with the method of the present invention.

Fig 2. shows in 1250X the microstructure and the thickness of the coating from the cross section of a T-shape crack in the coating. The network of the coating is observed clearly. The crack has been formed during the cooling step because of difference in thermal

expansion coefficient between coating and cemented carbide.

According to the method of the present invention one or more metal salts of at least one iron group metal containing organic groups are dissolved and complex bound in at least one polar solvent with at least one complex former comprising functional groups in the form of OH or NR_3 , ($\text{R}=\text{H}$ or alkyl). Optionally, a soluble carbon source is added to the solution which is applied onto the cemented carbide inserts. The solvent is evaporated and the coated inserts are heat treated in an inert and/or reducing atmosphere. As a result coated cemented carbide inserts are obtained which can be brazed to a tool according to standard practice.

The process according to the invention comprises the following steps where $\text{Me}=\text{Co}$, Ni and/or Fe , preferably Co :

1. At least one Me -salt containing organic groups such as carbo-oxylates, acetyl-acetonates, nitrogen containing organic groups such as schiff bases, preferably Me -acetates, is dissolved in at least one polar solvent such as ethanol, acetonitrile, dimethyl-formamide or dimethyl-sulfoxide and combinations of solvent such as methanol-ethanol and water-glycol, preferably methanol. Triethanolamine or other complex former especially molecules containing more than two functional groups, i. e. OH or NR_3 with $\text{R}=\text{H}$ or alkyl (0.1-2.0 mole complex former/mole metal, preferably about 0.5 mole complex former/mole metal) is added under stirring.

2. Optionally, sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) or other soluble carbon source such as other types of carbohydrates and/or organic compounds which decompose under formation of carbon in the temperature interval $100\text{-}500^\circ\text{C}$ in non-oxidizing atmosphere is added (0.1-2.0 mole C/mole metal,

preferably about 0.5 mole C/mole metal), and the solution is heated to 40°C in order to improve the solubility of the carbon source. The carbon is used to reduce the MeO formed in connection with heat treatment and to regulate the carbon-content in the coating layer.

3. The solution is applied at least onto the surface/surfaces to be brazed by dipping into the solution or by spraying or painting with the solution.

4. The coated inserts obtained in the preceding step are heat treated in nitrogen at about 700-1100°C. To achieve a full reduction a holding temperature might be needed. The time of reduction (5-120 minutes) is influenced by process factors such as coating thickness and reduction temperature. Nitrogen is normally used but argon, hydrogen, NH₃, CO and CO₂ (or mixtures between them) can be used whereby the composition and micro-structure of the coating can be modulated.

5. As a result of the heat treatment cemented carbide inserts coated with Me are obtained which e.g. can be brazed to a tool in the conventional way, however, with improved strength of the brazed joint.

The thickness of the final coating can be varied by varying the thickness of the initial coating. For brazing purposes a thickness of 0.1 - 0.5 µm is suitable. For other purposes, however, the coating can be thicker.

Because of the difference in thermal expansion the coating generally shows cracks. These cracks however, do not affect the brazing properties of the coating.

The method according to this invention can be used to provide coatings also on Ti-based carbonitrides so called cermets, binderless carbide and ceramics.

In these applications the coating can be tailor-made to form a good wetting to the base material. In addition to or instead of the carbon source mentioned above e.g.

Ti can be added as soluble salt in the metal salt-solution to form a good adhesion to a Ti containing base material.

Most of the solvent can be recovered which is of
5 great importance on an industrial production scale.

Example 1

134.89 g cobalt acetate-tetrahydrate
($\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 800 ml
10 methanol(CH_3OH). 36.1 ml triethanol-amine ($(\text{C}_2\text{H}_5\text{O})_3\text{N}$
(0.5 mole TEA/mole Co) was added during stirring and
after that 7.724 g sugar (0.5 mole C/mole Co) was added.
The solution was heated to about 40°C in order to
dissolve all the sugar added. About 100 cemented
15 carbide, grade SANDVIK DC03, saw tooth inserts were
dipped into the solution and dried in a drying cabinet
at a temperature of about 70°C.

The inserts were placed onto net trays and heat
treated in a furnace with nitrogen atmosphere. The
20 heating rate was 10°C/min to 700°C, no holding
temperature, cooling 10°C/min and finally completed with
reduction in hydrogen, holding temperature 800°C for 90
minutes.

As a result the cemented carbide inserts had been
25 coated with a 0.3 µm coating of cobalt.

Example 2

The inserts from Example 1 were brazed onto a saw
blade according to the following:

30	Steel	DIN75Cr1
	Brazing material	Degussa 49 Cu
	Flux	Degussa Special H
	Brazing temperature	690°C

As a reference a saw blade was manufactured using
35 the same materials, but the inserts had been coated with

cobalt in the conventional way, i.e. by electrochemical deposition. The strength of the brazing joint was determined on both saw blades by pushing off the inserts in a compression tester, using a special fixture to
5 support the steel blade in the interface between the brazing joint and the steel. The force needed to remove (push off) the inserts was measured with the following results:

10		Conventional coating	Coating acc. to the invention
	Number of inserts	100	100
	Force N per mm ² , mean	246	287
15	standard dev	19	11

The inserts according to the invention show both higher mean value and lower spread in the force required to remove them than the inserts coated in the conventional way.

Claim

1. Method of coating metal composites bodies formed by carbides, nitrides, carbonitrides with a binder phase consisting of Co and/or Ni at least partly with a layer of at least one iron group metal preferably Co characterised in comprising the following steps
- dissolving and complex binding at least one salt of at least one iron group metal containing organic groups in at least one polar solvent with at least one complex former comprising functional groups in the form of OH or NR₃, (R=H or alkyl)
 - optionally adding a soluble carbon source and/or other soluble agents to improve the wetting properties into the solution
 - applying the solution at least partly on said bodies by dipping, spraying or painting
 - drying the inserts to evaporate the solvent
 - heat treating the dried bodies in inert and/or reducing atmosphere to obtain said bodies at least partly coated with said at least one iron group metal.

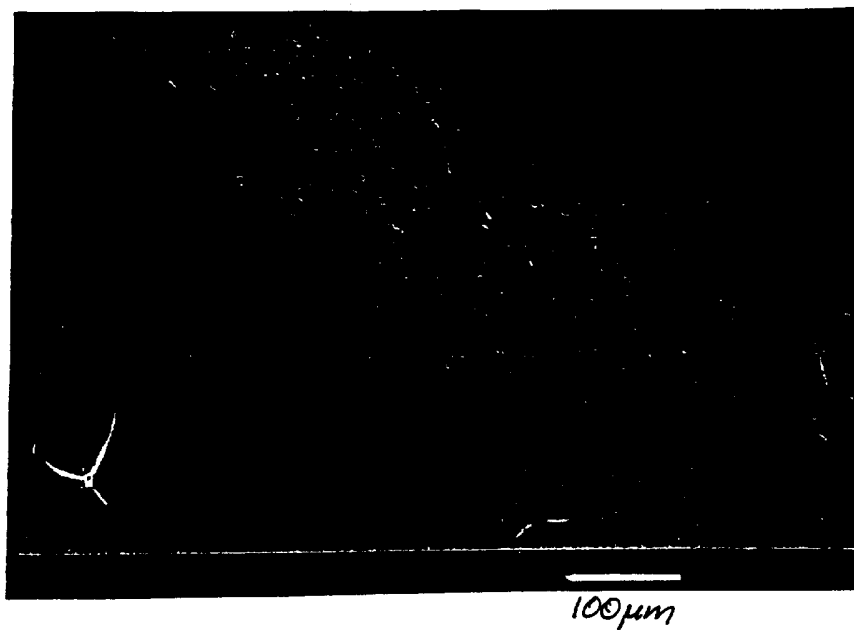


Fig. 1

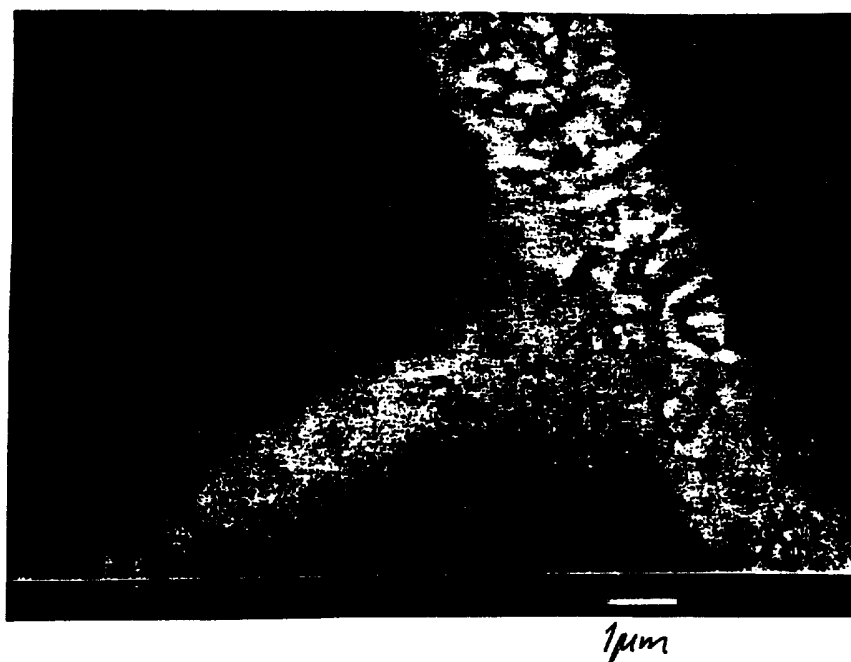


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 95/01586

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 18/08, C04B 41/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C, C04B, B23B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, Volume 121, No 10, 5 Sept 1994 (05.09.94), (Columbus, Ohio, USA), page 438, THE ABSTRACT No 115335x, JP, 649651, A, (Nippon Aluminium Mfg) 22 February 1994 (22.02.94) --	1
X	Patent Abstracts of Japan, Vol 8, No 99, E-243, abstract of JP, A, 59-17223 (NIPPON DENKI K.K.), 28 January 1984 (28.01.84) --	1
A	Patent Abstracts of Japan, Vol 13, No 501, C-652, abstract of JP, A, 1-201091 (IBIDEN CO LTD), 14 August 1989 (14.08.89) -- -----	1

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Date of the actual completion of the international search

29 May 1996

Date of mailing of the international search report

12.06.1996

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INTERNATIONAL SEARCH REPORT
Information on patent family members

01/04/96

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A- 649651	22/02/94	NONE	