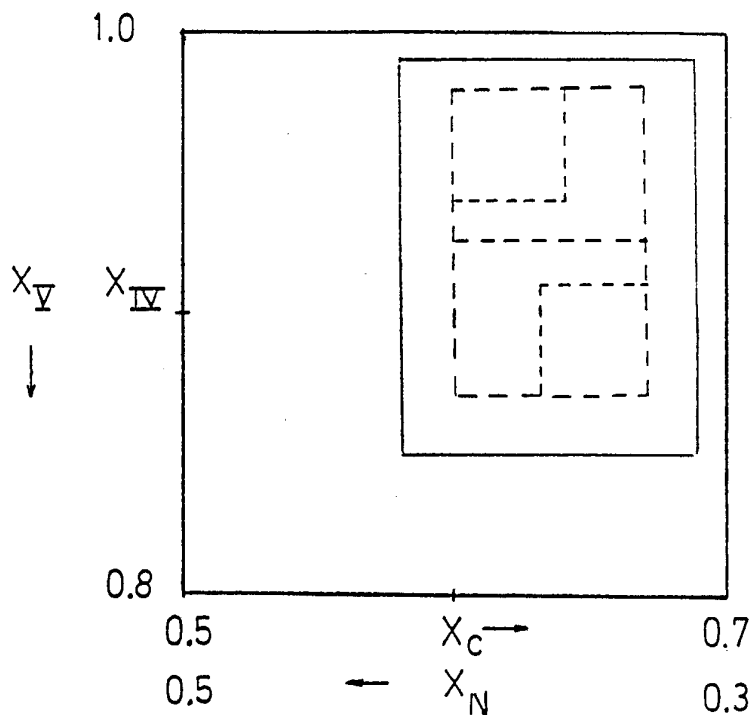




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C22C 29/04</p>	<p>A1</p>	<p>(11) International Publication Number: WO 92/11394 (43) International Publication Date: 9 July 1992 (09.07.92)</p>
<p>(21) International Application Number: PCT/SE91/00886 (22) International Filing Date: 19 December 1991 (19.12.91) (30) Priority data: 9004117-9 21 December 1990 (21.12.90) 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) : WEINL, Gerold [SE/SE]; Långsjövägen 128, S-125 51 Älvsjö (SE). OSKARSSON, Rolf [SE/SE]; Svampstigen 82, S-144 00 Rönninge (SE). (74) Agent: ÖSTLUND, Alf; Patent Department, Sandvik AB, S-811 81 Sandviken (SE).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report.</i></p>

(54) Title: METHOD OF PRODUCING A SINTERED CARBONITRIDE ALLOY FOR SEMIFINISHING MACHINING



(57) Abstract

According to the invention there now is provided a method of producing a sintered titanium based carbonitride alloy with 3-25 weight-% binder phase with extremely good properties at semifinishing operations at turning. The method relates to the use of a raw material comprising a complex cubic carbonitride containing the main part of the metals from groups IV and V of the periodic system and carbon and nitrogen to be found in the finished alloy whereby said alloy has the composition: $0.85 \leq X_{IV} \leq 0.99$, $0.58 \leq X_C \leq 0.69$, where X_{IV} is the molar ratio of the group IV elements of the alloy and X_C is the molar ratio of carbon.

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Method of producing a sintered carbonitride alloy for
semifinishing machining

The present invention relates to a method of producing a
5 sintered carbonitride alloy with titanium as main constituent
for semifinishing machining.

Sintered carbonitride alloys based on mainly titanium usually
referred to as cermets have during the last years increased
10 their use at the expense of more traditional cemented carbide
i.e. tungsten carbide based alloys.

US 3,971,656 discloses the production of an alloy with a duplex
hard constituent where the core has a high content of Ti and N
15 and the surrounding rim has a lower content of these two
elements which is compensated for by a higher content of group
VI metals i.e. in principle Mo and W and by higher carbon
content. The higher content of Mo, W and C has inter alia the
advantage that the wetting against the binder phase is improved
20 i.e. the sintering is facilitated. As a raw material a
carbonitride of titanium and a group VI metal is used.

By changing the raw material it is possible to vary the core-
rim-composition. In e.g. Swedish Patent Specification 459 862
25 it is shown how it is possible to use (Ti,Ta)C as a raw
material to get a duplex structure with cores with a high
content of titanium and tantalum but low content of nitrogen.
The surrounding rims have higher contents of group VI-metals,
i.e. molybdenum and tungsten and higher contents of nitrogen
30 than the cores. This leads inter alia to an improved resistance
against plastic deformation.

Furthermore, it has in Swedish Patent Application 8902306-3
been shown how by mixing various types of core-rim structures
35 in one and the same alloy advantages and drawbacks can be
balanced out in such a way that optimized alloys are obtained.

EP-A-259192 discloses a sintered alloy comprising a mixed carbonitride of titanium and at least one element from the group consisting of group IV, V and VI elements except titanium in a binder phase based on Co and/or Ni. The alloy is produced
5 by mixing powders of the hard constituents, heating the mixture in a nitrogen atmosphere at a temperature of at least the sintering temperature to form a solid solution, milling said solid solution to obtain a carbonitride powder which is mixed with Co and/or Ni and sintered.

10

It has now turned out that if sintered titaniumbased carbonitride alloys are produced using complex cubic carbonitride raw material which contains the main part, preferably >90%, most preferably >95% of the metals at least
15 two preferably at least three from the groups IV and V in addition to carbon and nitrogen being part of the finished sintered carbonitride alloy unique structures as well as unique properties are obtained. Preferably all of the nitrogen shall be present in the mentioned carbonitride raw material.

20

In particular of the above-mentioned metals all titanium and tantalum shall be present in the raw material according to the invention. Preferably also vanadium, niobium and suitably also zirconium and hafnium are present if they are part of the
25 finished sintered alloy. Metals from group VI, Cr, Mo and W, shall, if they are present, be added as multiple carbides, single carbides and/or as metal+carbon, but they may also be part of the raw material according to the invention provided that the raw material remains cubic.

30

The raw material according to the invention is produced directly by carbonitriding of the oxides of the metals or the metals themselves. As a result a carbonitride powder with essentially equiaxial grains and a narrow grain size distribution is
35 obtained with a mean grain size of 0.8 - 3 μm , preferably 1 - 2 μm .

As mentioned interesting properties of a sintered carbonitride alloy are obtained if the special raw materials according to this invention are used. Thus, it has turned out that a carbonitride alloy with extremely positive properties at semifinishing operations at turning i.e. with somewhat lower cutting speeds and higher feeds than finishing i.e. pure finishing operations, >250 m/s, for carbon steel and low alloyed steel, and low feeds, <0.3 mm/rev, is obtained, if a complex raw material with e.g. the composition

($Ti_{0.96}, Ta_{0.04}$) ($C_{0.62}, N_{0.38}$) is used. This effect is further increased if in addition vanadium is added whereby the corresponding formula will be ($Ti_{0.89}, Ta_{0.04}, V_{0.07}$) ($C_{0.65}, N_{0.35}$). Corresponding inserts made from simple raw materials and in exactly the same equipment give considerably decreased properties in toughness inter alia greater scatter at the same wear resistance. This means that the reliability of such inserts is considerably decreased which means that they are not as efficient when producing with limited manning a production form with increased importance due to increasing labour costs.

One of the reasons for this positive behaviour has turned out to be that a considerably lower porosity level is obtained with this complex raw material compared to conventional raw materials without having to use any other means such as HIP and this with even lower compaction pressure than for conventional material. This is a great advantage from production point of view inter alia due to reduced tool wear and considerably lower risk for unfavourable pressing cracks.

The invention thus relates to a method of producing a titanium based carbonitride alloy with 3-25 % by weight binder phase based on Co, Ni and/or Fe using the above mentioned complex raw material. This raw material is milled together with carbides from group VI, if any, and binder phase elements and carbon addition, if any, and minor additions of e.g. TiC, TiN, TaC, VC or combinations thereof due to small deviations in composition of the complex raw material whereafter compaction and

sintering, preferably in an inert atmosphere, is performed according to known technique.

Fig 1 shows the 'window' in the composition diagram for Group IV-Group V - C-N, expressed in molar ratio, of the complex raw material which shows the above mentioned advantages in high magnification, whereas fig 2 shows where in the total molar ratio diagram this small area is situated.

Group IV metals are Ti, Zr and/or Hf and Group V metals are V, Nb and/or Ta.

As is evident from figure 1 the window comprises the composition area:

15

$$0.85 \leq X_{IV} \leq 0.99$$

$$0.58 \leq X_C \leq 0.69$$

and in particular:

20

$$0.87 \leq X_{IV} \leq 0.98$$

$$0.60 \leq X_C \leq 0.67$$

The latter restricted window can be divided into two, one without other group V metals than Ta:

25

$$0.925 \leq X_{IV} \leq 0.98$$

$$0.60 \leq X_C \leq 0.67$$

and another one with other group V elements than Ta i.e. V and Nb:

30

$$0.87 \leq X_{IV} \leq 0.925$$

$$0.60 \leq X_C \leq 0.67$$

35

Particularly good properties are obtained for the compositions

$$0.94 \leq X_{IV} \leq 0.98$$

$$0.60 \leq X_C \leq 0.64$$

respectively

5

$$0.87 \leq X_{IV} \leq 0.91$$

$$0.63 \leq X_C \leq 0.67$$

For titanium the following applies $x_{Ti} > 0.7$ preferably $x_{Ti} > 0.75$.

10

In the above given molar ratios for carbon and nitrogen usual amounts of oxygen may be present i.e. substitute carbon and nitrogen even if it is desirable to keep such amounts of oxygen low <0.8 %, preferably <0.5 %. The invention comprises

15 stoichiometric as well as usually substoichiometric carbonitrides.

Example

20 Titanium-based carbonitride alloys with 16.5 % Ni+Co binder phase were produced with the use of a complex raw material according to the invention ($Ti_{0.89}, Ta_{0.04}, V_{0.07}$) ($C_{0.65}, N_{0.35}$) as well as with the use of simple raw material: TiN, TiC and VC. In both cases also WC and Mo_2C were added in addition to Co

25 and Ni. The following compaction pressure and porosity after milling and sintering to the same grain size were obtained:

	Porosity	Compaction pressure, N/mm ²
30 Alloy according to the invention	A00	137
Simple raw materials	A06-A08 B02	171

Claims

1. Method of producing a sintered titanium based carbonitride alloy with 3-25 weight-% binder phase by milling, pressing and sintering according to known technique
5 characterized in that a raw material is used comprising a complex cubic carbonitride containing the main part of the metals from groups IV and V of the periodic system and carbon and nitrogen to be found in the finished alloy
10 whereby said alloy has the composition

$$0.85 \leq X_{IV} \leq 0.99$$

$$0.58 \leq X_C \leq 0.69$$

15 where X_{IV} is the molar ratio of the group IV elements of the alloy and X_C is the molar ratio of carbon.

2. Method according to claim 1 characterized in that the carbonitride raw material comprises essentially
20 equiaxial grains with a narrow grain size distribution with a mean grain size of 0.8 - 3 μm , preferably 1 - 2 μm .

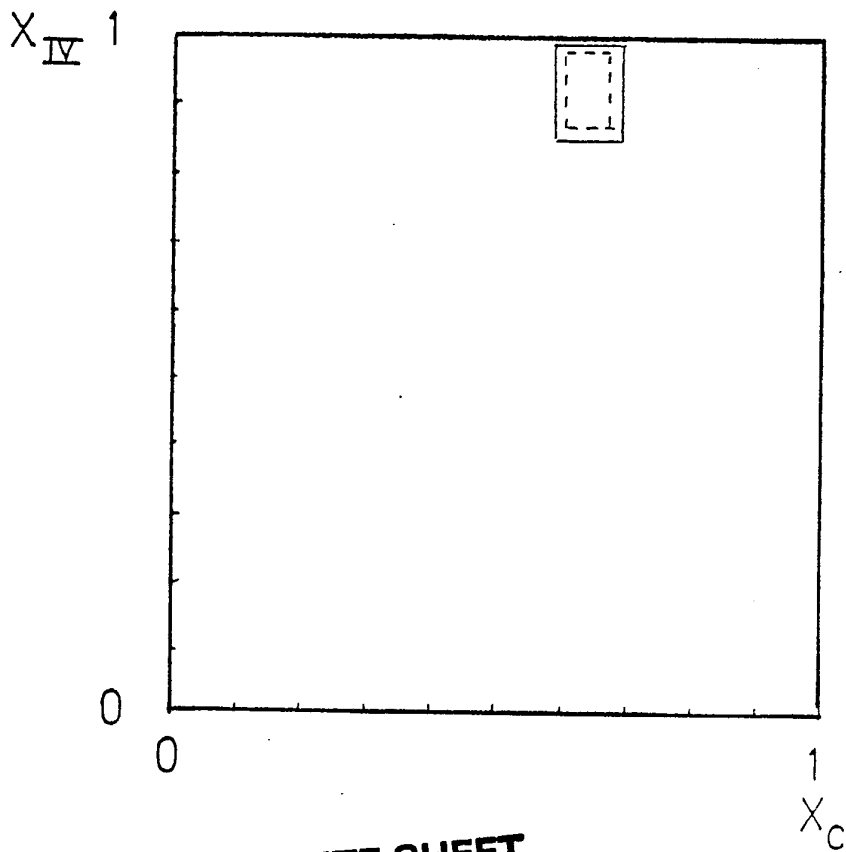
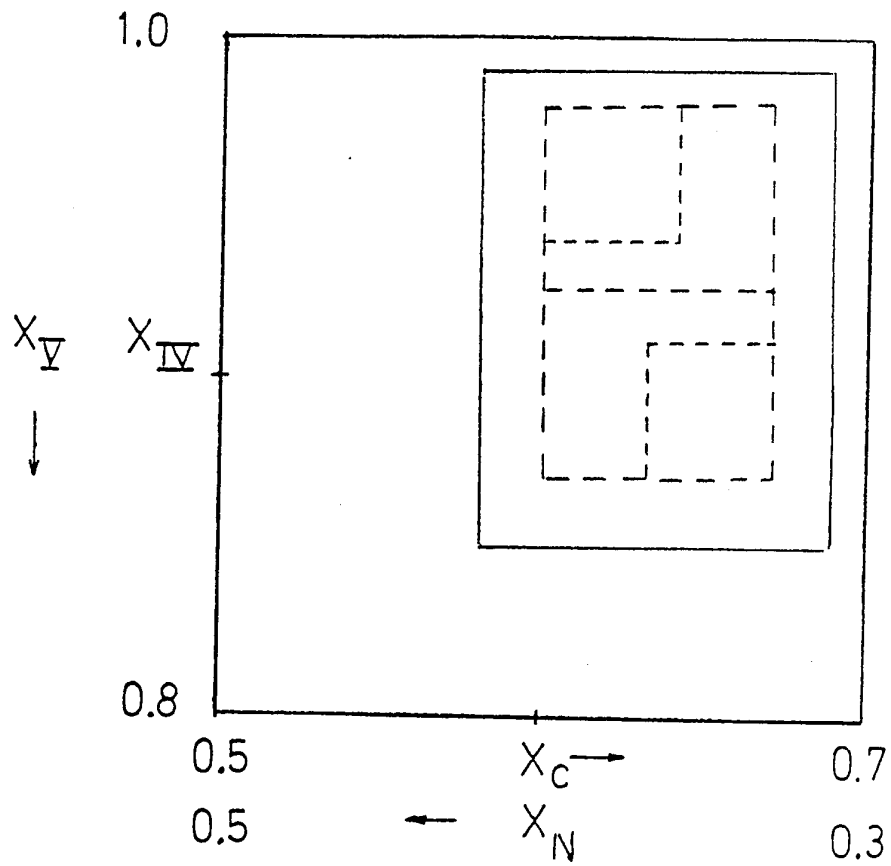
3. Method according to claim 1 or 2 characterized in that the composition of the complex raw material is
25

$$0.87 \leq X_{IV} \leq 0.98$$

$$0.60 \leq X_C \leq 0.67$$

4. Method according to any of the preceding claims
30 characterized in that said raw material is produced directly by carbonitriding of the oxides of the metals or the metals themselves.

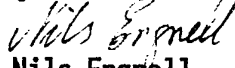
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SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00886

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁸ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 22 C 29/04				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁷				
Classification System	Classification Symbols			
IPC5	C 22 C			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸				
SE,DK,FI,NO classes as above				
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹				
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³		
A	EP, A2, 0259192 (SUMITOMO ELECTRIC INDUSTRIES LIMITED) 9 March 1988, see the whole document --	1-4		
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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top; border: none;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
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IV. CERTIFICATION				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report			
19th March 1992	1992 -03- 23			
International Searching Authority	Signature of Authorized Officer			
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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