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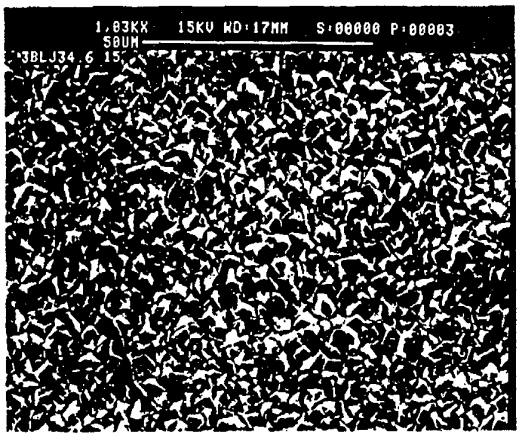

(57) Abstract

According to the present invention there is provided a body coated with refractory single- or multilayers, wherein specific layers are characterized by a controlled microstructure and phase composition with crystal planes preferably grown in a preferential direction with respect to the surface of the coated body. Said coating comprises one or several refractory layers of which at least one layer is a dense, fine-grained layer of α-Al_2O_3 textured in the (104) direction. The Al_2O_3-coating is obtained by control of the oxidation potential of the CVD-reactor atmosphere prior to the nucleation of Al_2O_3, which is initiated by a controlled sequencing of the reactant gases. During the growth of the Al_2O_3 a sulphur dopant is added, preferably H_2S. The coated tool according to the invention exhibits excellent surface finish and shows much improved wear and toughness properties compared to prior art objects when used for machining steel, cast iron and, particularly, when machining nodular cast iron.

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OXIDE COATED CUTTING TOOL

The present invention relates to a coated cutting tool for chipforming machining.

Chemical Vapour Deposition (CVD) of alumina on cutting tools has been an industrial practice for more than 15 years. The wear properties of Al_2O_3 as well as of other refractory materials have been discussed extensively in the literature.

The CVD-technique has also been used to produce coatings of other metal oxides, carbides and nitrides, the metal being selected from transition metals of the IVB, VB and VIB groups of the Periodic Table. Many of these compounds have found practical applications as wear resistant or protective coatings, but few have received as much attention as TiC, TiN and Al_2O_3.

Cemented carbide cutting tools coated with various types Al_2O_3-coatings, e.g., pure κ-Al_2O_3, mixtures of κ-and α-Al_2O_3 and very coarse-grained α-Al_2O_3 have been commercially available for many years. Al_2O_3 crystallizes in several different phases: α, κ, γ, β, θ etc. The two most frequently occurring phases in CVD of wear resistant Al_2O_3-coatings are the thermodynamically stable, hexagonal α-phase and the metastable κ-phase. Generally, the κ-phase is fine-grained with a grain size in the range 0.5-2.0 µm and often exhibits a columnar coating morphology. Furthermore, κ-Al_2O_3 coatings are free from crystallographic defects and free from micropores or voids.

The α-Al_2O_3 grains are usually coarser with a grain size of 1-6 µm depending upon the deposition conditions. Porosity and crystallographic defects are in this case more common.

Often both α- and κ-phase are present in a CVD alumina coating deposited onto a cutting tool. In commer-

cial cutting tools, Al_2O_3 is always applied on TiC coated carbide or ceramic substrates (see, e.g. U.S. Pat. No. 3,837,896, now Reissue U.S. Pat. No. 29,420) and therefore the interfacial chemical reactions between the TiC-surface and the alumina coating are of particular importance. In this context the TiC layer should also be understood to include layers having the formula $TiC_xN_yO_z$ in which the carbon in TiC is completely or partly substituted by oxygen and/or nitrogen.

The practice of coating cemented carbide cutting tools with oxides to further increase their wear resistance is in itself well known as is evidenced in e.g. U.S. Pat. Reissue No. 29,420 and U.S. Pat. Nos. 4,399,168, 4,018,631, 4,490,191 and 4,463,033. These patents disclose oxide coated bodies and how different pretreatments e.g. of TiC-coated cemented carbide, enhance the adherence of the subsequently deposited oxide layer. Alumina coated bodies are further disclosed in U.S. Pat. No. 3,736,107, 5,071,696 and 5,137,774 wherein the Al_2O_3 layers comprise α, κ resp $\alpha+\kappa$ combinations.

US 4,619,866 describes a method for producing fast growing Al_2O_3 layers by utilizing a hydrolysis reaction of a metal halide under the influence of a dopant e.g. hydrogen sulphide(H_2S) in the concentration range 0.01-0.2 % at a CVD deposition temperature 1000-1050°C. Under these process conditions, essentially two phases of Al_2O_3, the α- and the κ phases, are produced. The resulting coating consists of a mixture of the smaller κ-grains and the larger α-grains. The process yields coatings with an even layer thickness distribution around the coated body.

Swedish patent application 9101953-9 discloses a method of growing a finegrained κ-alumina coating.

In Swedish Patent Application No. 9203852-0 a method is disclosed for obtaining a fine grained, (012)-textured α-Al_2O_3-coating. This particular Al_2O_3-coating applied on cemented carbide tools has been found particularly useful for machining of cast-iron.

Swedish Patent Application No. 9304283-6 discloses a body with a coating comprising one or more refractory layers of which at least one layer is a layer of α-Al_2O_3 textured in the (110) direction. The alumina layer is essentially free of cooling cracks and comprises platelike grains with a length of 2-8 µm and a length/width-ratio of 1 - 10.

The object of the present invention is, thus, to provide onto a hard substrate or preferably onto aforementioned $TiC_xN_yO_z$ coating at least one single phase Al_2O_3 layer of the polymorph α with a desired microstructure and crystallographic texture using suitable nucleation and growth conditions such that said properties of the Al_2O_3 layer are stabilized.

It is a further object of the invention to provide an alumina coated cutting tool insert with improved cutting performance in steel, stainless steel, cast iron and in nodular cast iron.

Fig 1 shows a Scanning Electron Microscope (SEM) top-view micrograph at 1000X magnification of a typical Al_2O_3-coating according to the invention.

According to the invention there is provided a cutting tool comprising a body of a hard alloy onto which a wear resistant coating has been deposited. The coating comprises one or several refractory layers of which at least one layer is a dense, fine-grained and preferably textured Al_2O_3-layer of the polymorph α.

A coated cutting tool according to the present invention exhibits improved wear and toughness properties compared to prior art tools when used for machining

steel or cast iron particularly if the surface has been further smoothened by wet blasting.

More specifically, the coated tool comprises a substrate of a sintered cemented carbide body, cermet or a ceramic body preferably of at least one metal carbide in a metal binder phase. The individual layers in the coating structure may be TiC or related carbide, nitride, carbonitride, oxycarbide and oxycarbonitride of a metal selected from the group consisting of metals in the Groups IVB, VB, and VIB of the Periodic Table, B, Al and Si and/or mixtures thereof. At least one of said layers is in contact with the substrate. However, at least one of the layers in the coating structure comprises a fine-grained, dense, single phase α-Al_2O_3 coating free of microporosity and crystallographic defects. This coating is preferentially textured with a thickness of d = 0.5-25 µm with an average grain size (s) of

0.5 µm < s < 1 µm for 0.5 µm < d < 2.5 µm and

0.5 µm < s < 4 µm for 2.5 µm < d < 25 µm

The fine-grained microstructure comprises a narrow grain size distribution. Most often 80 % of the Al_2O_3 grains have a grain size of ± 50 % of the average grain-size.

The grain-size of the Al_2O_3-coating is determined from a SEM top view micrograph at 5,000X magnification. Drawing three straight lines in random directions, the average distances between grain boundaries along the lines, are taken as a measure of the grain-size.

The Al_2O_3-layer according to the invention has a preferred crystal growth orientation in the (104) direction which is determined by X-ray Diffraction (XRD) measurements. A Texture Coefficient, TC, can be defined as:

$$TC(hkl) = \frac{I(hkl)}{I_o(hkl)} \left\{ \frac{1}{n} \sum \frac{I(hkl)}{I_o(hkl)} \right\}^{-1}$$

where

I(hkl) = measured intensity of the (hkl) reflection

I_o(hkl) = standard intensity of the ASTM standard powder pattern diffraction data

n = number of reflections used in the calculation, (hkl) reflections used are: (012), (104), (110), (113), (024), (116)

According to the invention TC for the set of (104) crystal planes is larger than 1.5, preferably larger than 2.5, and most preferably larger than 3.0.

The coated body according to the invention is further characterized by a surface roughness (R_a) of the refractory coating of less than 0.3 µm over a measured length of 0.25 mm. Preferably, the Al_2O_3-layer is an exposed outermost layer.

The textured Al_2O_3-coating according to the invention is obtained by careful control of the oxidation potential of the CVD-reactor atmosphere prior to the nucleation of Al_2O_3. The total concentration level of H_2O or other oxidizing species should preferably be below 5 ppm. However, the nucleation of Al_2O_3 is initiated by a controlled sequencing of the reactant gases as follows: CO_2 and CO are first entering the reactor in a H_2 free atmosphere e g in the presence of N_2 or/and Ar then H_2 and $AlCl_3$ are allowed into the reactor. The temperature shall be 850-1100 ^oC, preferably 950-1000^oC, during the nucleation. However, the exact conditions depend to a certain extent on the design of the equipment used. It is within the purview of the skilled artisan to determine whether the requisite texture and coating morphology have been obtained and to modify the nucleation and the deposition conditions in

accordance with the present specification, if desired, to effect the amount of texture and coating morphology.

Example 1

A) Cemented carbide cutting inserts with the composition 6.5 % Co, 8.5 % cubic carbides and balance WC were coated with a 5.5 μm thick layer of TiCN. In subsequent process steps during the same coating cycle, a 6 μm thick layer of α-Al_2O_3 was deposited. Prior to the nucleation, the oxidation potential of the hydrogen carrier gas, i.e. the water vapour concentration, was explicitly set forth to a low level, less than 5 ppm (See also U.S. Pat. No. 5,071,696).

A hydrogen free reaction gas mixture comprising N_2, CO_2 and CO was first introduced into the CVD-reactor. The reaction gases were sequentially added in the given order. After a preset time H_2 and $AlCl_3$ were allowed into the reactor. During the deposition of Al_2O_3, H_2S was used as a dopant.

The gas mixtures and other process conditions during the Al_2O_3 deposition steps comprised:

Step	1.	2
CO_2	4%	4%
$AlCl_3$	4%	4%
CO	2%	-
H_2S	-	0.2%
HCl	1%	4%
H_2	balance	balance
Pressure	55 mbar	100 mbar
Temperature	1000°C	1000°C
Duration	1 hr	7.5 hr

XRD-analysis showed a texture coefficient, TC(104), of 3.2 of the (104) planes in the single α phase of the Al_2O_3 coating.

SEM-studies showed a fine grained, 6 μm thick Al_2O_3-coating with an average grain size of = 2.1 μm.

B) The cemented carbide substrate of A) was coated with TiCN (5.5 μm) and Al_2O_3 (6 μm) as set forth in A) except that the Al_2O_3 process was carried out according to prior art technique resulting in a mixture of coarse α- and fine κ-Al_2O_3 grains in the coating.

Coated tool inserts from A), and B) were all wet blasted with 150 mesh Al_2O_3 powder in order to smoothen the coating surface.

The cutting inserts were then tested with respect to edge line and rake face flaking in a facing operation in nodular cast iron (AISI 60-40-18, DIN GGG40). The shape of the machined work piece was such that the cutting edge is intermitted twice during each revolution.

Cutting data:
Speed = 150 m/min,
Cutting Depth = 2.0 mm and
Feed = 0.1 mm/rev.

The inserts were run one cut over the face of the work piece.

The results are expressed in the table below as percentage of the edge line in cut that obtained flaking as well as the rake face area subjected to flaking in relation to total contact area between the rake face and the work piece chip.

	Flaking (%)		
	Edge line	Rake face	
A) single phase/textured α-Al_2O_3	5	6	(acc. to the invention)
B) α+κ Al_2O_3	90	86	

Example 2

The cutting inserts from A) and B) were also tested with respect to edge line flaking in a facing operation in an alloyed steel (AISI 1518, W-no. 1,0580). The shape of the machined work piece was such that the cutting edge is intermitted three times during each revolution.

Cutting data:

Speed = 130-220 m/min,

Cutting Depth = 2 mm and

Feed = 0.2 mm/rev.

The inserts were run one cut over the face of the work piece.

The result below is expressed as percentage of the edgeline in cut that obtained flaking.

	Flaking (%) Edge line	
D) single phase/textured α-Al_2O_3	0	(according to the invention)
E) $\alpha+\kappa$ Al_2O_3	28	

CLAIMS

1. Body at least partially coated with one or more refractory layers of which at least one layer is alumina c h a r a c t e r i z e d in said alumina layer having a thickness of d = 0.5-25 μm with grain size (s):

0.5 μm < s < 1 μm for 0.5 μm < d < 2.5 μm and

0.5 μm < s < 4 μm for 2.5 μm < d < 25 μm.

and consisting of single phase α-structure textured in the (104)-direction with a texture coefficient larger than 1.5 preferably larger than 2.5. and most preferably larger than 3.0 the texture coefficient being defined as below:

$$TC(hkl) = \frac{I(hkl)}{I_o(hkl)} \left\{ \frac{1}{n} \sum \frac{I(hkl)}{I_o(hkl)} \right\}^{-1}$$

where

I(hkl) = measured intensity of the (hkl) reflection

I_o(hkl) = standard intensity of the ASTM standard powder pattern diffraction data

n = number of reflections used in the calculation

(hkl) reflections used are: (012), (104), (110), (113), (024), (116).

2. Body according to any of the preceding claims c h a r a c t e r i z e d in that said alumina layer is an exposed outermost layer.

3. Body according to any of the preceding claims c h a r a c t e r i z e d in that said alumina layer is in contact with a $TiC_xN_yO_z$-layer.

4. Body according to claim 5 c h a r a c t e r i z e d in that said $TiC_xN_yO_z$-layer is the innermost layer of the coating.

5. Body according to any of the preceding claims c h a r a c t e r i z e d in that said body is a cut-

ting tool insert of cemented carbide, titanium based carbonitride or ceramics.

6. Method of coating a body with an α-alumina coating at which the body is brought in contact with a hydrogen carrier gas containing one or more halides of aluminium and a hydrolyzing and/or oxidizing agent at high temperature c h a r a c t e r i z e d in that the oxidation potential of the CVD-reactor atmosphere prior to the nucleation of Al_2O_3 is kept at a low level using a total concentration of H_2O or other oxidizing species preferably below 5 ppm, that the nucleation of Al_2O_3 is started up by controlled sequencing of the reactant gases that CO_2 and CO are entering the reactor first in an N_2 and/or Ar atmosphere followed by H_2 and $AlCl_3$, that the temperature is preferably between 950-1000°C during the nucleation and that during the growth of the Al_2O_3 a sulphur dopant is added, preferably H_2S.

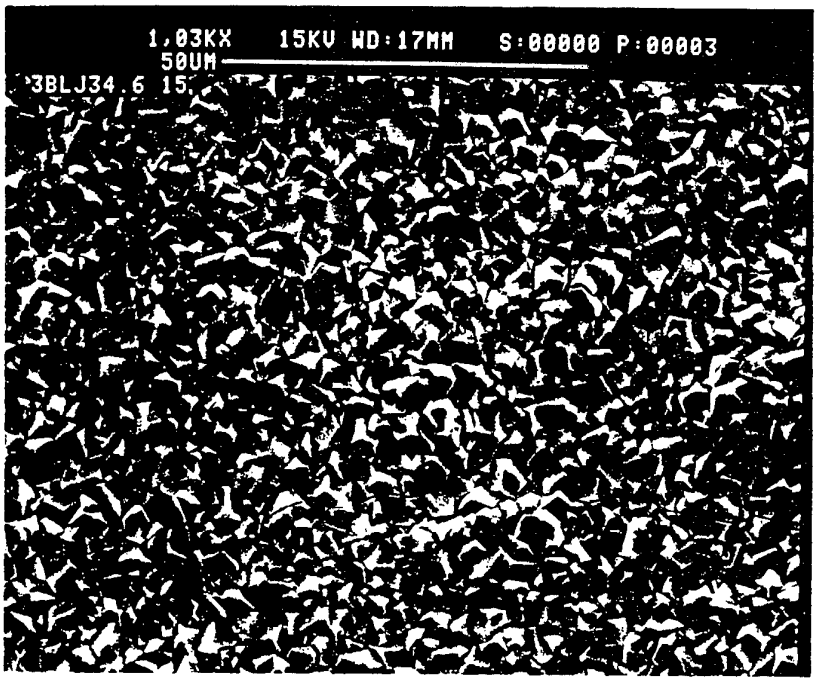

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/00018

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 16/40, C23C 16/30, B23B 27/14
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, B23B

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP, A1, 0603144 (SANDVIK AKTIEBOLAG), 22 June 1994 (22.06.94), claims 1,3-7, abstract	1-5
P,Y	claim 8	6
	--	
Y	EP, A1, 0523021 (SANDVIK AKTIEBOLAG), 13 January 1993 (13.01.93), page 3, line 12 - line 23; page 4, line 10 - line 24, claims 7,8, abstract	6
A	claims 2,3,5,6	2-5
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0403461 (SANDVIK AKTIEBOLAG), 19 December 1990 (19.12.90), page 2, line 21 - line 25, claims 4,5, abstract -- --------	1-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

25/02/95

International application No.
PCT/SE 95/00018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0603144	22/06/94	NONE	
EP-A1- 0523021	13/01/93	CA-A- 2072160	26/12/92
		JP-A- 5230620	07/09/93
EP-A1- 0403461	19/12/90	CA-A- 2019077	16/12/90
		JP-A- 3150364	26/06/91
		SE-B,C- 464818	17/06/91
		SE-A- 8902179	17/12/90
		US-A- 5071696	10/12/91