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(54) Title: COATINGS FOR CUTTING TOOLS

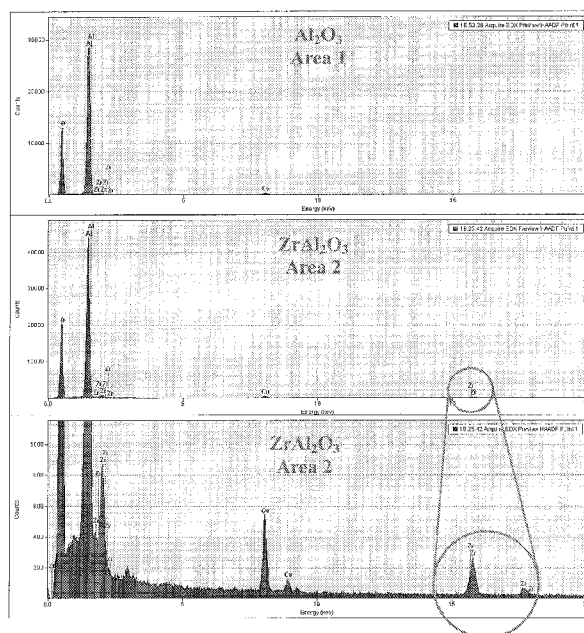


FIG. 4

(57) **Abstract:** In one aspect, cutting tools are described having coatings adhered thereto which, in some embodiments, can demonstrate desirable wear resistance and increased cutting lifetimes. A coated cutting tool, in some embodiments, comprises a substrate and a coating adhered to the substrate, the coating comprising at least one Zr doped layer deposited by chemical vapor deposition comprising ZrAl_2O_3 .



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COATINGS FOR CUTTING TOOLS

RELATED APPLICATION DATA

The present application claims priority pursuant to 35 U.S.C. § 119(e) to United States
5 Provisional Patent Application Serial Number 61/804,077 filed March 21, 2013, which is hereby
incorporated by reference in its entirety.

FIELD

The present invention relates to coatings for cutting tools.

BACKGROUND

Cutting tools, including cemented carbide cutting tools, have been used in both coated
15 and uncoated conditions for machining various metals and alloys. In order to increase cutting
tool wear resistance, performance and lifetime, one or more layers of refractory material have
been applied to cutting tool surfaces. TiC, TiCN, TiN and/or Al₂O₃, for example, have been
applied to cemented carbide substrates by chemical vapor deposition (CVD) and by physical
vapor deposition (PVD). While effective in inhibiting wear and extending tool lifetime in a
20 variety of applications, refractory coatings based on single or multi-layer constructions of the
foregoing refractory materials have increasingly reached their performance limits, thereby
calling for the development of new coating architectures for cutting tools.

In an effort to increase performance, some have tried to modify Al₂O₃. DE2736982 to
Hillnhagen describes a ceramic matrix (e.g. alumina), into which a further material (e.g. ZrO₂) is
25 stored and the stored material has clearly distinct coefficients of thermal expansion producing a
coating with very fine micro-cracks.

US4702970 to Sarin et al. and US4749629 to Sarin et al. describe a hard ceramic
substrate coated with a ceramic coating having at least two phases. The first phase is a
continuous oxide matrix layer of alumina, zirconia, or yttria. At least one discontinuous second
30 or additional phase of oxides of aluminum, zirconium, or yttrium, or solid solutions thereof, is
dispersed as discrete particles within the matrix layer. The additional phase material is different
from the matrix material.

In Russell, W.C., Strandberg, C., "Wear Characteristics and Performance of Alumina-Zirconia CVD Coatings", *Int. J. of Refractory Metals & Hard Materials*, 14 (1996) 51-58, the authors describe using various doped amounts of ZrO_2 within an alumina matrix. Further, this article discloses a Ti layer adjacent the substrate followed by a pure alumina layer for adhesion followed by an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ coating.

US7276301 to Tsushima et al. discloses an α -type $(\text{Al,Zr})_2\text{O}_3$ layer with a TiO_y upper layer. The $(\text{Al,Zr})_2\text{O}_3$ is deposited having a β -type crystal structure. Post coat heat treatment is described as a method of converting the $(\text{Al,Zr})_2\text{O}_3$ an α -type crystal structure.

US7597511 to Tomita et al. discloses an aluminum oxide layer with α -type crystal structure and containing Zr. The Zr containing coating is claimed to have a particular crystallographic orientation where a defined $\Sigma 3$ value is greater than 60%.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a photomicrograph of a section of a coated cutting insert demonstrating layers of the coating architecture according to one embodiment described herein.

Figure 2 illustrates a substrate of a coated cutting tool according to one embodiment described herein.

Figure 3 is an a high angle annual dark field image of a section of ZrAl_2O_3 produced by a scanning transmission microscopy, hereinafter STEM HAADF. The selected areas differed by composition via x-ray energy dispersive spectrum analysis according to one embodiment described herein.

Figure 4 illustrates Energy Dispersive X-ray (EDS) spectrographs of the area 1 and area 2 from the image of Figure 3.

Figure 5 is an optical image of section of ZrAl_2O_3 produced according to one embodiment described herein.

DETAILED DESCRIPTION

Embodiments described herein can be understood more readily by reference to the following detailed description and examples and their previous and following descriptions. Elements, apparatus and methods described herein, however, are not limited to the specific embodiments presented in the detailed description and examples. It should be recognized that

these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations will be readily apparent to those of skill in the art without departing from the spirit and scope of the invention.

In one aspect, cutting tools are described having coatings adhered thereto which, in some
 5 embodiments, can demonstrate desirable wear resistance and increased cutting lifetimes. A coated cutting tool, in some embodiments, comprises a substrate and a coating adhered to the substrate, the coating comprising at least one Zr doped layer deposited by chemical vapor deposition comprising ZrAl_2O_3 . In some embodiments, zirconium is present in a polycrystalline ZrAl_2O_3 layer in an amount selected from Table XI.

Table XI – Zr of Polycrystalline ZrAl_2O_3 Layer

Zr Content (wt.%)
0.01-5
0.1-4
0.15-3
0.2-2

In being a dopant, zirconium can be incorporated into the lattice of an Al_2O_3 phase. In such embodiments, zirconium does not form oxide phase(s) separate from the Al_2O_3 phase.

Turning now to specific components, a coated cutting tool described herein comprises a
 15 substrate. Substrates of coated cutting tools can comprise any material not inconsistent with the objectives of the present invention. In some embodiments, a substrate comprises cemented carbide, carbide, ceramic, cermet, steel, PCD, PcBN or a combination of those listed.

A cemented carbide substrate, in some embodiments, comprises tungsten carbide (WC).

WC can be present in a substrate in an amount of at least about 70 weight percent. In some
 20 embodiments, WC is present in a substrate in an amount of at least about 80 weight percent or in an amount of at least about 85 weight percent. Additionally, metallic binder of a cemented carbide substrate can comprise cobalt or cobalt alloy. Cobalt, for example, can be present in a cemented carbide substrate in an amount ranging from about 3 weight percent to about 15 weight
 25 percent. In some embodiments, cobalt is present in a cemented carbide substrate in an amount ranging from about 5 weight percent to about 12 weight percent or from about 6 weight percent

to about 10 weight percent. Further, a cemented carbide substrate may exhibit a zone of binder enrichment beginning at and extending inwardly from the surface of the substrate.

A cemented carbide substrate can also comprise one or more additives such as, for example, one or more of the following elements and/or their compounds: titanium, niobium, vanadium, tantalum, chromium, zirconium and/or hafnium. In some embodiments, titanium, niobium, vanadium, tantalum, chromium, zirconium and/or hafnium form solid solution carbides with the WC in the substrate. The substrate, in some embodiments, comprises one or more solid solution carbides in an amount ranging from about 0.1 weight percent to about 5 weight percent. Additionally, a cemented carbide substrate can comprise nitrogen.

In some embodiments, a substrate of a coated cutting tool described herein comprises one or more cutting edges formed at the juncture of a rake face and flank faces of the substrate. In other embodiments, a substrate of a coated cutting tool is an insert, drill bit, saw blade or other cutting apparatus.

Figure 1 is photomicrograph of a section of a coated cutting insert demonstrating layers of the coating architecture according to one embodiment described herein. Figure 2 illustrates a coated cutting insert according to the embodiment shown in Figure 1. The cutting insert of Figures 1 and 2 comprises a substrate 1 of cemented WC. The substrate 1 is coated with multilayer coating. Beginning from the substrate and progressing outward the coating comprises an inner layer 2 of TiN, a MT TiCN layer 3, a TiCN layer 4, a $ZrAl_2O_3$ layer 5, a penultimate TiCN layer 6 and an outer TiN layer 7.

Figure 3 is a HAADF image of a section of a $ZrAl_2O_3$ produced by STEM. The selected areas differed by composition via x-ray energy dispersive spectrum analysis according to one embodiment described herein. Area 1 of Figure 3 highlights a section of a single grain of the $ZrAl_2O_3$ coating in which no Zr is present. Area 2 highlights a second area of the same grain in which Zr can be detected. Figure 4 illustrates Energy Dispersive X-ray (EDS) spectrographs of the Area 1 and Area 2 from Figure 3. The EDS confirm the presence of Zr in Area 2 and absence of Zr in Area 1. This variable doping has shown be advantageous in certain metalcutting conditions.

Figure 5 is an optical image of section of $ZrAl_2O_3$ produced according to one embodiment described herein. In Figure 5 a $ZrAl_2O_3$ coating is shown. Doped and undoped regions of the coating are indicated.

Further, a polycrystalline ZrAl_2O_3 layer of a coating described herein can have any thickness not inconsistent with the objectives of the present invention. In some embodiments, a ZrAl_2O_3 layer has a thickness selected from Table XII.

5 Table XII – ZrAl_2O_3 Layer Thickness (μm)

ZrAl_2O_3 Layer Thickness (μm)
0.5-15
1-12
1.5-10
2.5-8

A ZrAl_2O_3 layer can be deposited directly on the cutting tool substrate surface.

Alternatively, a coating described herein can further comprise one or more inner layers between the ZrAl_2O_3 layer and the substrate. One or more inner layers, in some embodiments, comprise one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements selected from the group consisting of non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table. In some embodiments, one or more inner layers between the substrate and ZrAl_2O_3 layer comprise a carbide, nitride, carbonitride, oxide or boride of one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table. For example, one or more inner layers are selected from the group consisting of titanium nitride, titanium carbonitride, titanium carbide, titanium oxide, zirconium oxide, zirconium nitride, zirconium carbonitride, hafnium nitride, hafnium carbonitride and alumina and mixtures thereof.

Inner layers of coatings described herein can have any thickness not inconsistent with the objectives of the present invention. An inner layer of a coating can have a thickness ranging from 0.5 μm to 25 μm . In some embodiments, thickness of an inner layer is selected according to the position of the inner layer in the coating. An inner layer deposited directly on a surface of the substrate as an initial layer of the coating, for example, can have a thickness ranging from 0.5 to 2.5 μm . An inner layer deposited over the initial layer, such as a TiCN layer, can have a thickness ranging from 2 μm to 20 μm . Further, an inner layer on which a ZrAl_2O_3 layer described herein is deposited, such as a layer comprising alumina, can have a thickness ranging from 1 to 6 μm .

In some embodiments, a ZrAl_2O_3 layer described herein is the outermost layer of the coating. Alternatively, a coating described herein can comprise one or more outer layers over the ZrAl_2O_3 layer. One or more outer layers, in some embodiments, comprise one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements selected from the group consisting of non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table. In some embodiments, one or more outer layers over the ZrAl_2O_3 layer comprise a nitride, carbonitride, oxide or boride of one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table. For example, one or more outer layers are selected from the group consisting of titanium nitride, titanium carbonitride, titanium carbide, zirconium nitride, zirconium carbonitride, hafnium nitride, hafnium carbonitride, titanium oxycarbonitride, zirconium oxycarbonitride, hafnium oxycarbonitride and alumina and mixtures thereof.

Outer layers of coatings described herein can have any thickness not inconsistent with the objectives of the present invention. An outer layer of a coating, in some embodiments, can have a thickness ranging from 0.5 μm to 5 μm .

Additionally, in some embodiments, a coating described herein can comprise one or more bonding layers. A bonding layer can demonstrate various positions in the coating. In some embodiments, a bonding layer is disposed between two inner layers of the coating, such as between a titanium nitride or titanium carbonitride inner layer and an inner layer comprising alumina. A bonding layer can also be disposed between an inner layer and a ZrAl_2O_3 layer described herein. Further, a bonding layer can be disposed between a ZrAl_2O_3 layer and an outer layer of the coating. In some embodiments, bonding layers are used to increase adhesion between layers of the coating and/or nucleate the desired morphology of a coating layer deposited on the bonding layer. A bonding layer, in some embodiments, is of the formula $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$, wherein M is a metal selected from the group consisting of metallic elements of Groups IVB, VB and VIB of the Periodic Table and $x \geq 0$, $y \geq 0$ and $z \geq 0$ wherein $x + y + z = 1$. For example, in one embodiment, a bonding layer of TiC is employed between an inner layer of TiCN and an inner layer comprising alumina.

A bonding layer of the formula $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$ can have any thickness not inconsistent with the objectives of the present invention. In some embodiments, a $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$ layer has a

thickness of about 0.5 μm . Moreover, a $\text{M}(\text{O}_x\text{C}_y\text{N}_z)$ layer can have a thickness ranging from 0.5 μm to 5 μm .

A coating adhered to a substrate can have any architecture of ZrAl_2O_3 layer, inner layer(s) and/or outer layer(s) described herein. In some embodiments, a coating described herein
5 has an architecture selected from Table VII.

In some embodiments, a coating described herein has a nanoindentation hardness of 2866. The load is about 80mN with penetration depth of 0.20 μm in 15s. The hardness is 2866 for certain embodiments described herein.

Additionally, a coating described herein can demonstrate a critical load (L_c) up to about
10 90 N. L_c values for coatings described herein were determined according to ASTM C1624-05 – Standard Test for Adhesion Strength by Quantitative Single Point Scratch Testing wherein a progressive loading of 10 N was used. A coating, for example, can exhibit a L_c value of 60 to 90 N.

In some embodiments the coatings may be post coat blasted. Post coat blasting can be
15 administered in any desired manner. In some embodiments, post coat blasting comprises shot blasting or pressure blasting. Pressure blasting can be administered in a variety of forms including compressed air blasting, wet compressed air blasting, pressurized liquid blasting, wet blasting, pressurized liquid blasting and steam blasting.

In one embodiment, for example, post coat treatment of a coating described herein can be
20 administered by dry blasting the coating with alumina and/or ceramic particles. Alternatively, the coating can be wet blasted using a slurry of alumina and/or ceramic particles in water at a concentration of 5 volume percent to 35 volume percent. Alumina and/or ceramic particles of post-coat blasting techniques described herein can have a size distribution of 60 μm to 120 μm . Additionally, blasting pressures can range from 2 bar to 3 bar for a time period of 1 to 15
25 seconds, wherein the blast nozzle is 2 to 8 inches from the coating surface being blasted. Further, angle of impingement of the alumina and/or ceramic particles can be chosen to range from 45 degrees to 90 degrees.

In another aspect, methods of making coated cutting tools are described herein. A
method of making a coated cutting tool, in some embodiments, comprises providing a
30 substrate and depositing over the substrate by chemical vapor deposition at least one ZrAl_2O_3

layer of a coating, the ZrAl_2O_3 layer comprising at least one Zr doped region and one undoped region.

Turning now to specific steps, a method described herein comprises providing a substrate. A substrate can comprise any substrate recited in Section I hereinabove. In some embodiments, for example, a substrate is cemented carbide, such as cemented tungsten carbide described in Section I herein. Moreover, a polycrystalline ZrAl_2O_3 layer deposited according to methods described herein can have any construction, compositional parameters and/or properties described in Section I herein for a ZrAl_2O_3 layer.

In a method described herein, a ZrAl_2O_3 layer can be deposited from a gaseous mixture comprising an aluminum source, oxygen source, nitrogen source and source for the zirconium. In some embodiments, for example, the aluminum source is AlCl_3 , and the zirconium source is a ZrCl_4 . In one embodiment a ZrAl_2O_3 layer is made by alternating Cycle A and Cycle B according to the CVD processing parameters of Table I.

Table I			
	Cycle A	Cycle B	Cycle A
Temp. ($^{\circ}\text{C}$)	950-1010	950-1010	950-1010
Press. (mbar)	60-80	60-80	60-80
Time (min.)	20-90	20-90	20-90
H_2	balance	balance	balance
AlCl_3	1.5-3 vol. %	1.5-3 vol. %	1.5-3 vol. %
ZrCl_4	----	0.2-1 vol. %	----
CO_2	3-6 vol. %	3-6 vol. %	3-6 vol. %
HCl	1-3 vol. %	1-3 vol. %	1-3 vol. %
H_2S	0.15- 0.6 vol. %	0.15- 0.6 vol. %	0.15- 0.6 vol. %
Ar	----	1-2%	----

In another embodiment a ZrAl_2O_3 coating is made according to the CVD processing parameters provided in Table II. The embodiment described in Table II provides a Zr doping gradient in the Zr doped section of the ZrAl_2O_3 coating. Cycles C-I may be shortened and repeated to induce alternating intragranular doped and undoped regions.

Table II							
	Cycle C	Cycle D	Cycle E	Cycle F	Cycle G	Cycle H	Cycle I
Temp. (°C)	950-1010	950-1010	950-1010	950-1010	950-1010	950-1010	950-1010
Press. (mbar)	60-80	60-80	60-80	60-80	60-80	60-80	60-80
Time (min.)	20-90	20-90					20-90
H ₂	balance	balance	balance	balance	balance	balance	balance
AlCl ₃ (vol. %)	1.5-3	1.5-3	1.5-3	1.5-3	1.5-3	1.5-3	1.5-3
ZrCl ₄ (vol. %)	----	0.10-0.15	0.18-0.21	0.24-0.26	0.18-0.21	0.10-0.15	----
CO ₂ (vol. %)	3-6	3-6	3-6	3-6	3-6	3-6	3-6
HCl (vol. %)	1-3	1-3	1-3	1-3	1-3	1-3	1-3
H ₂ S (vol. %)	0.15- 0.6	0.15- 0.6	0.15- 0.6	0.15- 0.6	0.15- 0.6	0.15- 0.6	0.15- 0.6
Ar (vol %)	----	1-2	1-2	1-2	1-2	1-2	----

In another embodiment a ZrAl₂O₃ coating is made according to the CVD processing parameters provided in Table III. The embodiment described in Table III provides a Zr doping gradient in the Zr doped section of the ZrAl₂O₃ coating. Cycles J-P may be shortened and repeated to induce alternating intragranular doped and undoped regions.

Table III							
	Cycle J	Cycle K	Cycle L	Cycle M	Cycle N	Cycle O	Cycle P
Temp. (°C)	990-1000	990	990	990	990	990	990-1000
Press. (mbar)	75	75	75	75	75	75	75
Time (min.)	20-90	20-90					20-90
H ₂	balance	balance	balance	balance	balance	balance	balance
AlCl ₃ (vol. %)	1.96	1.84	1.84	1.83	1.84	1.84	1.96
ZrCl ₄ (vol. %)	----	0.4	0.61	0.80	0.61	0.4	----
CO ₂ (vol. %)	3.44	4.2	4.19	4.18	4.19	4.2	3.44
HCl (vol. %)	1.38	1.29	1.29	1.29	1.29	1.29	1.38
H ₂ S (vol. %)	0.26	0.24	0.24	0.24	0.24	0.24	0.26
Ar (vol %)	----	4.84	4.83	4.82	4.83	4.84	----

In another embodiment a ZrAl_2O_3 coating is made according to the CVD processing parameters provided in Table IV. The embodiment described in Table IV provides a Zr doping gradient in the Zr doped section of the ZrAl_2O_3 coating. Cycles Q-S may be shortened and repeated to induce alternating intragranular doped and undoped regions.

5

Table IV			
	Cycle Q	Cycle R	Cycle S
Temp. (°C)	990-1000	990	990-1000
Press. (mbar)	75	75	75
Time (min.)	20-90	20-90	20-90
H ₂	balance	balance	balance
AlCl ₃ (vol. %)	1.96	1.65	1.96
ZrCl ₄ (vol. %)	----	0.72	----
CO ₂ (vol. %)	3.44	3.76	3.44
HCl (vol. %)	1.38	1.16	1.38
H ₂ S (vol. %)	0.26	0.22	0.26
Ar (vol. %)	----	14.45	----

In another embodiment a ZrAl_2O_3 coating is made according to the CVD processing parameters provided in Table V. The embodiment described in Table V provides a Zr doping gradient in the Zr doped section of the ZrAl_2O_3 coating. Cycles T-V may be shortened and repeated to induce alternating intragranular doped and undoped regions.

10

Table V			
	Cycle T	Cycle U	Cycle V
Temp. (°C)	990-1000	990	990-1000
Press. (mbar)	75	75	75
Time (min.)	20-90	20-90	20-90
H ₂	balance	balance	balance
AlCl ₃ (vol. %)	1.96	1.44	1.96
ZrCl ₄ (vol. %)	----	0.63	----

CO ₂ (vol. %)	3.44	3.28	3.44
HCl (vol. %)	1.38	1.01	1.38
H ₂ S (vol. %)	0.26	0.19	0.26
Ar (vol. %)	----	24.26	----

A ZrAl₂O₃ layer, in some embodiments, is deposited directly on a surface of the substrate. Alternatively, a ZrAl₂O₃ layer is deposited on an inner layer of the coating. An inner layer of the coating can have any construction, compositional parameters and/or properties recited in Section I hereinabove for an inner layer. An inner layer can comprise one or more metallic elements selected from the group consisting of aluminum and one or more metallic elements of Groups IVB, VB, and VIB of the Periodic Table and one or more non-metallic elements selected from the group consisting of non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table. In some embodiments, an inner layer is a carbide, nitride, carbonitride, oxide or boride of one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table. An inner layer over which a ZrAl₂O₃ layer is deposited, for example, can be selected from the group consisting of titanium nitride, titanium carbide, titanium carbonitride, titanium oxide, zirconium oxide, zirconium nitride, zirconium carbonitride, hafnium nitride, hafnium carbonitride and alumina and mixtures thereof. In one embodiment, for example, an inner layer comprises a mixture of alumina, zirconium oxide and titanium oxide (Al₂O₃/ZrO₂/TiO_x).

As with the ZrAl₂O₃ layer, inner layer(s) of a coating described herein can be deposited by CVD. In some embodiments, an inner layer of the coating, such as a TiCN layer, is deposited by medium-temperature (MT) CVD.

Further, methods described herein can also comprise depositing over the ZrAl₂O₃ layer one or more outer layers. Outer layer(s) of a coating described herein, in some embodiments, are deposited by CVD. An outer layer of the coating can have any construction, compositional parameters and/or properties recited in Section I hereinabove for an outer layer. An outer layer can comprise one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements selected from the group consisting of non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table. In some embodiments, one or more outer layers over

the ZrAl_2O_3 layer comprise a nitride, carbonitride, oxide or boride of one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table. For example, one or more outer layers are selected from the group consisting of titanium nitride, titanium carbonitride, titanium carbide, zirconium nitride, zirconium carbonitride, hafnium nitride, hafnium carbonitride, titanium oxycarbonitride, hafnium oxycarbonitride, zirconium oxycarbonitride and alumina and mixtures thereof.

Coatings of cutting tools described herein can be subjected to post-coat treatments. Coatings, for example, can be blasted with various wet and/or dry particle compositions. Post coat blasting can be administered in any desired manner. In some embodiments, post coat blasting comprises shot blasting or pressure blasting. Pressure blasting can be administered in a variety of forms including compressed air blasting, wet compressed air blasting, pressurized liquid blasting, wet blasting, pressurized liquid blasting and steam blasting. Wet blasting, for example, is accomplished using a slurry of inorganic and/or ceramic particles, such as alumina, and water. The alumina particle slurry can be pneumatically projected at a surface of the coated cutting tool body to impinge on the surface of the coating. The alumina particles can generally range in size between about 20 μm and about 100 μm .

Blasting parameters include pressure, angle of impingement, distance to the part surface and duration. In some embodiments, angle of impingement can range from about 45 degrees to about 90 degrees, i.e., the particles impinge the coating surface at an angle ranging from about 45 degrees to about 90 degrees. Suitable pressures can range from 30-55 pounds per square inch (psi) at a distance to the coated surface of 1-6 inches. Further, duration of the blasting can generally range from 1-10 seconds or longer. Blasting can be generally administered over the surface area of the coating or can be applied to select locations such as in a workpiece contact area of the cutting tool. A workpiece contact area can be a honed region of the cutting tool.

In other embodiments, a coating is subjected to a polishing post-coat treatment. Polishing can be administered with paste of appropriate diamond or ceramic grit size. Grit size of the paste, in some embodiments, ranges from 1 μm to 10 μm . In one embodiment, a 5-10 μm diamond grit paste is used to polish the coating. Further, grit paste can be applied to the CVD coating by any apparatus not inconsistent with the objectives of the present invention, such as brushes. In one embodiment, for example, a flat brush is used to apply grit paste to the CVD coating in a workpiece contact area of the cutting tool.

A coating described herein can be blasted or polished for a time period sufficient to achieve a desired surface roughness (R_a) and/or other parameters such as reducing residual tensile stress in the coating. In some embodiments, a coating subjected to post-coat treatment has a surface roughness (R_a) selected from Table VI.

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Table VI - Post-Coat Surface Roughness (R_a)

Polished Coating Surface Roughness (R_a) - nm
≤ 500
≤ 250
< 200
10-250
50-175
25-150

Coating surface roughness can be determined by optical profilometry using WYKO® NT-Series Optical Profilers commercially available from Veeco Instruments, Inc. of Plainview, New York.

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Further, a post-coat treatment, in some embodiments, does not remove one or more outer layers of the coating. In some embodiments, for example, a post-coat treatment does not remove an outer layer of TiN and/or TiCN. Alternatively, a post-coat treatment can remove or partially remove one or more outer layers, such as TiN and/or TiCN.

15

By alternating Zr doped and undoped regions of a $ZrAl_2O_3$ coating and by providing a Zr gradient in the Zr doped regions of the $ZrAl_2O_3$ coating, the inventors have improved the material properties and wear resistance of the $ZrAl_2O_3$ coatings. The $ZrAl_2O_3$ coatings are believed to have an increased micro-hardness due to a grain size decrease along with enhanced local bonding along grain boundaries due to Zr atoms segregating to localized regions along the grain boundaries. Sequential doped and undoped regions also are believed to affect the grain growth kinetics, defect levels and interfacial structure compared to Al_2O_3 thin films.

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These and other embodiments are further illustrated in the following non-limiting examples.

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EXAMPLE 1 – Coated Cutting Tool Body

Coated cutting tools 1 and 2 described herein were produced by placing cemented tungsten carbide (WC) cutting insert substrates [ANSI standard geometry CNMG432RN] into an axial flow hot-wall CVD reactor. The cutting inserts each comprised 7 wt.% cobalt binder with the balance WC grains of size 1 to 5 μm . A coating having an architecture provided in Table VII was deposited on the cemented WC cutting inserts according to the CVD process parameters provided in Table II. ZrCl_4 was presented in the CVD gas mixture in gradient steps to provide a polycrystalline ZrAl_2O_3 layer having an intra-layer compositional gradient of Al_2O_3 stages alternating with a gradient ZrAl_2O_3 stage.

Table VII – CVD Coating Architecture

Substrate	CVD Coating Architecture
WC-Co	TiN*-TiCN(MT)-TiCN(HT)/TiOCN-ZrAl ₂ O ₃ -TiN/TiCN

*Innermost layer adjacent to the substrate

The multilayered coatings of cutting inserts 1 and 2 comprising the polycrystalline ZrAl_2O_3 layer exhibited the properties provided in Table VIII.

Table VIII - Properties of CVD Coating

Coating Layers	Thickness (μm)
TiN*	0.3-0.7
TiCN(MT)	8.5-9
TiCN(HT)/TiOCN	0.8-1.2
ZrAl ₂ O ₃	6.8-7.2
TiN/TiCN	1.3-1.7

*Coating Layer adjacent to WC-Co Substrate

Figure 1 is a cross-sectional SEM image of a coated cutting insert of this Example 1 demonstrating layers of the coating architecture. Further, cutting insert 1 was subjected to dry polishing with diamond paste and cutting insert 2 was subjected wet-blasting with alumina grit as a post coat treatment.

EXAMPLE 2 – Metal Cutting Testing

Coated cutting inserts (1-2) of Example 1 and Comparative coating insert 3 were subjected to continuous turning testing of 1045 steel according to the parameters below.

Comparative cutting insert 3 displayed a coating architecture and properties set forth in Table IX.

- 5 Comparative cutting insert 3 employed a WC-Co substrate of substantially similar composition as Example 1 and an ANSI standard geometry CNMG432RN. Comparative cutting insert 3 was subjected to a wet blasting with alumina grit as a post coat treatment.

Table IX - Comparative cutting insert 3

Coating Layers	Thickness (μm)
TiN*	0.1-0.5
TiCN(MT)	7.0-9.0
TiCN(HT)/TiOCN	0.8-1.3
Al ₂ O ₃	7.1-8.5
TiN/TiCN	removed

- 10 *Coating Layer adjacent to WC-Co Substrate

Coated cutting inserts 1 and 2 of Example 1 and Comparative coating insert 3 were subjected to continuous turning testing as follows:

Workpiece - 1045 Steel

- 15 Speed - 1000 sfm (304.8 m/min)

Feed Rate - 0.012 ipr (0.3048 mm/min)

Depth of Cut - 0.08 inch (0.08 mm)

Lead Angle: -5°

End of Life was registered by one or more failure modes of:

- 20 Uniform Wear (UW) of 0.012 inches

Max Wear (MW) of 0.012 inches

Nose Wear (NW) of 0.012 inches

Depth of Cut Notch Wear (DOCN) Of 0.012 inches

Trailing Edge Wear (TW) of 0.012 inches

- 25 Two cutting inserts were tested for each coating architecture (1-3) providing repetition 1 and 2 data as well as mean cutting lifetime. The results of the continuous turning testing are provided in Table X.

Table X - Continuous Turning Testing Results

Cutting Insert	Repetition I Lifetime (minutes)	Repetition 2 Lifetime (minutes)	Mean Cutting Lifetime (minutes)
1	21.3	24.5	22.9
2	23.1	23.1	23.1
3	20.4	19.9	20.2

As provided in Table X, coated cutting tools 1 and 2 demonstrated the better mean cutting lifetime. Coating cutting tools 1 and 2 demonstrated about 14.0% improvement in cutting lifetime than coated cutting tool 3.

Various embodiments of the invention have been described in fulfillment of the various objects of the invention. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1. A coated cutting tool comprising:
a substrate; and
a coating adhered to the substrate comprising a polycrystalline layer of ZrAl_2O_3 , the
5 polycrystalline ZrAl_2O_3 layer having an intra-layer compositional gradient formed of an Al_2O_3
stage and ZrAl_2O_3 stage.
2. The coated cutting tool of claim 1, wherein Al_2O_3 stages and ZrAl_2O_3 stages alternate
throughout the polycrystalline layer.
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3. The coated cutting tool of claim 1, wherein the ZrAl_2O_3 stage has a zirconium gradient
therein.
4. The coated cutting tool of claim 1, wherein an individual grain of the polycrystalline
15 ZrAl_2O_3 layer displays a compositional gradient formed of an Al_2O_3 stage and ZrAl_2O_3 stage.
5. The coated cutting tool of claim 1, wherein zirconium is located in the ZrAl_2O_3 stage
adjacent to one or more grain boundaries.
- 20 6. The coated cutting tool of claim 1, wherein zirconium is present in the polycrystalline
 ZrAl_2O_3 layer in an amount 0.01-2 wt.%.
7. The coated cutting tool of claim 1, wherein the polycrystalline ZrAl_2O_3 layer has a
thickness of 2.5 to 8 μm .
25
8. The coated cutting tool of claim 1, wherein the coating further comprises one or more
base layers between the substrate and the ZrAl_2O_3 polycrystalline layer.
9. The coated cutting tool of claim 8, wherein a base layer comprises one or more metallic
30 elements selected from the group consisting of aluminum and metallic elements of Groups IVB,

VB and VIB of the Periodic Table and one or more non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table.

10. The coated cutting tool of claim 9, wherein the one or more base layers are selected from the group consisting of TiN, TiCN and TiOCN.
11. The coated cutting tool of claim 1, wherein the coating further comprises one or more outer layers over the polycrystalline ZrAl_2O_3 layer.
12. The coated cutting tool of claim 11, wherein an outer layer comprises one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table.
13. The coated cutting tool of claim 11, wherein the coating is post-coat blasted with ceramic or inorganic particles.
14. The coated cutting tool of claim 11, wherein the coating is polished.
15. The coated cutting tool of claim 1, wherein the polycrystalline ZrAl_2O_3 layer is deposited by CVD.
16. The coated cutting tool of claim 1, wherein the substrate comprises cemented tungsten carbide or polycrystalline cubic boron nitride.
17. The coated cutting tool of claim 1, wherein the substrate is an insert, drill bit or saw blade.
18. The coated cutting tool of claim 1, wherein the coating exhibits a critical load (L_c) of 60 to 90 N according to ASTM C1624-05 – Standard Test for Adhesion by Quantitative Single Point Scratch Testing.

19. A coated cutting tool comprising:
a substrate; and
a coating adhered to the substrate, the coating comprising a polycrystalline layer of ZrAl_2O_3 having a zirconium gradient along one or more ZrAl_2O_3 grains.
- 5
20. The coated cutting tool of claim 19, wherein the zirconium gradient is formed of an Al_2O_3 stage and a ZrAl_2O_3 stage.
21. The coated cutting tool of claim 20, wherein the ZrAl_2O_3 stage has a zirconium gradient
- 10 therein.
22. The coated cutting tool of claim 20, wherein Al_2O_3 stages alternate with ZrAl_2O_3 stages along the one or more ZrAl_2O_3 grains.
- 15
23. The coated cutting tool of claim 19, wherein zirconium is present in the polycrystalline ZrAl_2O_3 layer in an amount 0.01-5 wt.%.
24. The coated cutting tool of claim 19, wherein the polycrystalline ZrAl_2O_3 layer has a
- 20 thickness of 2.5 to 8 μm .
25. The coated cutting tool of claim 19, wherein the coating further comprises one or more base layers between the substrate and the polycrystalline layer of ZrAl_2O_3 .
26. The coated cutting tool of claim 25, wherein a base layer comprises one or more metallic
- 25 elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table.
27. The coated cutting tool of claim 26, wherein the one or more base layers are selected
- 30 from the group consisting of TiN, TiCN and TiOCN.

28. The coated cutting tool of claim 19, wherein the coating further comprises one or more outer layers over the polycrystalline $\text{TiZrAl}_2\text{O}_3$ layer.

29. The coated cutting tool of claim 28, wherein an outer layer comprises one or more metallic elements selected from the group consisting of aluminum and metallic elements of Groups IVB, VB and VIB of the Periodic Table and one or more non-metallic elements of Groups IIIA, IVA, VA and VIA of the Periodic Table.

30. The coated cutting tool of claim 28, wherein the coating is post-coat blasted with ceramic or inorganic particles.

31. The coated cutting tool of claim 28, wherein the coating is polished.

32. The coated cutting tool of claim 19, wherein the polycrystalline ZrAl_2O_3 layer is deposited by CVD.

33. The coated cutting tool of claim 19, wherein the substrate comprises cemented tungsten carbide or polycrystalline cubic boron nitride.

34. The coated cutting tool of claim 19, wherein the substrate is an insert, drill bit or saw blade.

35. The coated cutting tool of claim 19, wherein the coating exhibits a critical load (L_c) of 60 to 90 N according to ASTM C1624-05 – Standard Test for Adhesion by Quantitative Single Point Scratch Testing.

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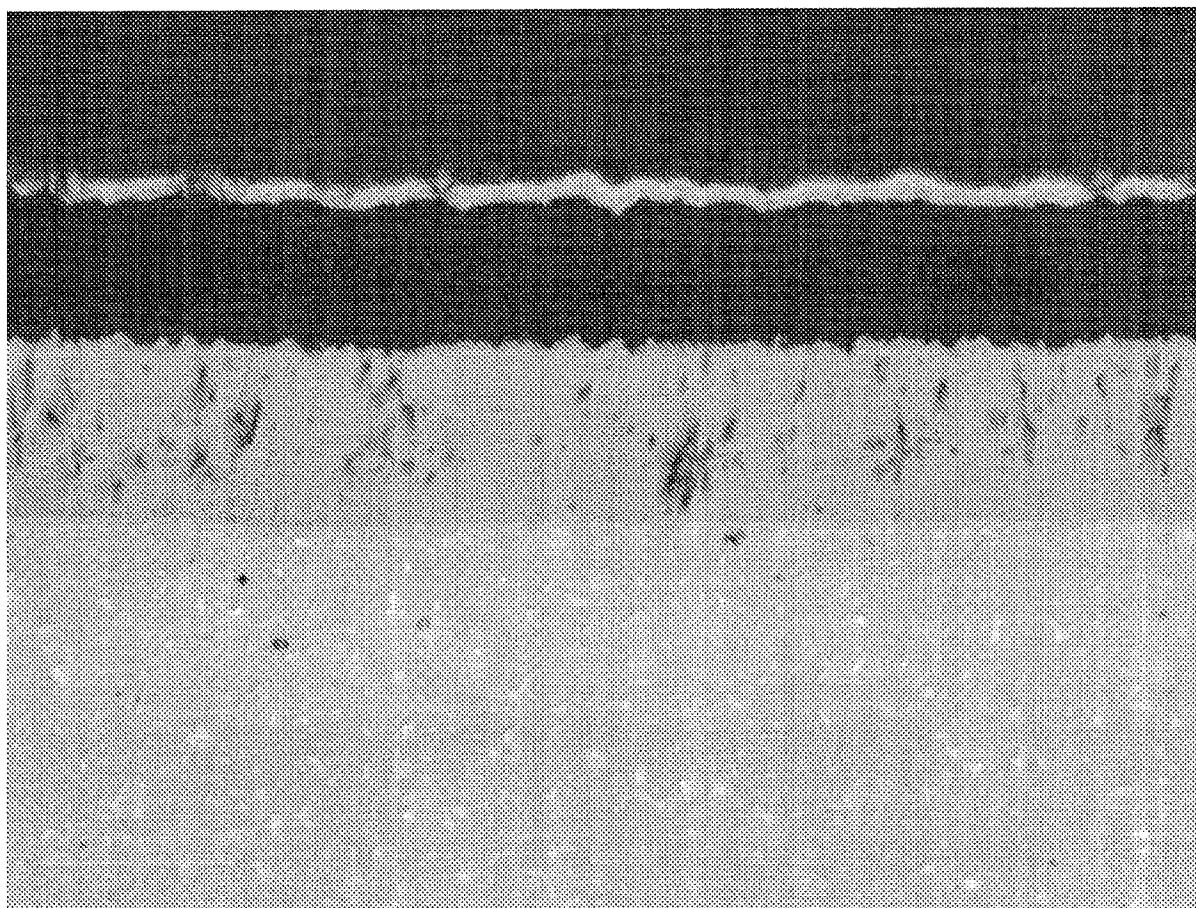


FIG. 1

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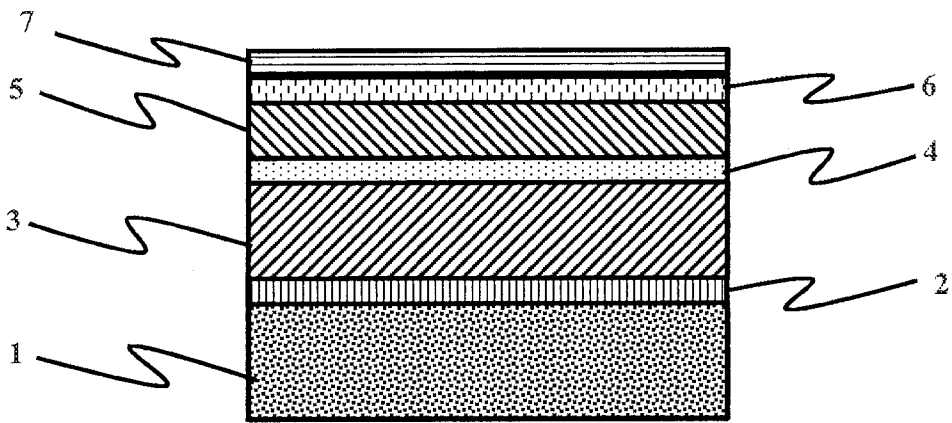


FIG. 2

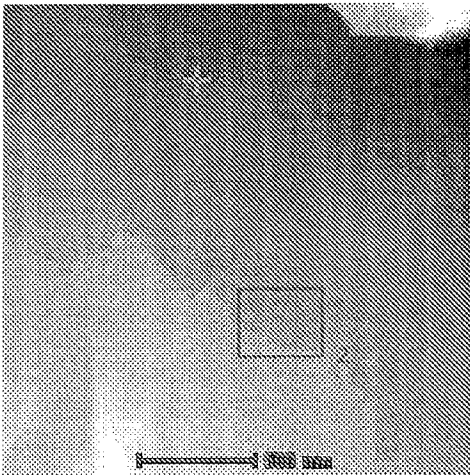


FIG. 3

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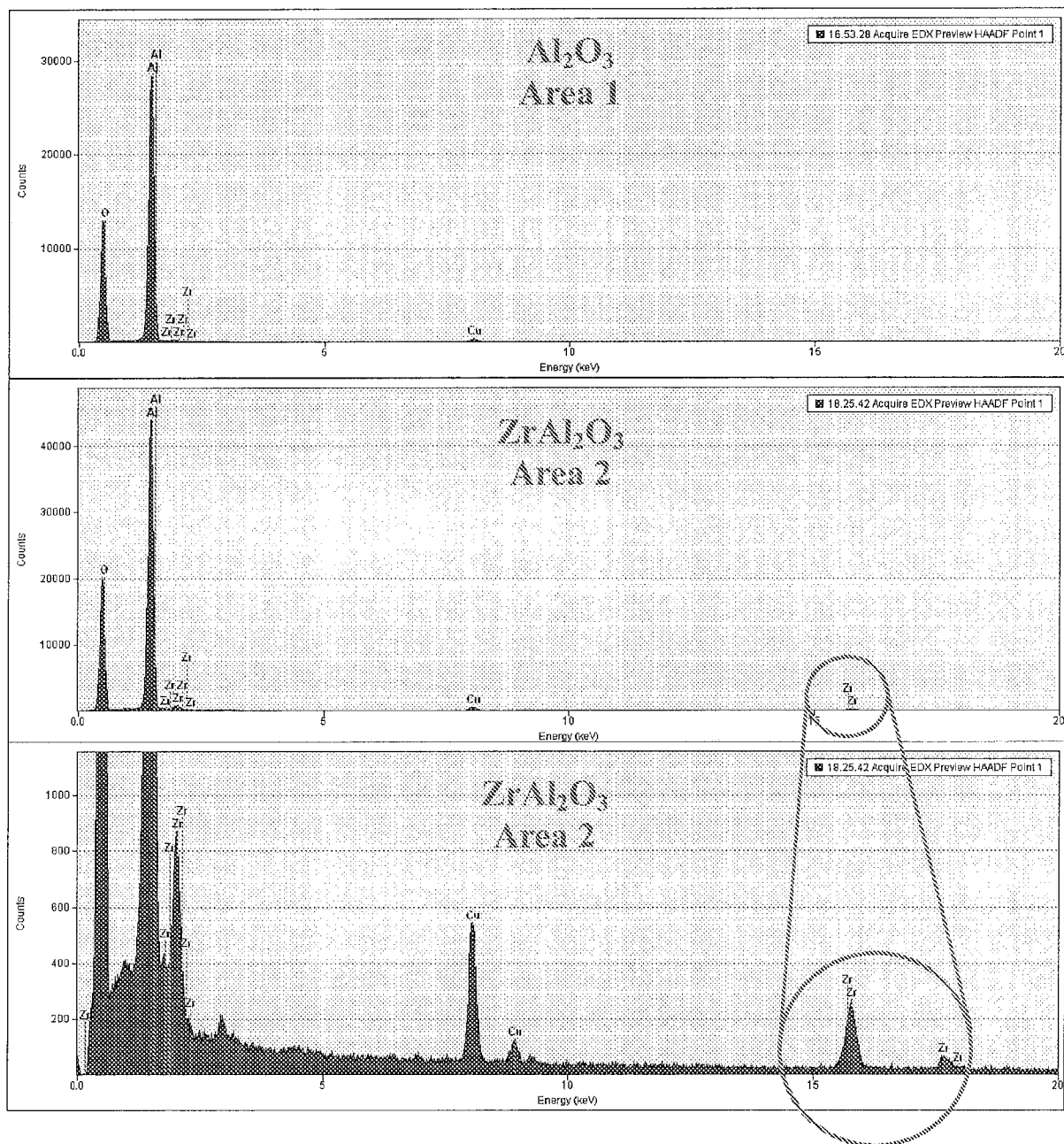


FIG. 4

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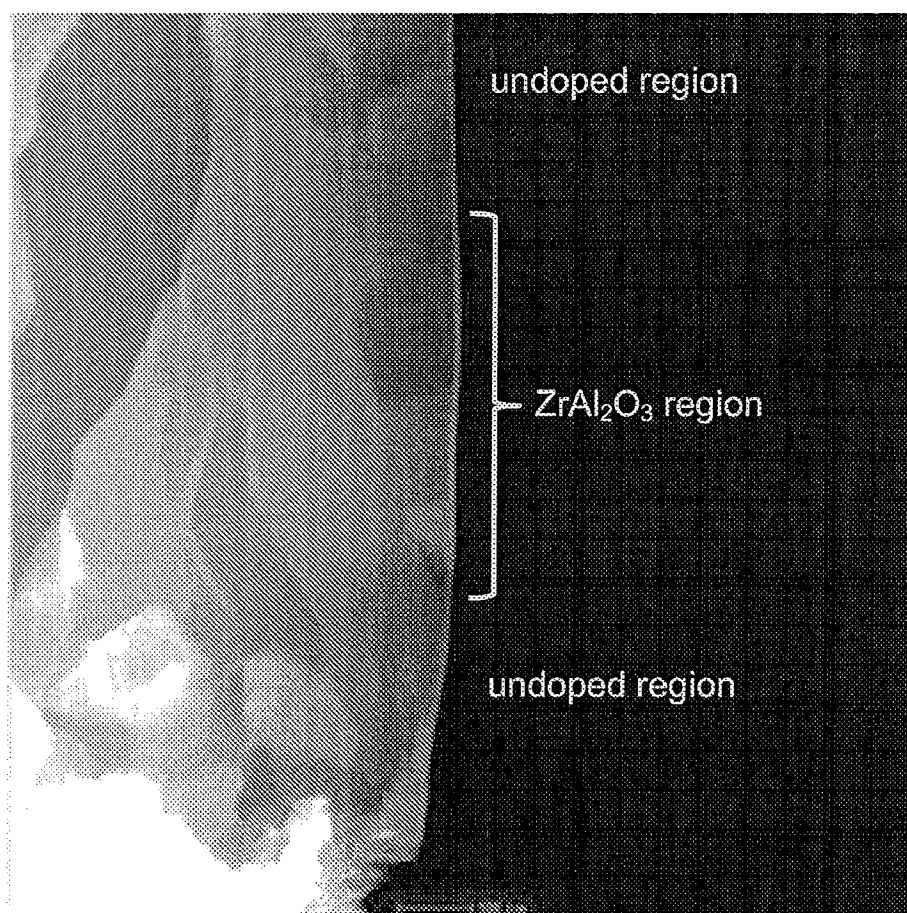


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/031358**A. CLASSIFICATION OF SUBJECT MATTER****C23C 16/06(2006.01)i, C23C 16/455(2006.01)i**

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)

C23C 16/06; B32B 15/04; B23B 27/14; C30B 29/20; C23C 16/40; H01L 21/31; B05D 1/18; B22D 25/00; C23C 16/00; C23C 16/455

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: cutting tool, coating, zirconium, aluminum oxide, and gradient

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A		1-18,20-22
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A	EP 1655387 B1 (SECO TOOLS AB) 07 May 2008 See paragraphs [0015],[0018]; and claims 1,4.	1-35



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

"&" document member of the same patent family

Date of the actual completion of the international search

02 July 2014 (02.07.2014)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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