United States Patent [19]

Hale

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[54] **ALUMINUM OXIDE COATED TITANIUM-CONTAINING CEMENTED CARBIDE PRODUCT**

[75] Inventor: **Thomas E. Hale**, Warren, Mich.

[73] Assignee: **General Electric Company**, Hudson Falls, N.Y.

[21] Appl. No.: **597,582**

[22] Filed: **Apr. 9, 1984**

Related U.S. Patent Documents

Reissue of:

[64] Patent No.: **3,736,107**
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Appl. No.: **147,240**
Filed: **May 26, 1971**

U.S. Applications:

[60] Continuation of Ser. No. 909,699, May 25, 1978, abandoned, which is a division of Ser. No. 577,584, May 15, 1975.

[51] **Int. Cl.**^{4} **B32B 9/04**

[52] **U.S. Cl.** **428/336;** 427/248.1; 427/255; 428/698; 428/926; 428/932

[58] **Field of Search** .... 427/248 A, 248 B, 255; 428/336, 457, 539, 552, 924, 926, 932

[56] **References Cited**

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Primary Examiner—Jerome Massie
Attorney, Agent, or Firm—Morgan, Finnegan, Pine, Foley & Lee

EXEMPLARY CLAIM

A high-strength, coated cemented carbide product comprising a cemented carbide substrate and a fully dense alpha aluminum oxide coating on the substrate. The coating has a thickness of from 1–20 microns and is firmly and adherently bonded to the cemented carbide substrate through a thin intermediate nonmetallic layer [of an iron group metal aluminate]. The coated product combines a wear resistance substantially as high as aluminum oxide cutting materials and a transverse rupture strength of at least 150,000 p.s.i. The coated product is prepared by passing water vapor, hydrogen gas and an aluminum halide over the substate at a temperature of from 900°–1250° C., the ratio of water vapor to hydrogen gas being between about 0.025 and 2.0.

32 Claims, No Drawings

ALUMINUM OXIDE COATED TITANIUM-CONTAINING CEMENTED CARBIDE PRODUCT

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This is a continuation, of application Ser. No. 909,699 filed May 25, 1978, now abandoned; which in turn is a division of reissue application Ser. No. 577,584, filed May 15, 1975, which is reissue of U.S. Pat. No. 3,736,107.

BACKGROUND OF THE INVENTION

This invention relates to a high-strength, coated cemented carbide product and to process for its preparation.

Cemented carbides are well known for their unique combination of hardness, strength and wear resistance and are accordingly extensively used for such industrial applications as cutting tools, drawing dies and wear parts. It is known that the wear resistance of cemented carbides may be enhanced by the application of a thin coating of a highly wear-resistant material, such as, for example, titanium carbide, and such coated cemented carbides are finding increasing commercial utility for certain cutting tool and machining applications. However, the increased wear resistance of such coated products has been at the sacrifice of the strength of the substrate which is substantially reduced after coating.

Because of its high hardness, wear resistance and low reactivity with a wide variety of metals, aluminum oxide has excellent potential as a tool material, and this potential has to some extent been realized with a variety of aluminum oxide cutting materials that are commercially available. The principel drawback to the more widespread use of aluminum oxide tools in their low strength which rarely exceeds 100,000 p.s.i., using the standard transverse rupture or bend test. This compares with a strength of from 200,000 to 300,000, or even more, for cemented carbide cutting tools. The low strength of aluminum oxide tools limits their use to cutting applications where the tool is not highly stressed, such as in finishing cuts. The low strength of aluminum oxide also precludes the use of such materials in certain types of insert shapes which encounter high stresses when locked in a toolholder.

It is an object of this invention to provide a hard, wear-resistant material which combines the extremely high wear resistance of aluminum oxide with the relatively high strength and hardness of cemented carbide.

It is an additional object of this invention to improve the wear resistance of cemented carbides without substantially reducing their strength. It is still an additional object of this invention to provide a process for producing a firmly adherent, nonporous, dense coating of aluminum oxide on a cemented carbide substrate.

SUMMARY OF THE INVENTION

The foregoing and other objects of this invention are achieved by the vapor deposition under carefully controlled conditions of an alpha aluminum oxide coating of from 1-20 microns thickness on a cemented carbide substrate. The product contains a cemented carbide substrate and a fully dense alpha aluminum oxide coating firmly and adherently bonded to the substrate. In addition, there is present a very thin, intermediate nonmetallic layer [of cobalt-, iron-, or nickel aluminate], which acts to metallurgically bond the coating to the substrate. The coated product has a wear resistance substantially equivalent to aluminum oxide base cutting materials and a transverse rupture strength of at least 150,000, in most cases greater than 200,000 pounds/sq. inch. At very high cutting speeds, greater than about 1,500 surface ft./minute in some applications, possibly higher in others, the higher heat resistance of solid aluminum oxide may result in higher wear resistance. But in all cutting tests other than those above these levels, the wear resistance of the present coated products has proven to be substantially as high as aluminum oxide cutting materials.

While the broad range of coating thicknesses useful in the invention is from 1-20 microns, most coating thicknesses are preferably less than 15 microns. As will be shown in more detail below, certain applications require even narrower ranges within these limits, e.g. 1-3 microns has proven optimum for machining high temperature alloys and for milling applications; 6-12 microns has proven optimum for steel machining.

The process of the invention comprises passing an aluminum halide, water vapor and hydrogen gas over the carbide substrate at a temperature of from 900°-1250° C., the ratio of water vapor to the hydrogen gas being maintained between about 0.025 and 2.0, and preferably between 0.05 and 0.20.

There have previously been references in the literature of attempts or suggestions to coat a variety of substrates with aluminum oxide. However, insofar as is known, the coating of a cemented carbide substrate with aluminum oxide to produce a fully dense and adherent coating has never previously been disclosed. Nor has the unusual combination of properties exhibited by the present products been previously attainable in either coated or uncoated cutting tool materials. The products ot the invention are remarkable in several respects. Their strength as compared with comparable known coated cemented carbide materials is considerably higher and their cutting performance is superior in terms of tool life at intermediate and higher cutting speeds. The basis for the foregoing statements will become apparent from the discussion and test results set forth below.

The term cemented carbide as used herein means one or more transitional carbides of a metal of Groups IVb, Vb, and VIb of the Periodic Table cemented or bonded by one or more matrix metals selected from the group iron, nickel and cobalt. A typical cemented carbide contains WC in a cobalt matrix or TiC in a nickel matrix.

Because of the demanding requirements normally placed upon a cemented carbide cutting material, the properties of any coating, the manner in which it is bonded to the substrate and its effect on substrate strength are extremely critical. The coating layer must have high integrity in terms of density and smoothness—porosity or nonuniformity cannot be tolerated. The coating must also be firmly and adherently bonded to the cemented carbide substrate to prevent spalling or separation in use. In addition, the coating must not reduce the strength of the cemented carbide substrate significantly. The products of the present invention have been extensively tested and have been found to satisfy all of the foregoing requirements. The coatings are uniform and fully dense, they are firmly bonded to the substrate and the coated composite retains a high proportion of its strength, usually greater than 85% of the transverse rupture strength of the uncoated substrate. The achievement of these characteristics in the coated product is believed to be quite unexpected, particularly in view of the substantial strength reductions known to result from the addition of wear-resistant coatings to cemented carbide substrates. The coated materials of the invention also produce a surface finish in machining operations which appears to be fully equivalent in quality to solid aluminum oxide cutting materials, the latter being known to produce the best surface finishes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The outstanding properties of the aluminum oxide-coated product of the invention depend upon careful control of the process parameters. The process involves the use of a gaseous mixture of hydrogen, water, and an aluminum halide such as aluminum trichloride. Carbon monoxide and carbon dioxide may be optionally added. The primary overall deposition reaction is:

$$3H_2O+2AlCl_3 \rightarrow Al_2O_3+6HCl$$

The most important ingredients in the gaseous reaction mixture are therefore water vapor and aluminum chloride vapor. However, the aluminum chloride vapor can be formed in several ways during the deposition reaction, as for example by heating solid $AlCl_3$ powder or by passing chlorine gas over aluminum metal. The water vapor is most conveniently formed by reacting hydrogen with carbon dioxide in the deposition chamber to form carbon monoxide and water vapor by the water gas reaction:

$$H_2+CO_2 \rightleftarrows CO+H_2O$$

The amount of water vapor formed in this manner depends upon the temperature and the initial concentrations of hydrogen, carbon dioxide, carbon monoxide and water vapor in the input gas stream. In order to form a good quality coating of desirable thickness in the temperature range of 900°-1250° C., the ratio of water to hydrogen gases present, after the water gas reaction, should be between about 0.025 and 2.0.

Hydrogen has been found to be necessary in the vapor deposition process to obtain a dense, adherent coating. Hydrogen appears to insure oxidation of the aluminum at the carbide surface. Oxidation in the reaction zone above the carbide substrate creates a condition known as dusting—which must be avoided. The absence of hydrogen creates a porous coating which is not fully dense. Thus the three necessary ingredients of the process are aluminum halide vapor, water vapor and hydrogen. In its preferred form, the process includes the use of aluminum chloride vapor, hydrogen and carbon dioxide, the latter reacting with H_2 to form water vapor.

The amount of water vapor present, after the reaction of known input concentrations of H_2 and CO_2 and CO and H_2O if used, can be calculated using the following equation:

$$(H_2O)_f = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

where

$a=1-K$; K=the equilibrium constant for the water gas reaction;

$b=(CO)_i—(H_2O)_i+K(H_2)_i+(CO_2)_i+2(H_2O)_i)$; and

$c=-K((H_2)_i(CO_2)_i+(H_2)_i(H_2O)_i+(H_2O)_i(CO_2)_i+(-H_2O)_i^2)$

The parentheses denote the concentration of the gaseous species enclosed within the terms of partial pressure, and the subscripts f and i denote the final or equibrium concentrations and the initial or input concentrations, respectively. The amount of H_2 present, and thus the H_2O/H_2 ratio, can then be determined from the relationship:

$$(H_2)_f=(H_2)_i+(H_2O)_i-(H_2O)_f$$

A series of coated products were prepared in accordance with the invention by passing aluminum chloride vapor, hydrogen and carbon dioxide over cemented carbide inserts. The examples were prepared at various input gas compositions and at various final H_2O/H_2concentrations. In all cases, deposition was at 1050° C. and a 45-minute deposition cycle was used with 2-3 grams of aluminum chloride and an aluminum chloride generator temperature of about 200° C. The use of more $AlCl_3$ shifts the desired H_2O/H_2 ratio to a higher value and vice versa. The coatings were deposited on a cemented carbide substrate having the following composition in percent by weight: WC-72, Co-8.5, TiC-8, TaC-11.5. Table I bellow shows the effect of gas composition on coating thickness. When coating with both higher and lower ratios of H_2O/H_2(i.e. outside range of about 0.025 to 2.0), it wasn't possible to get a coating of sufficient thickness, i.e., >1 micron. Coating quality was good for all examples having more than 1 micron thickness coating. Coating quality was judged to be good if the coating could withstand an adherency test consisting of sliding the coated insert under a diamond brale indentor of the same type used for the Rockwell hardness test using a load of 2 kilograms on the diamond. If the coating resisted spalling or crumbling during this test, it was judged to have good quality. If it did not, it was judged to have poor quality.

TABLE I

	Input gas partial pressures				Water gas reaction equilibrium partial pressures			Coating thickness
Example	(H_2)	(CO_2)	(CO)	(H_2O)	$(H_2)+$	$(H_2O)+$	$\frac{(H_2O)+}{(H_2)+}$	(microns)
1	.978	.022	.000	.000	.956	.0217	.023	<1
2	.960	.040	.000	.000	.921	.0391	.043	2½
3	.850	.150	.000	.000	.713	.137	.192	6
4	.750	.100	.150	.000	.665	.085	.127	6
5	.050	[.850]*.100*	[.100]*.850*	.000	.042	.0085	.205	3
6	.600	.400	.000	.000	.323	.277	.857	3
7	.450	.250	.300	.000	.307	.143	.466	9
8	.400	.600	.000	.000	.123	.277	2.26	<1
9	.100	.700	.200	.000	.019	.081	4.26	<1

TABLE I-continued

Example	Input gas partial pressures (H_2)	(CO_2)	(CO)	(H_2O)	Water gas reaction equilibrium partial pressures (H_2)+	(H_2O)+	(H_2O)+ / (H_2)+	Coating thickness (microns)
10	.975	.000	.000	.025	.975	.025	.026	1

The nature of coating obtained was determined by using X-ray diffraction analyses and optical microscopy. X-ray analyses showed the coating to be alpha Al_2O_3. At the higher deposition temperatures (greater than 1150° C.), significant amounts of the compound **[**W_3CO_3C**]** *W_3Co_3C* began to form due to reaction of the substrate carbide with the coating atmosphere. Optical microscopy revealed a gray, translucent coating of Al_2O_3 that was fully dense and well bonded to the substrate in those examples in which the coating quality was found to be good. A very thin (less than 1 micron) layer of another nonmetallic compound **[**, cobalt aluminate ($CoAl_2O_4$)**]** *formed by oxidation of the substrate (a titanium-containing oxide phase)*, was present between the Al_2O_3 layer and the cemented carbide substrate. The presence of this thin layer is necessary to achieve the proper bond strength between the coating and the substrate, that is, a bond strength sufficient to pass the adherency test set forth above. In those cases in which no observable intermediate nonmetallic layer was present, the coated inserts did not pass the above described adherency test. For this reason, **[**a cobalt (iron, or nickel) aluminate**]** intermediate layer is believed necessary to a good quality coating.

The preferred temperature range for deposition of the coating is 900° C. to 1250° C. At lower temperatures, the deposition rate becomes very low and the coating is poorly bonded to the substrate. At higher temperatures, excessive reaction occurs between the coating atmosphere and the cemented carbide substrate, weakening the bond between the coating and the substrate and lowering the strength of the overall composite body.

The strength of the Al_2O_3 coated cemented carbide composite was measured (as were all strength measurements disclosed herein), using a slightly modified standard transverse rupture test (ASTM No. B4066-63T), that included three roll loading and a span-to-thickness ratio of 3.5 to 1. Using a deposition temperature of 1050° C. and a cemented carbide substrate of the nature set forth in the first ten examples in Table I above, the average strength of bars having coating thicknesses of from 5–7 microns (the preferred thickness for this substrate in terms of wear resistance) was 241,000 p.s.i. This represents only a slight reduction (11%) from the 270,000 strength value obtained from the uncoated cemented carbide substrate.

In the following Table II, the metal cutting performance of coated inserts prepared in accordance with this invention is shown and compared with the corresponding performance of uncoated inserts. Examples 11 through 17 were ½"×½"×3/16" disposable cutting inserts, coated with **[**Al_2O_3 at 1050° C.**]** by the vapor deposition technique disclosed above for Examples 1 through 10. A range of coating thicknesses of from 1–10 microns was used. These inserts were then used ot machine SAE 1045 steel, 190 BHN hardness, at 700–1000- and 1500-surface-feet-per-minute speeds, 0.010 inch per revolution feed, and 0.100 inch depth of cut. The cutting times to a flank wear of 0.010 inch are shown in Table II, along with the crater wear depth at the 0.010 flank wear time. The transverse rupture strengths are also given. For comparison purposes, the cutting performance and strengths of the uncoated substrate material, Examples 18 and 19, a commercially available solid aluminum oxide base (89% Al_2O_3, 11% TiO) insert—Examples 20–22—and a TiC coated cemented carbide insert—all run under the same conditions—is also shown in Table II.

TABLE II

Example		Coating thickness (microns)	Cutting speed, s.f.p.m.	Time to .010 flank wear (min.)	Crater depth at .010 flank wear	Transverse rupture strength (p.s.i.)
11	Al_2O_4 coating on cemented carbide[1]	1	700	9	.003"	260,000
12	"	4	700	32	.002"	250,000
13	"	7	700	51	.001"	235,000
14	"	10	700	51	.008"	210,000
15	"	7	1,500	[2]4.2	[3].0003"	235,000
16	Al_2O_3 coating on cemented carbide[4]	7	1,500	17	.007"	175,000
17	"	12	1,000	26	.003"	160,000
18	Uncoated carbide[1]		700	4	.004"	270,000
19	"		1,000	5	.010"	230,000
20	Solid Al_2O_3		700	51	.001"	90,000
21	"		1,000	30	.002"	90,000
22	"		1,500	[2]4.5	[3].0002"	90,000
23	TiC coating on cemented carbide[1]	5	700	18	.011"	175,000
24	"	5	1,000	4	.011"	175,000

[1] 72% WC, 8% TiC, 11.5% TaC, 8.5% Co.
[2] To .004" wear.
[3] At .004" flank wear.
[4] 71% WC, 12.5% TiC, 12% TaC, 4.5% Co.

It can be seen that the cutting performance of the cemented carbide tool material is very substantially improved by the Al_2O_3 coating and that this improvement is substantially greater than a TiC coating on the same substrate. It is also evident that the amount of improvement obtained is dependent upon coating thickness up to a value of about 7 microns and that some evidence of performance decline occurs at 10 microns. At the optimum thickness value of 7 microns for this substrate, the performance of the Al_2O_3 coated tool was equivalent to that of the solid Al_2O_3 tool at all three speeds tested. The strength of the Al_2O_3 coated inserts was, however, considerably higher than solid Al_2O_3 and higher than the strength of the same substrate with a TiC coating.

It should be noted that, because of strength limitations, it has not been feasible to use solid aluminum oxide cutting materials in disposable cutting inserts of the type used in pin-type holders. These inserts have a centrally disposed hole for the reception of a pin which locks the insert in place. The strength of such inserts must be sufficient to resist the locking stresses. The strength of the present coated materials is sufficiently high to enable their use in such inserts. The present invention therefore makes possible the use of an insert, in such applications, having a higher wear resistance than any comparable insert presently available.

The following Table III shows the performance of the coated inserts of the invention in cutting a high temperature nickel-base alloy, specifically Inconel 718 in the solution-aged condition (BHN 390 hardness). The results, Example 25, are compared with the performance of an uncoated cemented carbide of the same composition (Example 26), and in addition with a commercial solid aluminum oxide tool (Example 27). The inserts were of the negative-rake disposable type (indexable and invertible) and were ½"×½"×3/16". The cemented carbide substrate for Examples 25 and 26 was 94% WC and 6% Co. The substrate was coated with Al_2O_3 [at 1050° C.] by vapor deosition process described above in connection with Examples 1 through 10.

TABLE III

Example	Insert type	Coating thickness (microns)	Time to .020" flank wear (min.)	Comments
25	Al_2O_3 coating on cemented carbide	2.5	8.5	
26	Uncoated cemented carbide		5.4	
27	Solid Al_2O_3		<1	Rapid edge breakdown.

The performance of the insert coated with 2.5 microns of Al_2O_3 was significantly better than that of the uncoated cemented carbide insert of the same substrate composition. From tests with other coating thicknesses, it has been determined that the optimum thickness for this kind of machining (i.e., high temperature alloys) is in the 1-3 micron range. Thicknesses greater than 3 microns in these tests decreased tool life. The superior strength of the Al_2O_3 coated tools is amply demonstrated by the rapid falure of the solid Al_2O_3 tool in Example 27, whereas no breakage or chipping was observed in the Al_2O_3 coated tools, Examples 25.

The foregoing is a description of illustrative embodiments of the invention, and it is applicant's intention in the appended claims to cover all forms which fall within the scope of the invention.

I claim:

1. A high strength, high-wear resistance coated cemented carbide product comprising:

a *titanium carbide-containing* cemented carbide substrate, and a *generally* fully dense *chemically vapor deposited* alpha aluminum oxide coating of from 1-20 microns thickness firmly and adherently bonded to said cemented carbide substrate through an intermediate layer [of an iron group metal aluminate] *comprising another non-metallic compound formed in situ by chemical vapor reaction, which acts to bond said coating to said substrate,*

said coated cemented carbide product having a wear resistance substantially equivalent to aluminum oxide base cutting materials and having a transverse rupture strength of at least 150,000 p.s.i.

[**2**. The coated cemented carbide product of claim **1** in which the cemented carbide substrate comprises tungsten carbide and a cobalt matrix.]

[**3**. The coated cemented carbide product of claim **2** in which the intermediate layer is cobalt aluminate.]

4. The coated cemented carbide product of claim **1** in the form of a disposable cutting insert for the machining of metal and other materials.

[**5**. The coated cemented carbide insert of claim **4** having a centrally disposed hole therein, the insert adapted to be mounted in a pin-type toolholder.]

6. The coated cemented carbide product of claim [**1**] *4* in which the coating is less than [**15**] *10* microns in thickness.

7. The coated cemented carbide product of claim **1** in which [the cemented carbide substrate comprises titanium carbide and a matrix selected from the group consisting of iron, nickel and cobalt] *said non-metallic compound is a titanium-containing oxide of the rutile type.*

[**8**. The coated cemented carbide product of claim **7** containing tantalum carbide.]

9. The coated cemented carbide product of claim [**1**] *6* in which [the] *said* cemented carbide substrate comprises tungsten carbide, titanium carbide and tantalum carbide [and] *in* a cobalt matrix *and said non-metallic compound comprises a rutile type oxide phase.*

10. A high-strength, high-wear resistance coated cutting insert for machining metals and other materials, comprising:

a substrate which includes a titanium-containing cemented carbide phase;

a generally fully dense, firmly adherent, chemically vapor deposited, aluminum oxide coating of from 1 to less than 10 microns thickness; and

another non-metallic compound formed between said substrate and said coating by oxidation, which non-metallic compound acts to enhance the adherence of said coating.

11. The coated cutting insert of claim 10 in which said non-metallic compound is a titanium-containing oxide phase of the rutile type.

12. A high-strength, high wear resistance coated cutting insert for machining metals and other materials comprising:

a substrate comprising a titanium-containing cemented carbide;

a generally fully dense, firmly adherent, chemically vapor deposited, alpha aluminum oxide coating of from 1-20 microns thickness and

an intermediate layer comprising another non-metallic compound containing titanium, which acts to enhance the adherence of said coating.

13. The coated cutting insert of claim 12, wherein said coating is less than 10 microns thick.

14. The coated cutting insert product of claim 12 or 13, wherein said non-metallic compound comprises a rutile-type oxide phase formed in situ by chemical vapor reaction.

15. A high-strength, high-wear resistance coated cutting insert for the machining of metal and other materials, comprising:

a cemented carbide substrate including tungsten carbide, titanium carbide, tantalum carbide and a cobalt matrix;

a generally fully dense alpha aluminum oxide coating of from 1 to less than 10 microns thickness firmly and adherently bonded to said cemented carbide substrate, and

an intermediate layer comprising another non-metallic compound of a titanium-containing oxide phase of the rutile type which acts to enhance the adherence of said coating to said substrate.

16. A cemented carbide tool comprising a titanium-containing cemented carbide substrate coated with a generally fully dense chemically vapor deposited layer of aluinum oxide of from about 1.0 to about 20 microns thickness, and a titanium containing non-metallic phase formed in situ by chemical reaction and located intermediate the coating and substrate which acts to enhance the adherence of said coating.

17. The cemented carbide tool of claim 16 in the form of a disposable cutting insert adapted to be mounted in a pin type tool holder for the machining of metal and other materials.

18. The cemented carbide tool of claim 16 in the form of metal cutting machine insert and in which the coating is less than 10 microns in thickness.

19. The cemented carbide tool of claim 16 in which the cemented carbide substrate comprises titanium carbide and a bonding matrix selected from the group consisting of iron, nickel and cobalt.

20. The cemented carbide tool of claim 16 in the form of an insert for machining metal and in which the aluminum oxide coating is between about 7 and about 10 microns thick.

21. The cemented carbide tool of claim 16, 32 or 34, in which the cemented carbide substrate comprises tungsten carbide, titanium carbide and tantalum carbide and a cobalt matrix and said non-metallic phase is a product of oxidation of said substrate.

22. A high-strength, high-wear resistance metal cutting tool comprising:

a titanium-containing cemented carbide substrate;

a generally fully dense coating of aluminum oxide of from 1 to less than 10 microns thickness; and

bonding means located intermediate said cemented carbide substrate and aluminum oxide coating for enhancing the adherence of said aluminum oxide coating such as to prevent spalling and separation of said coating when subjected to an adherency test of sliding the tool under a Rockwell hardness test type diamond brale indentor having a load of 2 kilograms.

23. The metal cutting tool of claim 22 in the form of a disposable insert having a centrally disposed hole for mounting in a pin type holder.

24. The metal cutting tool of claims 22 or 23, in which said bonding means comprises a phase formed by oxidation of said substrate.

25. The metal cutting tool of claim 22 or 23, in which the cemented carbide substrate comprises titanium carbide and a matrix selected from the group consisting of iron, nickel and cobalt, and said bonding means comprises an oxide phase containing titanium from said substrate.

26. The metal cutting tool of claim 22 or 23, in which the cemented carbide substrate comprises tungsten carbide, titanium carbide and tantalum carbide and a cobalt matrix, and said bonding means comprises a phase formed in situ by oxidation of said substrate.

27. A cemented carbide tool comprising a titanium-containing cemented carbide substrate coated with a generally fully dense, chemically vapor deposited, layer of aluminum oxide from 1.0 to 20 microns thick, and a titanium-containing oxide phase located intermediate the coating and substrate which acts to enhance the adherence between said coating and said substrate to prevent spalling and separation of said coating when subjected to an adherency test of sliding the tool under a Rockwell hardness diamond brale indentor having a load of 2 kilograms.

28. The cemented carbide tool of claim 27 in the form of a disposable cutting insert for the machining of metal and other materials.

29. The cemented carbide tool of claim 28 having a centrally disposed hole therein, the insert being adapted to be mounted in a pin type toolholder.

30. The cemented carbide tool of claim 27, 28 or 29 in which the coating is less than 10 microns in thickness.

31. The cemented carbide tool of claim 27, 28 or 29, in which the cemented carbide substrate comprises titanium carbide and a matrix selected from the group consisting of iron, nickel and cobalt, and wherein said oxide phase is a rutile phase formed by oxidation of said substrate, and said coating is less than 10 microns in thickness.

32. The article of manufacture according to claim 1, 6, 10, 11, 12, 13, 15, 22, or 27, wherein the phase which enhances coating adherence comprises an oxide of metal ions from said substrate.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : Re. 32,093
DATED : March 18, 1986
INVENTOR(S) : Thomas E. Hale

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the cover sheet, under the heading "References Cited, U.S. PATENT DOCUMENTS" insert the following:

2,707,691	5/55	Wheildon
3,031,331	1/62	Aves et al.
3,054,694	9/62	Aves
3,178,308	4/65	Oxley et al.
3,196,056	7/65	Ornitz
3,251,337	5/66	Latta et al.
3,502,493	3/70	Forestek
3,582,271	6/71	Minagawa et al.
3,640,689	2/72	Glaski et al.
3,640,757	2/72	Grubba
3,642,522	2/72	Gass et al.
3,656,229	4/72	Sakurai et al.
3,696,707	10/72	Schedler et al.
3,713,882	1/73	Debrunner et al.
3,770,512	11/73	Bopp

Under the heading "FOREIGN PATENT DOCUMENTS" insert the following:

268,003	1/69	Austria
547,937	6/56	Belgium
600,374	7/34	Germany
895,084	2/53	Germany
2,018,662		Germany
330,470	11/70	Sweden

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : Re. 32,093 Page 2 of 4
DATED : March 18, 1986
INVENTOR(S) : Thomas E. Hale

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Under the heading "OTHER PUBLICATIONS" insert the following:

Lee, et al., "The Effect of a Coated ... Tools" *Society of Manuf. Engr. CMEP* (1971)

Hinterman & Gass, "Chemical Deposition From The Gaseous Phase", *Schwizer Archiv.* pp. 157-163 (1967)

McCandless, et al., "Chemically Vapor Deposited Ceramic Coatings...Oxides", *J. Electromechanical Society* (March 1970)

Opitz, et al., "Oxides Make Steels Supermachineable", *Machining* (April, 1968)

Powell, et al., "Vapor Deposition", *Electrochemical Society, Inc.* pp. 384-389; 493-494 (1966)

Powell, et al., "Vapor-Plating", *Electrochemical Society, Inc.* (1955) pp. 136-143

Wong, et al., "Chemical Vapor Deposition...Al_2O_3" *J. Amer. Ceram. Soc.* 53[11] 617-21 (1970)

Parker, et al., "Vapor Growth Of Al_2O_3 Bicrystals", *J. Amer. Ceram. Soc.* 53[11] 583-85 (1970)

P.S. Schaffer, "Vapor-Phase Growth Of Alpha Alumina Single Crystals", *J. Amer. Ceram. Soc.* 48[10] 508-11 (1965)

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : Re. 32,093 Page 3 of 4

DATED : March 18, 1986

INVENTOR(S) : Thomas E. Hale

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the same sheet, under the heading EXEMPLARY CLAIM, on line 12, change "substate" to --substrate--.

IN THE SPECIFICATION

Col. 1, line 38, change "principel" to --principal--

Col. 4, line 17, change the italicized "H" in H_2O to bold --H--.

Col. 4, line 41, change "bellow" to --below--.

Col. 6, line 20, "[Al_2O_3 at" should be --Al_2O_3 [at--.

Col. 6, line 23, "ot" should be --to--.

Col. 7, line 29, change "deosition" to --deposition--.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : Re. 32,093 Page 4 of 4
DATED : March 18, 1986
INVENTOR(S) : Thomas E. Hale

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

IN THE CLAIMS

Claim 16, col. 9, line 22, change "*aluinum*" to --*aluminum*--

Claim 27, col. 10, line 33, change "2 kilograms" to --*2 kilograms*--

Claim 31, col. 10, line 47, change "10 microns in thickness" to "*10 microns in thickness*".

Signed and Sealed this

Seventh Day of October, 1986

[SEAL]

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks