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(54) **BRASAGE D'UNE PELLICULE DIAMANTEE ET DE CARBURE  
DE TUNGSTENE**

(54) **BRAZING OF DIAMOND FILM TO TUNGSTEN CARBIDE**

(57) The reliability of a braze joint formed between a diamond film and a tungsten carbide body is increased by use of a vanadium containing braze. The braze joint exhibits an average shear strength greater than about 40,000 pounds per square inch, (276 MPa) and the braze exhibits a contact angle with the diamond film of less than about 15°.

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ABSTRACT OF THE DISCLOSURE

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## BRAZING OF DIAMOND FILM TO TUNGSTEN CARBIDE

## FIELD OF THE INVENTION

The present invention is directed to cutting tools that contain a diamond cutting element. More particularly, the present invention is directed to a cutting tool in which the cutting element is a diamond film. Still more particularly, the present invention is directed to diamond film cutting tools containing cutting elements comprising a diamond film attached to a tungsten carbide body wherein the attachment is improved by the use of a vanadium containing braze composition.

## BACKGROUND OF THE INVENTION

It is important for the continued successful utilization of diamond tools that such tools be capable of withstanding extremely severe conditions of use without the diamond cutting surface breaking free from the tool. Diamond cutting tools are commonly prepared by adhering a diamond cutting element to an extremely hard and durable tool substrate material such as tungsten carbide. For flat tools, such as those intended for use on a metal lathe, the diamond cutting

elements are typically in the form of small triangular "inserts" which are clamped in place on a larger, bar-shaped "tool holder" which is held in a lathe or similar machine during actual use. Traditionally such inserts have been based upon a polycrystalline compact diamond (PCD) body which has tungsten carbide on one surface. Polycrystalline diamond compacts are a mixture of a binder such as cobalt and diamond powder. Such diamond compact materials are relatively thick, e.g. about 0.080" (2.03 mm), and relatively short in length, e.g. about 0.065" (1.65 mm) maximum. To form a cutting element, the tungsten carbide surface of the PCD is brazed to a larger tungsten carbide body.

In many applications, however, polycrystalline compact diamonds have been found unacceptable due to the presence of the cobalt or for insufficient hardness. Chemical vapor deposited (CVD) diamond film does not contain cobalt which can increase surface friction as well as be a contaminant for a workpiece. Moreover, CVD diamond film is harder than a PCD body. Accordingly, there is an increasing desire to utilize diamond film to form cutting elements. To do so in a manner which allows the direct commercial substitution for CVD diamond for PCD, however, requires adhering CVD diamond to a tungsten carbide strip so that it can be subsequently joined to a larger tungsten carbide body

by a braze.

Due to the high temperatures experienced by the cutting element both in use as well as during adherence of one tungsten carbide surface to another, high temperature brazes have been used to join a diamond film to tungsten carbide. However, CVD diamond films do not readily adhere to tungsten carbide, nor many other surfaces, and thus the art has previously used brazing alloys which contain metals which will improve the wetting of the braze alloy on the diamond film, generally by reacting with the carbon thereof to form carbides. Such metals have been referred to in the art as "active metals" or "reactive metals" and include such as titanium, tantalum, chromium, nickel, and the like. Prior to this invention, the art believed that the best active metal for adhering a CVD diamond film was titanium due to its known ability to react with carbon and form titanium carbide (TiC). Such alloys are generally referred to in the brazing art as "active metal brazes" or "active brazing alloys" or "reactive brazing alloys" or "reactive metal brazing alloys."

Specifically, U.S. Patent 5,326,195 issued 5 July 1994, entitled "Diamond Film Cutting Tool", assigned to the assignee of this application, discloses the brazing of a diamond film to a tungsten carbide surface

by standard active brazing techniques with a reactive metal braze alloy based upon silver, gold, palladium, and the like. In addition to the above metals, the braze further contained a metal capable of forming a carbide thereof at the interface with the diamond film, such as Ti, Ta, Cr, and Mn. The braze used in the Examples was an ordinary silver-copper braze containing Ti or Ta as the active/reactive metal.

U.S. Patent No. 5,020,394 discloses brazing a CVD diamond film to the rake face of a tool base by means of a two-step brazing process which is both expensive and results in a poor quality bond.

Saint-Gobain Corporation currently manufactures diamond film cutting elements wherein a CVD diamond film is joined to tungsten carbide by means of a commercially available reactive metal braze alloy (Lucanex 721 from Lucas-Milhaupt Inc., 5656 South Pennsylvania Avenue, Couda, Wisconsin 53110), which contains 72 parts silver, 28 parts copper, and 5 to 10 parts titanium.

It is an object of the present invention to improve the reliability of the bond between a diamond film cutting element and a tungsten carbide substrate to which the cutting element is attached.

## SUMMARY OF THE INVENTION

The present invention is directed to the formation of brazed joints between a diamond film and a tungsten carbide body which are more reliable than current commercially formed joints between the same materials. The braze in the joints is a vanadium containing alloy. Preferably, the braze is an alloy which contains a major amount of gold and a minor amount of vanadium.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a joint formed between a diamond film layer and a tungsten carbide body by means of a vanadium containing braze alloy.

The overall reliability, and thus commercial applicability, of a joint formed between two dissimilar surfaces (such as a diamond film and tungsten carbide) by means of a braze is dependent upon not only (i) the absolute shear strength of the joint but also (ii) the capacity of the braze to flow and thereby completely fill the space between the surfaces being joined, i.e. ability to avoid the creation of any voids therebetween. The shear strength of a particular joint can be determined by preparing multiple samples thereof and subjecting the samples to shear testing.

Generally, an average shear strength of at least about

40,000 pounds per square inch (276 MPa). This is equal to about 2500 pounds for a joint having an area of about 0.0625 square inches. The capacity of a braze to flow, commonly referred to as "wetting" or  
5 "wettability" or "flow characteristics" can be evaluated by determining the contact angle between the braze and a surface when the braze is melted on that surface. A low contact angle indicates a high capacity for wetting; thus the lower the contact angle the  
10 greater the likelihood of the absence of any voids and the increased reliability of the overall structure. For good wetting and spreading of a braze on a particular surface, a contact angle of less than about  $15^\circ$  is desired. Such a low contact angle provides sufficient  
15 capillary force to fill the interfacial voids and to flow into any asperities on the surface.

Diamond films suitable for use in this invention include those films which have been formed by a chemically deposited vapor process as well as  
20 polycrystalline diamond films prepared by other procedures known in the diamond film art. Also preferably, the diamond film has a cutting edge and a substantially flat surface to help prevent the formation of any gaps when the diamond film is attached  
25 to the surface of the tungsten carbide substrate. The diamond film preferably exhibits a high Young's

modulus, i.e. greater than about 1000 GPa, and also has a high thermal stability, i.e. greater than about 700°C.

5 A polycrystalline diamond film may be manufactured by any suitable technique known in the art which produces a diamond material with sufficient toughness for use in tool applications, including microwave plasma chemical vapor deposition (CVD) (generally described in Japanese Laid-Open Patent Appln. No. 58-100494), neutral ion CVD methods (generally disclosed 10 in Japanese Laid-Open Pat. Appln. No. 58-91100), plasma torch technology, or arc-jet processing. It is presently preferred to employ the arc-jet method to form the polycrystalline diamond film. The type of apparatus used for the arc-jet deposition is described, 15 for example, in U.S. Pat. No. 4,682,564. Presently known methods generally involve the disassociation of hydrogen as a facilitating gas and methane as a carbon source by heating the gases to a plasma with a hot 20 wire, combustion torch, plasma torch, microwave source, arc-jet, and the like. The heating occurs in a partial vacuum near the surface of a deposition substrate, such as silicone or molybdenum, to cause diamond to form as a layer thereon.

25 The tungsten carbide body of the invention is

preferably in the shape of a conventional diamond  
cutter element, typically a small triangular "insert."  
Such inserts are well known in the art and are  
conventionally used by attaching them onto a larger,  
5 bar-shaped "tool holder" which is held in a lathe.  
Alternatively, the tungsten carbide may be an assembly  
piece that has been or will be thereafter permanently  
affixed to a larger workpiece by brazing or other  
suitable chemical joining technique. Of course, the  
10 surface of the tungsten carbide body being joined  
should be relatively smooth so that it will easily be  
coated with the braze.

The braze used to form the joints of this  
invention must contain vanadium. The vanadium will be  
15 present in the braze in an amount sufficient to improve  
the performance of the braze in joining a diamond film  
to tungsten carbide as compared to a chemically similar  
braze containing titanium. Generally the vanadium will  
be present in the braze as a minor amount, i.e. about  
20 0.5 to 10%, preferably about 0.75 to 5%, most  
preferably about 1 to 3%, by weight. Such suitable  
brazes will have a melting temperature that is lower  
than the melting temperature of tungsten carbide. Such  
suitable brazes must further be capable of remaining in  
25 a liquid state for a sufficiently long period of time  
so that the diamond surface can be wetted by the braze

before the braze cools, solidifies, and bonds to the substrate. The melting (liquidus) temperature of the braze will vary with the particular composition thereof but is commonly in the range of about 750 to 1,200°C.

5 In addition to vanadium, the braze contains additional metals such as gold and nickel. Preferably, at least one of the additional metals will be gold. More preferably the additional metals will be a mixture of gold and nickel. Still more preferably, the braze will  
10 contain at least about 1 weight % vanadium, at least about 95 weight % gold, and the balance being nickel. Most preferably, the braze contains about 1.25-2.25% vanadium, about 96.5-98.5% gold, and about 0.25-1.25% nickel. Such a braze is available as a foil from Wesgo  
15 Division of GTW Products Corporation under the trade name Gold-ABA(H).

Unless the materials have been precleaned, the procedure for forming a brazed joint of this invention generally begins with the cleaning of the diamond film, the braze alloy, and the tungsten carbide surface of  
20 all contaminants. When the braze is used in the form of a foil, it is preferably cleaned ultrasonically by placing it in a beaker that contains an appropriate degreasing solvent (such as acetone or an alcohol), and  
25 then placing the beaker in a commercial ultrasonic cleaner and agitated ultrasonically for about 3 to 15

minutes continuously. Oil and grease can be removed from the tungsten carbide with a suitable degreasing solvent, by vapor degreasing or by alkaline cleaning. While not necessary, a conventional flux may be used.

5 Once the braze and tungsten carbide have been cleaned, a suitable amount of braze is placed between the diamond film and the tungsten carbide to be bonded, the three components held together in a predetermined relationship, and heated in a furnace, preferably a vacuum furnace, to a temperature sufficiently high to melt the braze and for a period sufficiently long to form the joint. Vacuums of better than  $1 \times 10^{-5}$  Torr, preferably better than  $5 \times 10^{-6}$  Torr, and most preferably better than  $1 \times 10^{-6}$  Torr should be used.

10

15 The heating from room temperature up to the brazing temperature should occur relatively quickly so as to minimize diffusion of any impurities present in the system. Preferably, a heating rate of about  $100^{\circ}\text{C}$  per minute is used until within  $20^{\circ}\text{C}$  of the solidus temperature of the braze. Then the rate is quickly decreased, for example to  $30^{\circ}\text{C}$ , until the temperature passes the liquidus temperature of the braze and reaches the brazing temperature. This procedure has been found to minimize the likelihood of overshooting the desired brazing temperature which, for certain brazes may be  $100^{\circ}\text{C}$  higher than the liquidus

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temperature of the braze which is commonly up to 50°C higher than the solidus temperature. More commonly, however, the brazing temperature is only about 5 to 60°C higher than the liquidus temperature of the braze.

5           After reaching the brazing temperature, the braze melts, wets the surfaces of the diamond film and tungsten carbide, and joins them together. When the braze melts, the carbon in the diamond film is believed to react with the vanadium in the brazing alloy and  
10           facilitate the formation of a strong adhesive bond. The joined materials are generally held at the brazing temperature for several minutes, e.g. about 2 to 10, before cooling to room temperature.

          The gap between the diamond film and the tungsten  
15           carbide which contains the brazing alloy will generally be in the range of from about 10 $\mu$ m to about 100 $\mu$ m depending upon the specific brazing alloy used. With the preferred gold-vanadium-nickel brazing alloy foil, no benefit was observed from using more than a single  
20           layer of foil and a joint gap more than about 30 $\mu$ m.

          A particularly advantageous way to join a diamond  
film to a tungsten carbide cutting element is by means of pre-brazing a diamond film with a vanadium-  
containing braze, and then joining the vanadium braze  
25           coated surface of the diamond film to the tungsten carbide cutting element by means of a conventional

braze. In this variation, a vanadium-containing braze is first substantially distributed on a diamond film surface. The resulting vanadium braze layer is then heated to its melting temperature, e.g. greater than about 1100°C, and bonds to the diamond film.

5 Thereafter, a conventional braze is substantially distributed on the braze surface of the diamond film. The conventional braze must melt at a lower temperature than the vanadium braze. The prebrazed diamond film, 10 the conventional braze, and the tungsten carbide substrate are then heated to the melting temperature of the conventional braze, and the brazed diamond film surface is then joined to the tungsten carbide, and cooled. Suitable conventional brazes may include 15 metals such as titanium, tantalum, chromium, nickel, and the like, in addition to conventional filler metals such as nickel, copper, silver and the like. This technique enables the tool manufacturer to braze a diamond film to a tungsten carbide cutting element 20 without the need of expensive equipment and exacting vacuum conditions which are ordinarily required to braze tungsten carbide to a diamond film.

The present invention will now be described with reference to the following examples in which all parts and percents are by weight unless otherwise specified. 25 It is understood that these examples are for

illustrative purposes only and should not be deemed to limit this invention.

EXAMPLE 1

A brazed joint was formed between a  
5 polycrystalline diamond film formed by the DC arc jet  
deposition techniques substantially as described in  
U.S. Patent No. 4,682,564 and tungsten carbide. The  
braze contained 97.5% gold, 1.75% vanadium, and 0.75%  
nickel and was used a single layer of foil about 0.002"  
10 thick. The diamond film and the tungsten carbide were  
held in place with a 30 $\mu$ m joint gap. The brazing was  
performed at a temperature of 1125°C and with a brazing  
time of 10 minutes. The braze was pre-cleaned  
ultrasonically for three minutes in alcohol, and the  
15 tungsten carbide surface was pre-cleaned with  
conventional oil-reducing chemical solvents. After  
pre-cleaning, the braze and the tungsten carbide were  
stored in a vacuum desiccator. Shortly before actual  
use, the tungsten carbide surface to be joined to the  
20 diamond film was recleaned with alcohol.

The brazing was conducted in a conventional three-  
zone tube vacuum furnace manufactured by Lindbergh,  
Inc. The furnace features three heating zones, wherein  
the two side zones are set up in a "slave"  
25 configuration and the central zone is set up in a

"master" configuration. The furnace's process chamber consists of a 2.75 inch dia. quartz tube that provides a vacuum level of more than  $1.0 \times 10^{-5}$  Torr.

To evaluate the quality of the brazed joint produced by the vanadium containing braze, multiple samples thereof were prepared as above and evaluated for shear strength. The shear strength was determined using an Instron Tester with a fixture which ensured that the shearing tool applied force in a direction perpendicular to the edge of the brazed specimen. The average shear strength was 2,706.7 pounds for a joint having an area of about 0.0625 square inches, i.e. 43,307 psi (299 MPa).

To determine the wettability of diamond film by the braze, a sample of the braze alloy was melted on an unpolished surface of a diamond film specimen and the contact angle between the braze and the diamond film identified. The braze exhibited an exceptionally low contact angle of only 7-8°.

#### COMPARATIVE EXAMPLE A

For comparison purposes, the procedure of Example 1 was repeated except that the vanadium containing braze was replaced by a titanium braze containing similar amount of gold and nickel as the vanadium braze of Example 1. Specifically the braze contained 96.4 parts gold, 3 parts nickel, and 0.6 parts titanium.



The average shear strength of the brazed sample was 1,684 pounds for a joint having an area of about 0.0625 square inches, (26,944 psi or 186 MPa) 62% of the strength of the vanadium braze of Example 1.

5 The contact angle of the braze on a diamond film surface was about 25°, more than 3 times that of the vanadium braze of Example 1.

#### COMPARATIVE EXAMPLE C

10 For comparison purposes, the procedure of Example 1 was repeated with a copper-silicon-titanium-aluminum braze in lieu of the vanadium containing braze of Example 1. Specifically the braze contained 92.75 parts copper, 3 parts silicon, 2.25 parts titanium, and 2 parts aluminum. The liquidus of this alloy is 1024°C and the maximum brazing temperature was 1050°C. Prior to use, the foil braze was dipped in 5 vol % nitric acid and distilled water solution to remove surface oxides that has formed on the alloy during storage.

20 The average shear strength of the copper-titanium braze sample was 2,772.8 pounds for a joint having an area of about 0.0625 square inches, (44,365 psi or 306 MPa), 2% higher than the vanadium alloy of Example 1.

25 The contact angle between the braze and a diamond film was determined to be 61°, vastly inferior to that observed with the vanadium braze of Example 1. Despite the excellent shear strength result, the extremely high

contact angle indicates that the likelihood of failure due to the braze forming voids with a diamond film is unacceptably high from a reliability standpoint. Thus the braze is unacceptable for commercial use.

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COMPARATIVE EXAMPLE D

The procedure of Example 1 was repeated with a further brazing alloy composition which contains an active metal and also has a high melting point.

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Nicrobraz 210 from Wall Colmoney Inc., which contains 51.52 parts cobalt, 19 parts chromium, 17 parts nickel, 8 parts silicon, 4 parts tungsten, 0.4 parts carbon, and 0.08 parts boron, has a liquidus of 1150°C. The brazing temperature was a maximum of 1230°C.

15

While the contact angle of the braze on a diamond film surface was excellent, about 12°, the average shear strength of the brazed sample was only 20 pounds for a joint having an area of about 0.0625 square inches. This is equivalent to merely 320 psi or 2 MPa. Despite the excellent contact angle result, the extremely low shear strength makes the braze unacceptable for commercial use.

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What is claimed is:

1. A brazed joint comprising a diamond film brazed to tungsten carbide by means of a braze which comprises a major component and a minor component wherein the major component comprises gold and the  
5 minor component comprises from 0.75 to 5 wt.% vanadium.
2. The brazed joint of claim 1, wherein the braze further contains nickel.
3. The brazed joint of Claim 2, wherein the  
10 braze comprises at least about 1 wt. % vanadium, at least about 95 wt. % gold, and the balance being nickel.
4. The brazed joint of Claim 1, wherein the braze, comprises about 1.25-2.25 wt. % vanadium, about  
15 96.5-98.5 wt. % gold, and about 0.25-1.25 wt. % nickel.
5. The brazed joint of Claim 1, wherein the diamond film has a Young's modulus greater than about 1000 GPa and a thermal stability of greater than about 700°C.
- 20 6. The brazed joint of claim 1, wherein the joint has an average shear strength of at least about 40,000 psi (276 Mpa) and the braze has a contact angle with the diamond film of less than about 15 degrees.
- 25 7. A cutting tool comprising a diamond film cutting element attached to a tungsten carbide

substrate by means of a braze therebetween, the braze comprising a major component and a minor component wherein the major component comprises gold and the minor component comprises from 0.75 to 5 wt.% vanadium.

5           8. The cutting tool of Claim 7, wherein the diamond film has a Young's modulus greater than about 1000 GPa and a thermal stability of greater than about 700°C.

9. A method for joining a diamond film to a tungsten carbide substrate comprising the steps of:

10           (a) placing a braze composition between a diamond film and a tungsten carbide substrate, the braze composition comprising a major component and a minor component wherein the major component comprises gold and the minor component comprises from 0.75 to 5 wt.% vanadium; and

15           (b) heating the braze to a temperature sufficiently high to melt the braze and form a brazed joint between the tungsten carbide substrate and the diamond film, wherein the joint has an average shear strength of at least 40,000 psi (276 Mpa) and the braze has a contact angle with the diamond  
20 film of less than 15 degrees.

10. A method for joining a diamond film to a tungsten carbide cutting element comprising the sequential steps of:

25           (a) distributing a first braze comprising vanadium on a diamond film surface, wherein the vanadium braze has a melting temperature greater than about 1100°C;

          (b) heating the first braze sufficiently high to

melt the braze and form an adhesive bond to the diamond film,  
and cooling the diamond film;

(c) distributing a second braze substantially on the  
first braze, wherein the second braze melts at a lower  
5 temperature than the first braze;

(d) placing a tungsten carbide cutting element on  
the second braze;

(e) heating the second braze sufficiently high to  
melt the second braze and form a brazed joint between the  
10 diamond film and the tungsten carbide cutting element;

(f) cooling the cutting element.

11. The method of Claim 10, wherein vanadium is present  
in the first braze in an amount of about 0.5 to 10 wt. % of  
the braze.

15 12. The method of Claim 11, wherein the first braze  
further comprises at least about 1 wt. % vanadium, at least  
about 95 wt. % gold, and the balance being nickel.

20 13. The method of Claim 10, wherein the diamond film is  
adhered to the first braze by vacuum brazing at a vacuum of  
greater than about  $1 \times 10^{-5}$  Torr.

14. The method of Claim 10, wherein the braze comprises  
a metal selected from the group consisting of titanium,  
tantalum, chromium, and nickel.

25 15. The method of Claim 10, wherein the second braze  
comprises a metal selected from nickel, copper, and silver.

16. The method of Claim 10, wherein the tungsten carbide

cutting element is spaced away from the second braze by a distance of less than about 100 $\mu$ m.

5 17. A diamond film substantially covered with a layer of braze comprising a major component and a minor component wherein the major component comprises gold and the minor component comprises from 0.75 to 5 wt.% vanadium.

18. The diamond film of Claim 17, wherein the braze comprising vanadium is covered with a braze having a lower melting temperature than the braze comprising vanadium.