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NITRIDED HAFNIUM-TANTALUM ALLOYS AND METHOD OF MAKING THE SAME

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U.S. Cl. 148—20.3 11 Claims

ABSTRACT OF THE DISCLOSURE

Improved alloys of hafnium-tantalum suitable for use as a cutting tool and the method of making the same. The alloys include a nitrided case layer formed by nitriding at temperatures between 2500° F. and 4000° F. until the nitrided layer is at least 2 mils thick.

This invention relates generally to hafnium-tantalum alloys, and more particularly it relates to nitrided hafnium-tantalum alloys of improved strength and high surface hardness.

Recent developments in the field of metallurgy have produced a wide range of high strength aloys. Because of the increased strength and hardness of such alloys, it is difficult to shape or machine the alloys to a desired configuration. In this connection, conventional cutting tools such as ferrous tool steels and high speed steels do not have a sufficient hardness to be able to be used as cutting tool for machining high strength alloys, for example AISI 4340, a high strength low alloy steel. Advances in high strength cutting tools has led to development of various ceramic, oxide and carbide cutting tools which have desired high strength. However, these materials are themselves quite difficult to form into desired tool shapes since most of such high strength tool materials are formed from powder compacts by sintering.

A principal object of the invention is to provide a material capable of use as a cutting tool for the shaping of high strength alloys. Another object is to provide a material suitable for use as a cutting tool which can be readily manufactured by conventional processing techniques.

These and other objects of the invention may be readily understood from the following detailed description.

Generally, the invention is directed to a nitrided hafnium-tantalum alloy which includes between about 20 and about 60 percent by weight tantalum, between 0 and about 10 percent by weight molybdenum, between 0 and about 10 percent by weight tungsten, and between 0 and about 1.5 percent by weight boron, the balance of the alloy being hafnium, the tantalum content of the alloy being at least about 30 percent by weight in the absence of at least one of molybdenum, tungsten and boron.

Hafnium is a ductile metal which has a melting point above 4000° F. The ductility of hafnium is such that it does not possess good structural strength, particularly at elevated temperatures. However, the addition of tantalum to hafnium provides a hafnium-tantalum alloy which has an increased strength, particularly at elevated temperatures. Furthermore, hafnium-tantalum alloys are also readily fabricated by hot working at 1800° F. to 2500° F., and when the alloys contain relatively large amounts of treatment and/or the addition of minor amounts of molybdenum. Hafnium-tantalum alloys have a desirable strength for use as cutting tools or bearing surfaces, but lack the surface hardness necessary for cutting high strength materials.

The hafnium and tantalum which form the major constituents of the described alloy are of high purity, that is, the purity normally available in commerce, and when the terms hafnium and tantalum are used it is understood that commercially pure hafnium and tantalum, along with impurities normally associated therewith, is intended.

The hafnium-tantalum alloy contains between about 20 and about 60 percent tantalum in order to provide a nitrided material having a desired surface hardness and metallurgical structure. If the nitrided alloy is composed essentially of hafnium and tantalum, that is, no additional molybdenum, tungsten or boron alloying agents are present, the tantalum content of the alloy is preferably above 30 weight percent tantalum, most preferably between about 30 about 50 weight percent tantalum. If the tantalum content is much below about 30 weight percent in the absence of the additional alloying agents, the nitrided hafnium-tantalum has a larger and coarser grain structure than is generally desired which may lead to reduced cutting tool life. Above about 70 percent tantalum the tantalum content of the alloy is sufficiently high that the nitrogen which is diffused in the alloy during nitriding tends to form a solid solution with the tantalum rather than forming a hard surfaced nitride case layer. Tantalum also forms stable nitrides, but hafnium tends to be preferentially nitrided during the nitridation treatment. As a result, the nitrides initially formed tend to be hafnium-rich, but all nitride phases are complex nitrides of all of the alloying elements in the alloy, except for tungsten and molybdenum which do not form nitrides. Above about 70 percent tantalum, the nitrided structure does not survive the stresses and thermal shock accompanying high speed cutting operations.

Hafnium-tantalum alloys containing between about 30 and about 60 percent by weight tantalum may be nitrided to form hard surfaced materials suitable for use as cutting tools, and which have extended life and low wear in machining many types of materials. For example, cutting tools formed from hafnium-tantalum alloys as described herein show very little wear in the removal of 4.5 cubic inches of AISI 4340 steel having a Rockwell hardness of 43, measured on the C scale, at 0.010 inch per revolution feed and a surface speed of 765 feet per minute (f.p.m.). Similar results have been obtained on slightly harder AISI 4340 stock having a R_c hardness of 44.5 at 0.05 inch depth of cut and a feed of 0.005 inch per revolution. The low wear rate results in a smooth finish of the surface machined under these conditions. Futhermore, the low friction coefficient of nitrided hafnium-tantalum alloys is evidenced by no significant heating of the tool during machining at these cutting rates. These results are equivalent or better than those obtained using commercial ceramic and cemented carbide cutting tools. However, the described alloys have the significant advantage of being able to be formed to the shape of the desired cutting tool by conventional machining, followed by nitriding. Commercial ceramic and cemented carbide tools on the other hand must be formed from powder.

It has been found that improved results can be obtained in the preparation of nitrided hafnium-tantalum alloys as cutting materials if the hafnium-tantalum alloy which is nitrided includes at least one additional alloying agent selected from molybdenum, tungsten and boron. Tools formed from nitrided hafnium-tantalum alloys containing such alloying agents show improved tool life and the ability to perform satisfactorily at high surface speeds. The primary reason for additions of the additional alloying elements is to modify the morphology of the nitrides formed during nitridation. The morphology of the nitrided case has considerable influence on performance as a cutting tool.

The molybdenum alloying agent may be present in an amount between 0 and about 10 percent by weight, preferably between about 2 and about 5 percent by weight of the alloy prior to nitriding. If the alloy contains amounts of molybdenum much in excess of about 5 percent by weight, ability of the hafnium-tantalum alloy to be hot worked prior to nitriding may be reduced. As indicated, one of the advantages of the described nitrided alloys as cutting tools is the ability to hot work the hafnium-tantalum alloy to a desired shape prior to nitriding. In such instances it is desirable to maintain the molybdenum content of the hafnium-tantalium alloy below about 5 percent by weight. If it is not necessary that the alloy be hot worked, the molybdenum content may be increased. Increasing of the molybdenum content much above about 10 percent by weight does not provide particular advantage, and is generally unnecessary.

The tungsten alloying agent may be added to the hafnium-tantalum alloy in an amount between 0 and about 10 percent by weight, preferably between about 2 and about 7.5 percent by weight of the alloy prior to nitriding. Similar to the addition of molybdenum as an alloying agent, if the tungsten content of the hafnium-tantalum alloy exceeds about 7.5 percent, the hot workability of the alloy may be affected.

Boron may be included as an alloying agent in the hafnium-tantalum alloy in amounts between 0 and about 1.5 percent by weight, preferably between about 0.1 and about 0.7 percent. The presence of boron in the hafnium-tantalum also influences the hot workability of the hafnium-tantalum alloy, and where hot working of the hafnium-tantalum alloy prior to nitriding is desired, the boron content is desirably maintained below about 1.0 percent by weight of the alloy prior to nitriding.

The addition of molybdenum, tungsten and boron alloying agents improves the ability of the nitrided alloy to withstand severe conditions when used as a cutting tool material. When at least one of such alloying agents is present, the tantalum content may be reduced to as low as about 20 percent by weight without sacrifice of properties, although alloys containing 20 weight percent tantalum, in the absence of one or more of the additional alloying agents, do not have sufficient hardness to be useful as cutting tools for machining high strength materials, e.g., AISI 4340 steel.

The hafnium-tantalum alloy may be fabricated to any desired shape, for example a single edge cutting tool, and the finished shape is then nitrided at an elevated temperature in order to provide a nitride case layer having a depth of at least about 2 mils, preferably between about 3 and about 15 mils. The depth of the nitrided case may be varied widely in accordance with known practices to provide specific surface properties for specialized machining operations. The reaction between nitrogen and hafnium at elevated temperatures is sufficient to drive the nitriding reaction, and the hafnium-rich nitride that is formed is stable.

The nitriding of the hafnium-tantalum alloy may be effected by heating the alloy to a temperature of between about 2500° F. and about 4000° F., preferably between about 3000° F. and about 3500° F. for a sufficient period of time to provide a desired nitride case layer. At temperatures within the range of 3000° F. and 3500° F. the nitriding may be carried out in between about 0.5 and about 4 hours. The isothermal nitriding rate is a parabolic function of nitriding time and is strongly dependent on the nitriding temperature. Generally, the preferred nitriding time and temperature are inversely related so that the longer nitriding times are generally carried out at lower nitriding temperatures. The nitriding rate has an effect upon the grain structure of the nitride case layer, and at lower temperatures the grain structure is generally smaller. Further, the amount of nitrogen in the nitriding atmosphere has an effect upon the grain structure, with lower nitrogen partial pressures, tending to result in smaller grain structures.

Because of the elevated temperatures utilized in the nitriding of the hafnium-tantalum alloys, the nitriding atmosphere may be diatomic nitrogen, or any other source of nascent nitrogen, rather than ammonia which is utilized in most conventional nitriding processes. At the temperatures and pressure utilized the diatomic nitrogen is disassociated into monoatomic nitrogen and readily reacts with the hafnium present in the hafnium-tantalum alloy to form stable hafnium nitride. Hafnium-tantalum alloys are strong getters for interstitial elements and therefore are capable of removing nitrogen from atmosphere with very low nitrogen concentrations. Generally, it is desirable to utilize a gaseous nitriding medium containing nitrogen gas at a partial pressure between about 0.01 atmosphere and about 1 atmosphere. Argon or helium may feed with the nitrogen to provide the nitriding medium. Any atmosphere in which monoatomic nitrogen can be generated, including diatomic nitrogen, at high temperatures, can be employed provided that the atmosphere does not introduce any major quantity of contaminants for example, any appreciable oxygen concentration should be avoided in the nitriding atmosphere. The oxygen concentrations in commercial nitrogen are not detrimental to the nitrided case layer that is formed during nitridation.

The nitriding process is also somewhat dependent upon the tantalum content of the hafnium-tantalum alloys and at high tantalum content, for example above about 30 percent tantalum, it is possible to lower the nitriding temperature slightly because of the ability of the nitrogen to diffuse through tantalum to a great degree and therefore enter the alloy surface.

The nitridation may be carried out in any suitable apparatus, for example a cold wall furnace, and the selection of a particular apparatus is considered to be within the skill of the art.

The hafnium-tantalum alloys may be prepared by conventional arc melting, or other manufacturing technique, and may be hot rolled to approximately one-eighth inch thick in order to prepare cutting tools. Tool inserts measuring one-half inch square may be cut from the rolled stock, machined to a desired shape, and surface hardened by elevated temperature exposure to nitrogen to form a nitride case layer. The tools may be formed in any of the conventional shapes, for example tools having positive and/or negative rake, as may be desired. It is also contemplated that after initial nitriding and use as a cutting tool, the tool inserts may be renitrided in order to provide further hardening of the tool surface.

There is set forth below in Table I compositions of several hafnium-tantalum alloy compositions:

TABLE I

		Nitriding condition	
	Alloy composition, weight percent	° F.	Hours
Example:			
1	Hf–29.7, Ta–0.66B	3,100	2
2	Hf–40, Ta–10 Mo	3,100	2
3	Hf–30, Ta–5W–0.15 B	3,300	2
4	Hf–25, Ta–3 Mo	3,300	2

Each of the above alloys was arc melted and hot rolled to about one-eighth inch in thickness. Various tool inserts were cut from the sheet, ground to a desired shape, and nitrided by exposure to a pure nitrogen atmosphere for two hours. The hafnium-tantalum alloys listed in Table I were utilized as a tool insert in cutting AISI 4340 alloy steel having a R_c hardness of 52. The cutting conditions were 0.050 inch depth of cut, and 0.005 inch per revolution of feed with no coolant being utilized. At a surface speed of 600 f.p.m. all of the alloys in Table I had a tool life in excess of about five minutes, the tool life end point being measured at 0.015 inch uniform flank wear or 0.030 inch localized flank wear. The alloy composition of Example 3 had a wear of 0.012 inch at 600 feet per minute after a test span of 51 minutes. The same alloy had a tool life of 22 minutes at 700 feet per minute cutting speed and a life of 11 minutes at a cutting speed of 800 feet per minute. This tool life exceeds that of commercial carbide and ceramic tool materials. For a 30 minute tool life, the hafnium-tantalum alloy of Example 3 has a permissible cutting speed 1.8 times that of a commercial oxide cutting tool.

There is set forth in Table II the results of cutting tests performed on AISI 4340 alloy steel having a R_c hardness of 40 which demonstrate the effect of edge honing on tool life when using a positive rake tool insert. The tool geometry was 0° back rake, 5° side rake, 6° relief and $\frac{1}{32}$ inch nose radius. The cutting speed was 750 feet per minute.

TABLE II

Tool treatment	SCEA, degrees	Feed, in./rev.	Tool life, minutes
No edge radius	15	0.005	0.2
0.001 inch edge radius	15	0.005	2.5
No edge radius	60	0.010	10.1
0.001 inch edge radius	60	0.010	10.1

It will be seen that the 2.5 minute life at 750 feet per minute indicates that the nitrided alloy had adequate edge strength to support positive rake geometry. No chipping was observed, the primary wearland being developed as a groove at the depth of cut line.

The effect of edge honing is also demonstrated by lathe turning AISI 4340, R_c hardness 40 barstock at 750 feet per minute and 0.010 inch per revolution feed. In order to achieve a flank wear of 0.012 inch for the alloy of Example 3 of Table I the as nitrided tool insert removed 18 cubic inches of barstock, while a similar tool which had been honed removed 36 cubic inches.

The force required to produce chipping of the edges of the described nitrided hafnium-tantalum alloys was measured by utilizing a three-eighth inch diameter carbide rod to apply a load to the cutting edge of a one-eighth by one-half inch tool insert. The carbide rod was inclined at an angle of 6° to the top surface of the tool, and loads were applied at a strain rate of 0.005 inch per minute using an Instron testing machine. The results indicate that the described hafnium-tantalum nitrided alloys are stronger than commercial ceramic tools. Further, the edge strength of the nitrided alloys of Table I was substantially improved after radiusing the cutting edge.

It can be seen that nitrided hafnium-tantalum alloys provide good results when utilized as cutting tools for alloy steels. The hafnium-tantalum alloys do not exhibit as good a tool life when cutting some nonferrous materials, for example titanium or nickel-base superalloys, it being believed that the abrasion and chipping in machining of nonferrous alloys is the prime factor for short tool life. However, in machining of ferrous alloys, the described hafnium-tantalum alloys are generally superior to conventional cutting tools and provide increased cutting speeds. The described hafnium-tantalum alloys have the further advantage of being capable of being hot worked to provide a desired tool shape prior to nitriding, thereby permitting ease of fabrication to intricate shapes which cannot be obtained with conventional oxide and carbide materials.

Although the invention has been described herein in connection with hafnium-tantalum alloys and modifications thereof, similar nitrided structures and properties are obtained for other combinations of Groups IV–B and V–B elements. For example, Ti and Zr may be substituted for Hf and V and Cb for tantalum in whole, or part. Furthermore, the additives which are effective in controlling the structure of hafnium-tantalum alloys are equally effective for other combinations of Groups IV–B and V–B alloys. Thus, the demonstrated cutting performance for hafnium-tantalum alloys can apply in general to combinations of Groups IV–B and V–B elements in the same atomic proportions as in the hafnium-tantalum alloys described herein.

The described hafnium-tantalum alloys, in addition to their use as tool materials, are also useful in other applications where wear is a factor, for example bearings, wear surfaces, gun barrel liners, and the like. The high structural strength of the hafnium-tantalum alloy, coupled with the hardness of the nitride case layer provides a particularly desirable material for such applications.

Various of the features of the invention are set forth in the following claims.

What is claimed is:

1. A nitrided hafnium-tantalum alloy of high surface hardness comprising a nitride case layer of at least about 2 mils thickness, the alloy having a composition prior to nitriding of betwen about 20 and about 60 percent by weight tantalum, between 0 and about 10 percent by weight molybdenum, between 0 and about 10 percent by weight tungsten, and between 0 and about 1.5 percent by weight boron, the balance being hafnium, and the tantalum content of the alloy being at least about 30 percent by weight in the absence of at least one of molybdenum, tungsten and boron.

2. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the hafnium-tantalum alloy prior to nitriding comprises between about 30 and about 50 percent by weight tantalum.

3. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the hafnium-tantalum alloy prior to nitriding comprises between about 2 and about 5 percent by weight molybdenum.

4. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the hafnium-tantalum alloy prior to nitriding comprises between about 2 and about 7.5 percent by weight tungsten.

5. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the hafnium-tantalum alloy prior to nitriding comprises between about 0.1 and about 0.7 percent by weight boron.

6. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the hafnium-tantalum alloy prior to nitriding comprises not more than about 5 percent by weight molybdenum, not more than about 7.5 percent by weight tungsten and not more than about 1.0 percent by weight boron.

7. A nitrided hafnium-tantalum alloy in accordance with claim **1** wherein the nitride case layer has a thickness of between about 2 and about 15 mils.

8. A method of forming a hard surfaced hafnium-tantalum article comprising providing a hafnium-tantalum alloy comprising between about 20 and about 60 percent by weight tantalum, between 0 and about 10 percent by weight molybdenum, between 0 and about 10 percent by weight tungsten, and between 0 and about 1.5 percent boron, the balance being hafnium, and the tantalum content being at least about 30 percent by weight in the absence of at least one of molybdenum, tungsten and boron, forming the hafnium-tantalum alloy into a deisred shape, and nitriding the formed halfnium-tantalum alloy at a temperature between about 2500° F. and about 4000° F. for a period of time sufficient to form a nitride case layer having a thickness of at least about 2 mils.

9. A method in accordance with claim **8** wherein the nitridation is carried out at a temperature of between about 3000° F. and about 3500° F. for between about 0.5 and about 4 hours.

10. A method in accordance with claim **8** wherein the hafnium-tantalum is formed in to the shape of a cutting tool.

11. A nitrided hafnium-tantalum alloy of high surface hardness comprising an outer nitrided case layer of at least about 2 mils thickness, an intermediate zone containing a limited amount of nitrogen in solid solution and an inner tough substrate of substantially less hardness, said alloy having a composition prior to nitriding of between about 20 and about 60 percent by weight tantalum, between 0 and about 10 percent by weight molybdenum, between 0 and about 10 percent by weight tungsten, and between 0 and about 1.5 percent by weight boron, the balance being hafnium, and the tantalum content of the alloy being at least about 30 percent by weight in the absence of at least one of molybdenum, tungsten and boron.

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CHARLES N. LOVELL, Primary Examiner

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75—134, 174; 148—31.5, 32

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,679,494 Dated April 30, 1969

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

Column 1, line 25, "aloys" should read --alloys--;

Column 1, line 31, "tool" should read --tools--;

Column 1, line 64, "large" should read --larger--;

Column 1, line 65, before "treatment" insert --tantalum, the alloy may be made cold workable by heat--.

Signed and sealed this 20th day of March 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents