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3,674,571

NITRIDED ZIRCONIUM ALLOYS

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No Drawing. Filed Mar. 4, 1970, Ser. No. 16,593

The portion of the term of the patent subsequent to

Dec. 22, 1987, has been disclaimed

Int. Cl. C22c 27/00; C23c 11/14

U.S. Cl. 148—31.5

7 Claims

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art the composition and properties of the materials disclosed in said referenced patents and patent applications are substantially different from those which are disclosed and claimed herein.

Accordingly, a principal object of our invention is to provide novel nitrided zirconium alloys characterized by excellent wear and abrasion resistance.

This and other objects, features and advantages of our invention will become evident from the following detailed disclosure thereof.

ABSTRACT OF THE DISCLOSURE

A novel group of nitrided alloys having excellent wear and abrasion resistance containing (a) zirconium, (b) one or more metals of the group vanadium, columbium, or tantalum, and (c) molybdenum or tungsten. The alloys can be readily fabricated to shape and then hardened by nitriding to produce high surface hardness.

BACKGROUND OF THE INVENTION

This invention relates to a novel group of ternary or higher alloyed metals which consist essentially of:

- (a) zirconium;
- (b) at least one metal selected from the group consisting of vanadium, columbium and tantalum; and
- (c) at least one metal selected from the group consisting of molybdenum or tungsten.

These alloys can be nitrided to produce a graded nitrided material having a high surface hardness and may be used in applications requiring wear and abrasion resistance.

It is well known that titanium can be nitrided to form a hard surface layer thereon, but such material shows a chipping propensity. The nitriding of titanium-rich alloys, i.e., containing about 90% titanium has been studied previously (for example, see E. Mitchell and P. J. Brotherton, J. Institute of Metals, vol. 93 (1964) p. 381). Others have investigated the nitriding of hafnium-base alloys (F. Holtz, et al., U.S. Air Force Report IR-718-7 (II) 1967); molybdenum alloys (U.S. Pat. No. 3,161,949); and tungsten alloys (D. J. Iden and L. Himmel, Acta Met, vol. 17 (1969) p. 1483). The treatment of tantalum or columbium and certain unspecified tantalum base alloys with air or nitrogen or oxygen is disclosed in U.S. Pat. 2,170,844 and the nitriding of columbium is discussed in the paper by R. P. Elliott and S. Komjathy, AIME Metallurgical Society Conference, vol. 10, 1961, p. 367.

In addition in IR-718-7 (III) there is disclosed nitrided alloys of the compositions Zr-46Ta-3Mo and Zr-30.5Cb-2Mo. As is shown herein we use substantially higher Mo addition, i.e., from 10 to 40% to achieve the desired results of our invention.

In our copending patent applications "Wear Resistant Materials" Ser. No. 755,658 now U.S. Pat. 3,549,427 and "Wear and Abrasion Resistant Materials" Ser. No. 755,662, we have disclosed and claimed certain nitrided three through seven metal alloy systems which are characterized by excellent cutting performance. Counterparts to said U.S. applications have now been issued as Belgium Pats. 720,398 and 720,399. Such applications and Belgium patents are directed to nitrided alloys containing

- (a) one or more metals of the group columbium, tantalum and vanadium;
- (b) one or both of the metals molybdenum and tungsten; and
- (c) titanium and/or zirconium,

in certain percentages by weight as is therein set forth.

As will be apparent to those skilled in this particular

SUMMARY OF THE INVENTION

We have discovered that by the specific alloying as taught herein, prior to nitriding, materials having a high surface hardness and graded, nitrided materials can be provided. The scope of applicability of the present alloys is different from that disclosed in the above identified pending U.S. patent applications and Belgium patents. The present alloys have a utility for wear and abrasion resistance and less severe cutting applications.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In our experimental work a series of alloys were melted under an inert atmosphere in a non-consumable electrode arc furnace using a water-cooled, copper hearth. High purity materials (greater than 99.5%) were used for the alloy charges and generally weighed about 50 grams. These procedures are of course quite well known to those skilled in the art.

The alloys were cut into specimens approximately 1/8 inch thick and reacted in nitrogen at atmospheric pressure. The resulting thickness and microhardnesses of the various reaction zone or layers were determined using standard metallographic techniques. Several tests were used to evaluate the strength and toughness of these materials for potential use in abrasive wear or metal cutting applications.

The metal cutting tests were performed using the nitrided materials as tool inserts 3/8 x 3/8 x 1/8 inch having a 0.030 inch nose radius which was used as a section of the cutting surface. Such radii were ground on the specimens prior to nitriding.

The alloy samples thus prepared were subsequently nitrided. For nitriding we used a cold wall furnace employing a molybdenum heating element and radiation shields with the furnace being evacuated to five microns pressure and flushed with nitrogen prior to heating. Temperatures were measured with an optical pyrometer, namely a Leeds and Northrop Optical Pyrometer, catalog number 862, sighting on an unnitrided molybdenum heating element which completely surrounded the specimens. The temperatures given herein are corrected from this source. We used a correction factor determined by using a tungsten-rhenium thermocouple in conjunction with the sightings of the aforesaid optical pyrometer.

Following nitrided sample preparation, lathe turning tests were run on AISI 4340 steel having a hardness of Rockwell C (Rc), 44. A feed rate of 0.005 inch per revolution and depth of cut of 0.050 inch were used. A standard negative rake tool holder was employed with a 5° back rake and a 15° side cutting edge angle.

Our principal criterion in determining whether the present nitrided materials are useful or not is whether they are a graded nitrided material having a high surface hardness and having little if any propensity towards chipping. We evaluated the toughness and chipping resistance by using a conical diamond hardness indentation (standard Rockwell A scale—60 kg. load) and evaluating whether chipping occurred around the hardness impressions using a 10X eyepiece magnifier.

We have discovered a novel group of alloys capable of being nitrided and which are then characterized by high surface hardness and useful wear resistance. These materials are formed when alloys within our prescribed compositional ranges as hereinafter taught are reacted with nitrogen or an environment which is nitriding to the alloys at elevated temperatures. The hardening reaction is typical of the internal oxidation or nitridation techniques well known in the art. The volume of hard constituents formed at the surface is high in our materials. Nitride formation decreases inwardly from the surface and this grading contributes to the thermal and mechanical shock resistance of the material. Our materials are characterized by being graded with the degree of nitride formation lessening as one moves inward from the surface.

Unalloyed zirconium, when nitrided, develops a discrete continuous nitride surface layer which is characterized by a tendency toward chipping under mechanical load. Serious chipping is observed around the conical indentation resulting from a standard Rockwell A hardness test (diamond indenter—60 kg. load). We nitrided several binary alloys, and for example, found chipping around the Ra impressions with the following:

Alloy:	Nitriding treatment
Zr-20Cb	2850° F.—2 hr.+3050° F.—2 hr.
Zr-20Ta	3250° F.—2 hr.
Zr-20V	2000° F.—2 hr.+2450° F.—2 hr.

This same tendency would be found in zirconium base ternary alloys containing only modest amounts of the alloying ingredients that we find necessary to develop the hard graded nitrided layers of our invention. In particular, in the ternary and higher order alloys of our invention, we find that a minimum of 10% of a metal selected from the group molybdenum and tungsten and a minimum of 15% of a metal selected from the group columbium, tantalum and vanadium is required, balance zirconium. Molybdenum and tungsten do not form stable nitrides at the temperatures required to produce the useful materials of our invention, and the presence of these elements is necessary to obtain the required toughness. In fact, we find that the preferred range of molybdenum and/or tungsten is above 15%.

In the Cb-Zr-(Mo,W) system we have found that useful materials can be produced when the columbium content is from 15% to 36%; the content of at least one metal selected from the group consisting of molybdenum and tungsten is from 10% to 40%; the content of zirconium is from 36% to 68%; with the ratio of columbium to zirconium being greater than $\frac{1}{3}$ but less than 0.7. Within the aforementioned range we have prepared two particularly useful nitrided alloys, 25Cb-50Zr-25Mo and 25Cb-50Zr-25W. These materials were nitrided at 2850° F. for four hours and then examined and tested. Both are a graded, nitrided material with a high surface hardness and were shown to pass a cutting test at 200 s.f.m.

Materials within Ta-Zr-(Mo,W) which are deemed desirable fall within the composition ranges given as follows: tantalum content is from 15% to 54%; the content of at least one metal selected from the group consisting of molybdenum and tungsten is from 10% to 40%; the content of zirconium is from 24% to 67%; with the ratio of tantalum to zirconium being greater than $\frac{1}{3}$ but less than 1.5. The materials within the above described ranges when nitrided meet the above described criteria. The materials 35Ta-35Zr-30W and 45Ta-35Zr-20Mo exhibit the desired properties of a graded nitrided layer and high surface hardness.

Turning now to V-Zr-(Mo,W) system, those materials which fall within the hereinafter presented ranges exhibit the desired high surface hardness and are graded. The vanadium content should be from 15% to 36%; the content of at least one metal selected from the group consisting of molybdenum and tungsten should be from 10% to 40%; the zirconium content should be from 36% to 68%

with the ratio of vanadium to zirconium being greater than $\frac{1}{3}$ and less than 0.7.

Our nitrided materials can contain from 3 to 6 components if at least one of the group vanadium, columbium, or tantalum, and at least one of the group molybdenum or tungsten is present in addition to zirconium. When 4 to 6 metallic components are present in the nitrided alloys the allowable compositional ranges are defined by the formulae set forth below; these formulae also define the limitations in a ternary system. Such formulae represent linear proportionate amounts based on weight percentages.

A modest mathematical statement is required. In the present disclosure and claims the following ratios shall have the following meanings:

$$A = \frac{V}{V + Cb + Ta}$$

(That is, the concentration in weight percent of vanadium to total vanadium, columbium and tantalum.) Similarly,

$$B = \frac{Cb}{V + Cb + Ta}$$

$$C = \frac{Ta}{V + Cb + Ta}$$

In making the various alloyed, nitrided systems of this invention—that is, alloys consisting essentially of zirconium; at least one metal selected from the group consisting of vanadium, columbium, and tantalum; and at least one metal selected from the group consisting of molybdenum and tungsten—the following composition requirements must be met for the nitrided materials:

- (1) The minimum combined molybdenum and tungsten content is 10% and the maximum is 40%.
- (2) The maximum zirconium content is given by the ratio:

$$\frac{Zr}{V + Cb + Ta} < 3$$

- (3) The minimum zirconium content is given by:

$$\frac{V + Cb + Ta}{Zr} < 0.7A + 0.7B + 1.5C$$

A variety of nitrogen containing environments can be used to produce similar hardened materials. However, upon reacting in a much lower nitrogen potential environment, the effect of lowered nitrogen availability may be observed and a somewhat modified reaction product obtained. Since our surface hardened materials are in a thermodynamically metastable condition, a variety of heat treatments, including multiple and sequential treatments, may be used to modify the reaction product and resulting properties whether performed as part of the over-all nitriding reaction or as separate treatments. The materials may also be nitrided at higher temperatures (and times) that normally would produce some embrittlement and then subsequently annealed in inert gas as a tempering or drawing operation to improve toughness. This duplex treatment results in a deeper reaction product with the hardness-toughness relationship controlled by the tempering temperature and time. The annealing treatment aforesaid may also be carried out in partial pressures of nitrogen.

The nitrided material may be modified by combining nitriding with oxidizing or boronizing. However, the amount of reaction with the other hardening agents must be limited, a majority of the weight pick-up is due to nitriding, and these are essentially nitrided materials. Up to 25% of the nitrogen pick-up can be replaced by oxygen and/or boron.

The present useful alloys could be produced by powder processing techniques. Also such alloys could be employed on another metal or alloy as a surface coating or cladding and with the proper selection, a highly ductile or essentially unreacted substrate can be obtained. The nitrided mate-

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rial can be used as a mechanically locked insert or it can be bonded or joined by brazing, for example, to a substrate.

Spraying and/or fusing the desired alloy onto the surface are among the various methods for depositing the ternary or more complex (Cb,Ta,V)-Zr-(Mo,W) alloys. Small other additions may be made to our alloys to enhance the coatability. A variety of direct deposition methods may be employed or alternate layers could be deposited followed by a diffusion annealing treatment. Another surface alloying procedure involves zirconizing—for example, a process whereby zirconium is diffused into a Ta-W alloy substrate.

The high surface hardness of the nitrided alloys has been confirmed by 50 and 200 gram diamond pyramid microhardness traverses on metallographically-polished cross-sections. For the 1/8 inch thick materials falling within our invention the hardness measured at about 0.5 mil from the surface is greater than 800 DPN and the hardness grades inwardly in a mostly continuous fashion.

The nitrogen pick-up is in excess of 1 mg. per sq. cm. for use in metal cutting. However, the amount of nitrogen required for an equivalent surface hardness is substantially reduced when the material is used as a thin blade edge or sheet or as a thin coating or cladding. Also, such materials may be used for a wide variety of applications requiring wear and abrasion resistance where the requirement for surface hardness may be less than that required for metal cutting. Thus, for certain applications, the nitrogen pick-up might be 0.1 to 1 mg./sq. cm. of surface area.

We have also observed the excellent corrosion resistance of both the alloys and the nitrided alloys in strong acids, and these materials could effectively be employed for applications requiring both corrosion and abrasion resistance. Both the alloys and the nitrided alloys possess good structural strength. Thus, the materials can be employed for applications involving wear resistance and structural properties (hardness, strength, stiffness, toughness) at room and elevated temperatures. Other useful properties of the nitrided materials include good electrical and thermal conductivity, high melting temperature, and thermal shock resistance.

Although the alloys receptive to nitriding can be produced by coating or surface alloying techniques, many uses involve the forming and machining of a homogeneous alloy. One of the advantages in utility of these materials is our ability to form some of the metallic alloys by cold or hot working and/or machining (or hone) to shape in the relatively soft condition prior to final nitriding. Only minimal distortion occurs during nitriding and replication of the starting shape and surface finish is excellent. The final surface is reproducible and is controlled by original surface condition, alloy composition, and nitriding treatment. For some applications, the utility would be enhanced by lapping, polishing, or other finishing operations after nitriding. The nitrided surface is quite hard but only a small amount of material removal is required to produce a highly finished surface.

It will be understood that various modifications and variations may be affected without departing from the spirit or scope of the novel concepts of our invention.

We claim as our invention:

1. A graded, nitrided ternary or higher alloyed material consisting essentially of:

- (a) zirconium;
- (b) at least one metal selected from Group I which consists of columbium (Cb), vanadium (V) and tantalum (Ta);
- (c) at least one metal selected from Group II which consists of molybdenum (Mo) and tungsten (W); wherein
- (d) the nitrogen weight pick up is at least 0.1 milligram per square centimeter of surface area;

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(e)

$$A = \frac{V}{V + Cb + Ta}$$

$$B = \frac{Cb}{V + Cb + Ta}$$

$$C = \frac{Ta}{V + Cb + Ta}$$

(f) the minimum Group II content is 10% and the maximum Group II content is 40%;

(g) the minimum zirconium content is defined by the expression

$$\frac{\text{Group I}}{\text{Zr}} < 0.7A + 0.7B + 1.5C$$

and the maximum zirconium content is defined by the expression

$$\frac{\text{Zr}}{\text{Group I}} < 3$$

and

(h) wherein the nitriding extends to at least a depth of 0.0005 inch.

2. The material defined in claim 1 wherein the surface microhardness is at least 800 diamond pyramid numerals and the reaction depth to which such hardness is developed is at least .0005 inch.

3. The material defined in claim 1 wherein:

- (a) the vanadium content is 15% to 36%;
- (b) the Group II content is 10% to 40%;
- (c) the zirconium content is 36% to 68%; with
- (d) the ratio of vanadium to zirconium being greater than 1/3 and less than 0.7.

4. The material defined in claim 1 wherein:

- (a) the columbium content is 15% to 36%;
- (b) the Group II content is 10% to 40%;
- (c) the zirconium content is 36% to 68%; with
- (d) the ratio of columbium to zirconium is greater than 1/3 but less than 0.7.

5. The material defined in claim 1 wherein:

- (a) the tantalum content is 15% to 54%;
- (b) the Group II content is 10% to 40%;
- (c) the zirconium content is 24% to 67%; with
- (d) the ratio of tantalum to zirconium being greater than 1/3, but less than 1.5.

6. The material defined in claim 1 wherein up to 25% of the nitrogen weight pick-up is replaced by a material selected from the group consisting of oxygen and boron.

7. The material as defined in claim 1 wherein the nitrogen pick-up is at least 1 milligram per square centimeter.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

29—182.2, 182.5; 75—134, 174, 175.5, 177; 117—130; 148—20.3, 32, 34