SURFACE DEPLETED NITRIDED ARTICLES
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Int. Cl. C22c 29/60; C23c 11/14

U.S. Cl. 148 — 31.5

1 Claim

ABSTRACT OF THE DISCLOSURE

Graded nitrided articles, surface modified in alloy composition wherein the surface zone consists of nitrided alloys consisting essentially of (a) one or more metals of the group columbium, tantalum, and vanadium; (b) zirconium and zirconium-titanium mixtures; and (c) one or both metals of the group molybdenum and tungsten. A minor portion of the nitrogen may be replaced by oxygen or boron. Nitrided materials prepared from homogeneous alloys are also included. The materials are characterized by excellent wear and abrasion resistance.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of Ser. No. 16,594, filed Mar. 4, 1970, now U.S. Pat. 3,674,573 which is a division-in-part of our pending application, Ser. No. 755,662 entitled "Wear and Abrasion Resistant Materials" filed Aug. 27, 1968 now U.S. Pat. 3,549,429.

BACKGROUND OF THE INVENTION

In our parent application, Ser. No. 755,662 references above, we have disclosed and claimed certain nitrided alloys consisting essentially of (a) at least one metal of the group columbium, tantalum and vanadium; (b) zirconium and zirconium-titanium mixtures; and (c) at least one metal of the group molybdenum and tungsten in certain percentages by weight and compositional relations as are therein set forth. Such nitrided materials are characterized by among others, excellent wear and abrasion resistance and offer substantial utility as cutting tool materials.

In such parent application, we have noted that the desired alloys to be nitrided may be formed as free-standing thin sections or clad or by various means formed as a coating upon different substrates. Similarly, in such parent application, we have noted that a variety of nitriding treatments may be employed to effectuate the desired results.

In the present application, we wish to elaborate upon the teachings of said parent application. The compositions hereof which are nitrided or otherwise treated are the same as the alloy compositions which are disclosed in our parent application.

Accordingly, our parent application, Ser. No. 755,662 now U.S. Pat. 3,549,429, in its entirety, is incorporated herein by reference. We would note that a counterpart of such parent application has issued as Belgium Pat. 720,399. As will be evident, we herein provide additional features to said basic invention and certain improvements thereover.

In our parent application, the temperatures are presented uncorrected. In the present application, temperatures are corrected. We used a correction factor determined by using a tungsten-rhenium thermocouple in conjunction with the sightings of the optical pyrometer mentioned in the parent case.

Furthermore, we would note that zirconium or titanium can be nitrided to form a hard surface layer thereon but such material shows a chipping propensity due to brittleness. In the practice of our invention, such brittleness is avoided by specific alloying as taught herein prior to nitriding. Additionally, the alloying elements present in typical commercially available titanium alloys do not produce the same improvement and nitrided commercial titanium alloys show chipping similar to nitrided titanium.


In the present application, we wish to clearly point out the significance of alloying surface treatments or coatings or claddings with the present materials and surface treatments wherein nitriding is employed as the major constituent along with relatively minor amounts of oxygen and/or boron.

It should be noted that the alloys of the present invention may be employed in another manner, i.e., as a surface coating or cladding and with the proper substrate selection, a highly ductile and/or essentially unreacted substrate can be obtained. For example, columbium or tantalum are much less reactive to nitrogen when used in conjunction with the alloys hereof and tungsten and molybdenum do not form stable nitrides at the nitriding temperatures employed. Spraying and/or fusioning the desired alloy onto the surface are included in the various coating methods available. A variety of direct deposition methods may be employed or alternate layers could be deposited followed by a diffusion annealing treatment.

As set out in our parent application in determining whether or not a material falls within the scope thereof, certain test criteria were used as are set forth therein. More particularly, following nitrided sample preparation lathe turning tests were run thereon at surface speeds from 100 to 750 surface feet per minute (s.f.m.) on AISI 4340 steel having a hardness of around Rockwell C, (.R.), 43 to 45. A feed rate of .001 in./rev. and depth of cut of .050 in. were used. A standard negative rake tool holder was employed with a 5° back rake and a 15° side cutting edge angle. Tool wear was measured after removing a given amount of material.

The principal criterion in our parent application in determining whether the nitrided materials pass or fail and thus whether or not they are included or excluded from the scope thereof was the ability to cut 2 cubic inch metal removal of the 4340 steel at speeds of both 100 and 750 s.f.m.

At 750 s.f.m. our high performance, nitrided materials readily pass the initial test of 2 cu. in. metal removal in about 1 minute. (We would note that by "s.f.m." is meant the linear rate at which the material being cut pass the cutter.)

In some aspects of the present invention such test criteria of the parent application are inoperative. This is particularly true of the thin sections and surface zones considered herein. The nitrided alloys are the same but
in some instance in thin sections the test criteria of the parent case are not met herein. However, the materials still offer substantial wear and abrasion resistant properties.

In evaluating tools and tool materials, failure is often assumed to occur when the wearland reaches 0.030 inch. With the materials of this invention, we selected a rather severe test—we indicate those which are good (i.e., pass the test), when at 705 s.f.m. and 2 cu. in. removal, there is a uniform wearland of less than 0.025 in. Furthermore, we would note that although chipping is seen in some compositions upon testing at 750 s.f.m. the chipping propensity is aggravated at lower speeds and better assessed at 100 s.f.m. The latter is one of the reasons for selecting both speeds.

Accordingly, a principal object of our invention is to provide certain novel articles wherein the surface zone thereof is a nitrided alloy consisting essentially of: (a) at least one metal of the group carbonium, tantalum and vanadium; (b) zirconium; and (c) at least one metal of the group molybdenum and tungsten.

Another object of our invention is to provide said novel articles aforesaid wherein up to 97% of the zirconium content is replaced by titanium. A further object of our invention is to provide such nitrided articles wherein the nitrogen pick-up is at least 0.1 milligram per square centimeter of surface area.

Still a further object of our invention is to provide such nitrided articles wherein up to twenty-five percent of the nitrogen weight pick-up replaced by oxygen and/or boron.

These and other objects and advantages of our invention will become apparent to those skilled in this art from the following detailed disclosure thereof.

**DESCRIPTION OF THE INVENTION**

Coatings of the zirconium-containing ternary alloys were made on molybdenum by fusing a deposited alloy material in argon. V-25Zr-20Mo and Ta-20Zr-20Mo were heated to 2870°F and 3110°F and a 3 and 5 mil coating was produced, respectively. The coatings wet the molybdenum substrate well and did not flow excessively, but the Ta-20Zr-20Mo alloy reacted deeply into the molybdenum. Subsequent nitriding at 2250°F, for one-half hour resulted in a nitrogen pick-up in the range of 1 to 2 mg. per sq. cm. At a depth of 1/2 mil from the surface, the hardness was 2000 and 1500 DPN for the samples coated with V-25Zr-20Mo and Ta-20Zr-20Mo, respectively.

We have coated the alloy V-25Zr-20Mo on steel and find that the coating temperature is substantially reduced because of the low melting alloys formed by interaction between iron and the zirconium-containing alloys.

Much thinner coatings could readily be produced by similar or other procedures. As the reactive alloy coating becomes thinner, the amount of nitrogen pick-up for surface hardening is reduced since the nitriding is concentrated near the surface. Obviously, the depth of hardening is reduced. In relatively thin coatings, the weight pick-up of nitrogen may be 0.1 mg. per sq. cm. or less and in thicker coatings the pick-up will be over 1 mg. per sq. cm. of surface area. It should be noted that in relatively thick materials the nitrides are graded and lesser from the surface inwardly. With thinner materials such grading is sometimes not readily seen.

In our pending parent application, it has been shown that for non-coated homogeneous alloy stock, the amount of nitrogen required for equivalent surface hardening is dependent upon sample thickness. As the thickness of the samples decreased, the required nitriding temperature and weight pick-up are reduced. We have observed a pronounced effect of specimen thickness, particularly at knife edges where the required nitrogen pick-up is greatly reduced. Also, such coated or homogeneous materials may be used for a wide variety of applications involving wear and abrasion resistance where the requirement for surface hardening or depth of hardening may be less than that required for metal cutting. Accordingly, in this sections of homogeneous alloy material, similar to thin coatings of the alloys, the weight pick-up of nitrogen may be 0.1 to 1 mg. per sq. cm.

Another useful method for utilizing our nitrided materials involves controlled evaporation of titanium and/or zirconium from the surface of an alloy. By this procedure, an alloy, for example with a zirconium and titanium content greater than that determined by our compositional limitations, can be depleted to bring the surface alloy content within our prescribed ranges prior to nitriding by heating alloys containing the required metals of our invention in vacuo at temperatures below the melting point of the alloy. This can be accomplished without the occurrence of significant amounts of porosity or any substantial change in geometry. Since titanium has a higher vapor pressure than zirconium, it is more readily removed. It will, of course, be appreciated that such surface evaporation techniques can be applied to alloys that are already within our prescribed composition ranges to effect desirable structural and property changes in the nitrided materials.

It should be noted that annealing per se, that is, annealing under conditions where significant evaporation does not occur, has an effect on the microstructural morphology. Such morphology effects due to annealing, which result in greater regularity of structure may produce improvements for certain uses, but the compositional effect due to treatment in vacuo is of value by itself. In most of our materials the hardness (and nitride content) grades and lessens as one moves from the surface inwardly. However, we would note that in some cases such grading extends from a plate or from a peak hardness slightly below the surface and grades inwardly therefrom.

Such materials can be effective cutting tools or abrasion resistant articles.

Since our nitrided materials possess as a homogeneous material or as a coated article in a thermodynamically metastable condition, those skilled in the art will realize that a variety of heat treatments, including multiple and sequential treatments, can be used to modify the reaction structure and resulting properties whether performed as part the over-all nitriding reaction or as separate treatments. Improvement in cutting properties has been noted by nitriding at lower temperatures for longer times and by nitriding at lower temperatures followed by nitriding at higher temperatures. However, the required weight pick-up for cutting at 750 s.f.m. is similar to the amount of nitriding necessary with a simple 2 hour nitriding treatment. The treatments have been followed by aging at lower temperatures in argon or nitrogen. We have also nitrided at high temperatures (and longer 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 greater reaction depth with the hardness-roughness relationship controlled by the tempering temperature and time. The required annealing treatment is dependent upon the material usage, alloy composition and degree of prior nitriding.

The microhardness traverse for the Cb-10Zr-10Ti-20Mo alloy nitrided at 3550°F for 8 hours is shown in Table I. Such treatment results in a brittleness propensity. Upon annealing this material in argon for one hour at 3450° F, a considerable softening occurs in the outer 3 mils. This surface softening can be controlled by annealing in A-O,1% N2, while thickness traverse to be reduced as illustrated in Table I. Whereas A-1% N2 is an effective softening medium for this highly nitrided alloy, such an atmosphere will harden unnitrided or moderately nitrided alloys. A 0.4 gram specimen of Cb-30Zr-10Mo picks up 6 mg. of nitrogen when treated for 2 hours at 3550°F. For comparison, treatment in essentially static nitrogen for the same temperature and time results in a pick-up of 24 mg.
The above treatments were at essentially atmospheric pressure.

<table>
<thead>
<tr>
<th>Nitriding treatment Subsequent treatment Microhardness (DPN) at depth (mils)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,764,404</td>
<td>None</td>
<td>2,100</td>
<td>1,100</td>
<td>1,560</td>
<td>1,220</td>
</tr>
<tr>
<td>3,500-15</td>
<td>Ar</td>
<td>1,400</td>
<td>1,500</td>
<td>1,700</td>
<td>1,700</td>
</tr>
<tr>
<td>3,500-15</td>
<td>A-15% N</td>
<td>1,000</td>
<td>1,400</td>
<td>1,600</td>
<td>1,100</td>
</tr>
</tbody>
</table>

These various alternate nitriding treatments may be applied to the materials of our invention whether used as a homogeneous alloy or as a coated or surface modified material. In all of the nitriding treatments and particularly for those involving reduced nitrogen potential, the effect of the varying stabilities of the metal nitrides must be considered since this can also contribute to surface compositional effects.

Surface alloying techniques are useful for the preparation of the alloys to be nitrided to produce the materials of our invention. Cb-15Mo, Cb-10W, and Ta-10W were zirconized by holding in vacuo in a pack of fine zirconium sponge which results in a pullout of zirconium inward and subsequently nitrided with the following procedure: vacuum pack zirconized 290°F—6 hours; annealed in argon 290°F—2 hours plus 350°F—2 hours; nitrided 2850°F—2 hours. Such treatment resulted in a relatively thin zirconized zone on Ta-10W but the zirconium diffusion zone was about 6 mils deep for the Cb-15Mo and Cb-10W substrates. As shown in Table II, these materials exhibit a graded reaction zone similar to nitrided homogeneous Cb-Zr-Mo or Cb-Zr-W materials. This contrasts with the 4 mil continuous nitride layer formed on Cb-15Mo without the prior diffusion treatment which exhibits cracking of the continuous nitride layer.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Microhardness (DPN) at depth (mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Cb-15 Mo...</td>
<td>2,410</td>
</tr>
<tr>
<td>Cb-10 W...</td>
<td>2,410</td>
</tr>
</tbody>
</table>

A cutter specimen of Cb-10W was prepared using the same zirconizing and nitriding treatment. It passed our cutting tests at both 750 and 100 s.f.m. although some limited chipping was noted at 750 s.f.m. The materials of our invention can receive titanium and zirconizing treatments prior to nitriding. Molybdenum, tungsten and alloys thereof can be coated or alloyed by a variety of methods including those given as examples herein to produce useful surfaces which upon nitriding result in the useful properties of our invention.

Use of surface alloying or coating techniques can enhance the utility of powder processing of the alloys prior to nitriding in a number of ways. For example, a powder processed alloy of Cb-Mo could be formed and then zirconized or a porous molybdenum or tungsten presintered compact could be infiltrated by coating methods. These and other techniques can (1) lower sintering temperatures, (2) enhance filling of pores, and (3) reduce shrinkage as compared to making a homogeneous powder part. Zirconium-titanium mixtures may also be used.

We have modified our nitrided material 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. The alloys may be preoxidized at a temperature where little reaction would occur with nitrogen alone and then subsequently nitrided. Also, we have alloyed the alloys with a combined oxidizing and nitriding environment although the relative oxidizing potential must be low since for example 3050°F for 2 hours and subsequently boronized at 2650°F for 4 hours. The structural features of such a material are very similar to the Alloy only nitrided; the hardness grades inwardly and of the total weight pick-up of 90% is due to nitriding. A smooth surface layer about 0.5 mil thick forms due to the boronizing treatment that is harder than the nitrided surface.

The Cb-30Zr-10Mo alloy nitried at 350°F for 2 hours exhibits a microhardness of 3025 DPN at a depth of 1/4 mil from the surface. After the subsequent boronizing treatment the hardness of the same depth was 3830 DPN. Up to 25% of the nitrogen pick-up can be replaced by oxygen and/or boron.

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 or a coated article. One of the advantages in utility of these materials is our ability to form the metallic alloys by cold or hot working and/or to machine (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.

One of the nitriding effects that we have noticed is an accentuation of sharp edges. Similar to the established technology for aluminum oxide ceramic insert tools, we have blunted sharp cutting edges prior to nitriding. This has been accomplished by simple tumbling prior to nitriding or by finishing subsequent to nitriding. High speed cutting performance will not be degraded if such edge preparation is limited. The nitrided material can be used as a mechanically locked insert or it can be bonded or joined by brazing, for example, to a substrate.

In the present invention, as in the invention disclosed and claimed in our copending parent application, when one wishes to determine whether or not the material is useful in the nitrided state for purposes hereof certain compositional ratios and formulae must be employed in some cases. 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:

\[ \text{Ratio } A = \frac{\text{Cb}}{\text{Cb} + \text{Ta} + \text{V}} \]

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

\[ \text{Ratio } B = \frac{\text{Ta}}{\text{Cb} + \text{Ta} + \text{V}} \]

\[ \text{Ratio } C = \frac{\text{Cb} + \text{Ta} + \text{V}}{\text{Ti}} \]

\[ \text{Ratio } D = \frac{\text{Ti} + \text{Zr}}{\text{Ti}} \]
In making the various alloyed, nitrided systems of this invention—that is, alloys consisting of one or more metals of Group I (Cb, Ta, V), Group II, zirconium and zirconium with up to 97% thereof replaced by titanium, and one or both Group III metals (Mo, W)—the following compositional requirements must be met for the nitrided material to be included within the scope hereof:

1. All alloys must contain at least 1% zirconium or 1% of total zirconium and titanium with up to 97% of the zirconium content being replaced by titanium;
2. Maximum combined columbium, tantalum and/or vanadium content is given by the expression:
   \[ \text{Cb} + \text{V} + \text{Ta} = C(90D + 75E) + 88B + 85A \]
3. The relationship of zirconium and titanium content to molybdenum and tungsten content is given by the expression:
   \[ \frac{\text{Zr} + \text{Ti}}{\text{Mo} + \text{W}} \]
   is equal to or less than 17.5(4A + B) + C(3E + 17.5D);
4. The relationship of total molybdenum and tungsten content to total columbium, tantalum and vanadium is given by the expression:
   \[ \frac{\text{Cb} + \text{Ta} + \text{V}}{\text{Mo} + \text{W}} \leq A(2F + 4G) + C[4G + 2F(D + 2E)] + B[4G + F(D + 2E)] \]
5. The relationship of columbium, tantalum and vanadium to titanium and zirconium is given by the expression:
   \[ \frac{\text{Cb} + \text{Ta} + \text{V}}{\text{Ti} + \text{Zr}} \geq B(0.7A + 1.5B + 0.7C) + D[A + 1.5B + 0.7C] \]
6. The Ti + Zr content is greater than 37%, Group III content must be greater than
   (percent Group II) = 35

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.

The excellent cutting properties and wear resistance of the nitrided materials can be effectively employed with the other useful properties of the alloys and nitrided materials to produce a wide range of products. Some of these are: single point cutting tools, multiple point cutting tools (including rotary burrs, files, routers and saws), drills, taps, punches, dies for extrusion, drawing, and other forming operations, armor, gun barrel liners, impeller or fan blades, EDM (Electrical Discharge Machining) electrodes, spinners, guides (thread, wire, and other), knives, razor blades, scrapers, slitters, shears, forming rolls, grinding media, pulverizing hammers and rolls, capstans, needles, gages (thread, plug, and ring), bearings and bushings, pivots, nozzles, cylinder liners, tire studs, pump parts, mechanical seals such as rotary seals and valve components, engine components, brake plates, screens, feed screws, sprockets and chains, specialized electrical contacts, fluid protection tubes, crucibles, molds and casting dies, and a variety of parts used in corrosion-abrasion environments in the papermaking or petrochemical industries, for example.

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

We claim as our invention:

1. Graded, nitrided ternary or higher refractory alloy material consisting essentially of: at least one metal selected from each of the Groups I, II and III wherein Group I consists of columbium, tantalum and vanadium; Group II is zirconium and zirconium with up to 97% of the content thereof replaced by titanium and Group III consists of molybdenum and tungsten and wherein:
   a. the nitrogen pick-up ranges from 0.1 to less than 1.0 milligram per square centimeter of surface area and the surface of the material is depleted in at least one metal of the group titanium and zirconium to the desired composition;
   b. there is from 1% and up to 50% Group II present;
   c. maximum Group I content is equal to or less than C(90D + 75E) + 88B + 85A;
   d. Group II/Group III content is equal to or less than 17.5(A + B) + C(3E + 17.5D);
   e. Group III/Group I is equal to or less than A(2F + 4G) + C(4G + 2F(D + 2E)) + B(4G + F(D + 2E));
   f. Group I/Group II is equal to or greater than E(0.7A + 1.5B + 0.7C) + D(A + 1.5B + 0.7C); and
   g. when Group II content is greater than 37%, Group III content must be greater than
   (percent Group II) = 35

and wherein the foregoing in weight percent concentrations
\[ A = \frac{\text{Cb}}{\text{Cb} + \text{Ta} + \text{V}} \]
\[ B = \frac{\text{Ta}}{\text{Cb} + \text{Ta} + \text{V}} \]
\[ C = \frac{\text{V}}{\text{Cb} + \text{Ta} + \text{V}} \]
\[ D = \frac{\text{Ti}}{\text{Ti} + \text{Zr}} \]
\[ E = \frac{\text{Zr}}{\text{Ti} + \text{Zr}} \]
\[ F = \frac{\text{Mo}}{\text{Mo} + \text{W}} \]
\[ G = \frac{\text{W}}{\text{Mo} + \text{W}} \]

(b) said depleted titanium and/or zirconium surface content being produced prior to nitriding by treating the refractory alloy material in a vacuum at a temperature below the melting point of the alloy for a time sufficient to produce the desired depletion in titanium and/or zirconium content and depth of depletion.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

148—20.3