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WEAR AND ABRASION RESISTANT MATERIALS

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FIG. 1

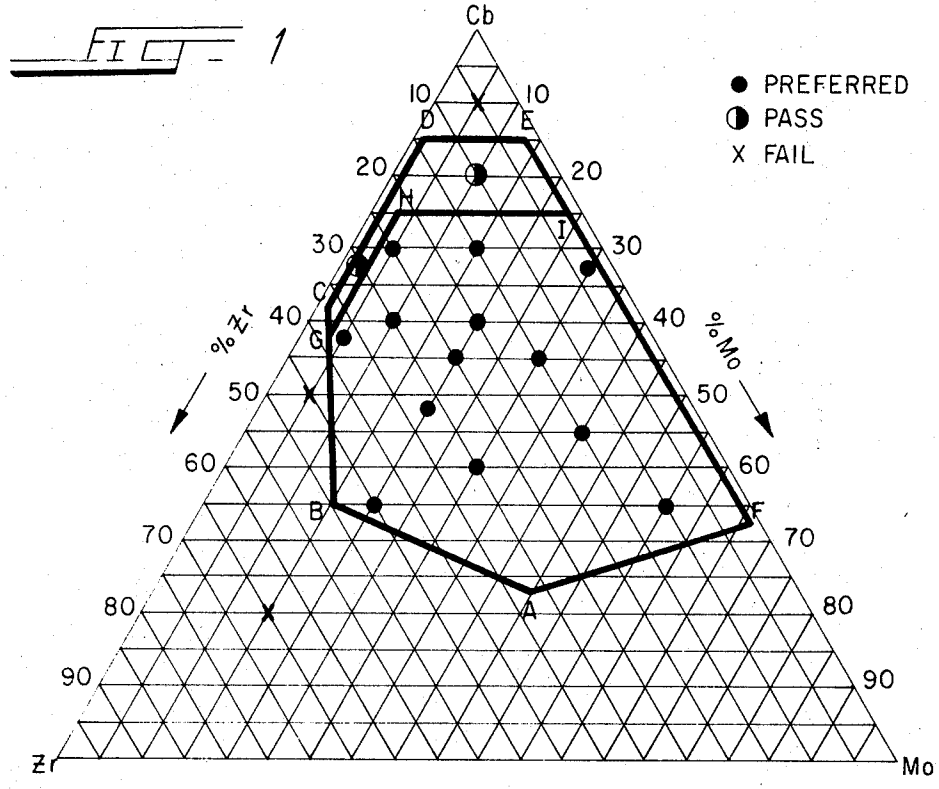
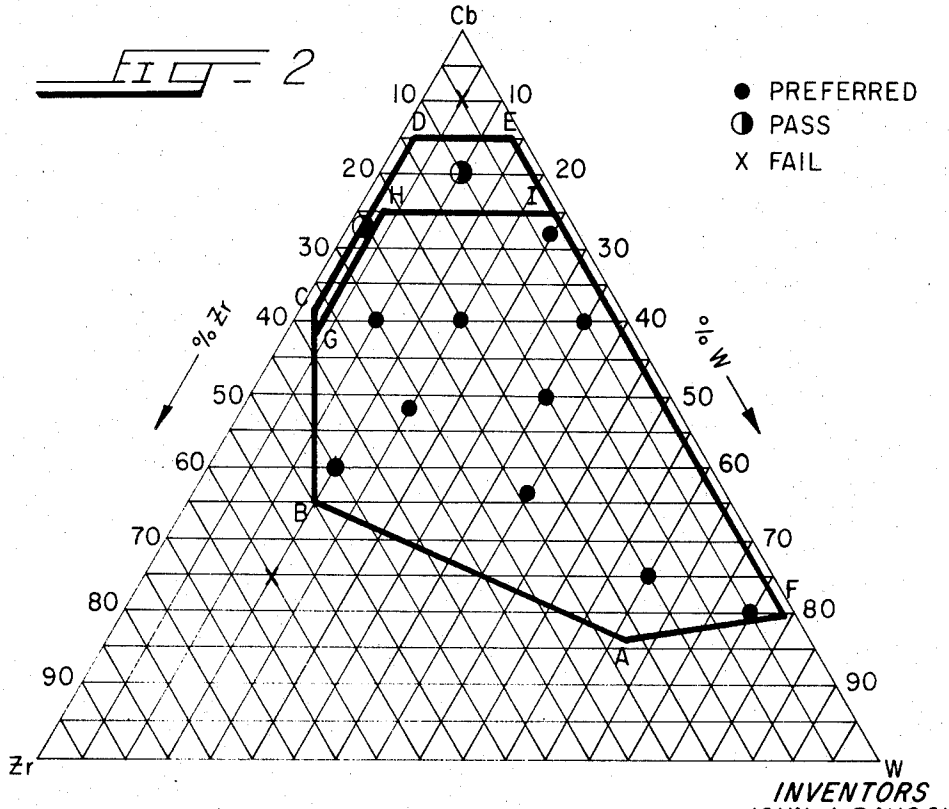


FIG. 2



INVENTORS
JOHN J. RAUSCH
RAY J. VAN THYNE

BY Albert Siegel ATTY

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WEAR AND ABRASION RESISTANT MATERIALS

John J. Rausch, Antioch, and Ray J. Van Thyne, Oak Lawn, Ill., assignors to Surface Technology Corporation, Stone Park, Ill., a corporation of Illinois

Continuation-in-part of application Ser. No. 665,510, Sept. 5, 1967. This application Aug. 27, 1968, Ser. No. 755,662

Int. Cl. C22c *15/00, 29/00*

U.S. Cl. 148—32 7 Claims

ABSTRACT OF THE DISCLOSURE

Nitrided materials consisting essentially of:

(I) columbium and/or tantalum and/or vanadium;
(II) zinconium and zirconium-titanium mixtures; and
(III) tungsten and/or molybdenum.

Such nitrided metals are characterized by excellent wear and abrasion resistance and illustrate utility as cutting tools.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending application Ser. No. 665,510 entitled "Composite Structures" filed Sept. 5, 1967, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a novel group of nitrided ternary or higher alloyed metals which illustrate superb cutting properties and which alloys contain essentially:

(I) one or more metals of the group columbium, tantalum and vanadium;
(II) zirconium alone and a mixture thereof with titanium wherein up to 97% of the zirconium content is replaced by titanium; and
(III) molybdenum or tungsten or both;

all in amounts by percent by weight and in accordance with the relationships as hereinafter set forth. We have discovered that such alloys when nitrided as herein taught form extremely useful high speed cutting materials (although they have other uses also) and offer considerable advantages in terms of cutter life, fabricability, performance and cost over presently known cutting tool materials, especially the sintered carbides. In addition such materials have excellent wear and abrasion resistance characteristics, all of which is hereinafter described. The commerical and technical significance of our invention will be immediately apparent to those skilled in this particular art.

Accordingly, a principal object of our invention is to provide novel, nitrided alloys consisting essentially of:

(I) one or more metals of the group columbium, tantalum and vanadium;
(II) zirconium and zirconium-titanium;
(III) one or more metals of the group molybdenum and tungsten.

This, and other objects, features and advantages of our invention will become apparent to those skilled in this particular art from the following detailed disclosure thereof and from the accompanying drawings.

DESCRIPTION OF THE PRIOR ART AND FURTHER BACKGROUND COMMENTS

To the best of our knowledge the products of our invention, which are fully set forth as this description proceeds, are nowhere described in the prior art. We have found nothing in the art which in anyway indicates the nitrided alloy composites of this disclosure or the utility thereof. In fact, there are certain teachings in the art

which would indicate that the nitrided alloys of our invention would be too brittle to be useful and accordingly it is with some surprise that the utility of such materials is as we have discovered.

We would note, however, that generally speaking, the reaction of various metals and alloys with the compound forming elements, carbon, oxygen and nitrogen to improve surface properties or in some instances, to develop certain composite materials is known. Most of the prior work along these lines has involved the carburizing or nitriding of ferrous base materials and there is extensive literature as regards that field.

In such prior art process the compound forming element usually is in the gaseous phase. Reaction temperatures vary from as low as 800° F. for ferrous metals to from 3500° F. to 5000° F. for tantalum and tungsten. (See M. R. Andrews, J. Am. Chem. Soc., 54:18–45 (1932); also U.S. Pat. 3,163,563.) The reaction product may be a continuous nitride, carbide or oxide layer formed on the metal surface, or an internal dispersion of the compound phase formed within the metal, or combination of these two.

It is also known that if an alloy consisting of copper with small amounts of aluminum is exposed to oxygen at elevated temperatures the oxygen goes into solution at the alloy surface, diffuses therein and reacts with the aluminum to form an aluminum oxide dispersion in a copper matrix. A similar effect occurs when molybdenum, alloyed with minor amounts of titanium and/or zirconium (i.e., up to 1.5%) is exposed to molecular nitrogen at elevated temperatures—a dispersion of titanium nitride and/or zirconium nitride is found within the molybdenum. (See: A. K. Mukherjie and J. W. Martin, J. of the Less Common Metals, 393 (1960).) With both such minor additions dispersion strengthened composites are produced.

Furthermore, it is known in the art that the nitriding at elevated temperatures of elemental tantalum, columbium or titanium, or dilute titanium alloys, generally results in the formation of continuous, hard nitrided surface layers thereon. These layers would usually be characterized as being brittle. Similarly, the carburizing of tantalum results in the formation of hard, continuous carbide surface layers. Additionally, if the tantalum is alloyed prior to carburizing substantial improvements in the adherence of the resulting layers to the substrate can be achieved. (See U.S. Pat. 3,163,563.) Similar improvements and modifications in phase distribution and surface layer adherence have been observed when columbium is alloyed with zirconium or titanium prior to oxidation.

In distinction to all of these prior art teachings, our invention relates chiefly to the making of an exceptionally useful group of materials which result from the reaction of certain alloy compositions with a nitrogen environment. Such alloy compositions contain columbium (Cb) and/or tantalum (Ta) and/or vanadium (V) as one constituent. Zirconium (Zr) is the second constituent. Up to 97% of the zirconium may be replaced with titanium (Ti). The third principal constituent is molybdenum (Mo) or tungsten (W) or both. Minor amounts of other materials and metals may be present either as impurities or as nondetrimental diluents which do not affect the basic teachings of our discovery. Upon being nitrided the present materials are characterized by a desirable combination of mechanical properties which make them extremely useful particularly under severe conditions of erosion or abrasion.

We would also note that the prior art indicates that when the elemental metals columbium, tantalum, vanadium or titanium are reacted at elevated temperatures in molecular nitrogen at one atmosphere pressure continuous nitride and subnitride layers are formed on the surface. In addition discrete particles of subnitride or solid solution phases may form below these outer layers. Such

nitrided metallic elements are in no way comparable in properties or utility to the nitrided structures of our invention. Although the hard outer layers have high hardness their structural value is quite limited. Their ability to support a mechanical load is poor as measured by tests which include diamond indentation, metal cutting and abrasion or impact under high load. Such materials are further characterized as having poor strength, little toughness and poor resistance to chipping or spalling. As is subsequently shown herein we have found that it is necessary to eliminate the continuity of the nitrided layers by using materials in which composition and properties are graduated in a mostly continuous fashion in order to achieve maximum performance for the test conditions described herein.

SUMMARY OF THE INVENTION

We have found that truly effective nitrided composites falling within the scope hereof can only be produced when certain combinations of metals in certain ranges and relationships are present in the alloys prior to nitriding. As noted above the present alloys prior to being nitrided must contain at least three metallic components, viz:

(I) one or more of the metals columbium, tantalum and vanadium;
(II) zirconium (or zirconium and titanium); and
(III) one or both of the metals molybdenum and tungsten.

The ranges and relationships, ratios, of the various metals which are nitrided to form the desirable products of our invention will be subsequently described.

Accordingly, our invention is directed to nitrided materials consisting essentially of the alloy system (Cb, Ta, V)-(Zr[Ti])-(Mo, W) and covers a number of desirable composites ranging from a three component up to a seven component alloy if titanium replaces a portion of the zirconium. In addition there may be present either or both of minor impurities or diluent metals which do not detract from the desirable properties of the nitrided materials.

Furthermore, as is likewise set forth below in some detail we find that within some of the compositional range hereof there are certain preferred compositions in terms of meeting the rather severe cutting test criteria we have established or materials for wear and abrasion resistance. All of the present materials of the alloy systems herein disclosed and claimed when nitrided may be used for cutting tools but these other aspects of the invention are also significant.

An important aspect of our invention lies in the achievement of high hardness and wear-resistance coupled with good toughness or chipping resistance in the same material. Normally it is quite difficult to develop a good balance between these properties while maintaining them at a relatively high value. For example, the wide usage of sintered carbides for wear and cutting purposes stems from a balance of such properties therein. (Yet we find that our materials are superior to and offer many advantages over the sintered carbides.) Although ceramic materials such as alumina may be much harder than sintered carbide their utilization is limited due to chipping.

We have used metal cutting tests at 100 and 750 surface feet per minute as a primary experimental evaluation technique since these are highly reproducible and metal cutting will certainly be one of the principal uses of the present materials. Cutting hardened steel at high speeds—750 s.f.m.—is a good measure of the high performance wear resistance of the material. At relatively low speeds (100 s.f.m.), the chipping propensity of the material under load can be evaluated. These inter-relationships will be more clearly understood as this description proceeds.

We are confident that to those skilled in this art such tests will appear quite severe but we have been able to develop a new family of materials which fulfill such requirements to a superb degree.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings appended hereto:

FIG. 1 is a ternary diagram for nitrided alloys in the columbium-molybdenum-zirconium system; and

FIG. 2 is a ternary diagram for nitrided alloys in the columbium-tungsten-zirconium system.

EXPERIMENTAL PROCEDURES

Before commencing the detailed discussion of our invention we consider it appropriate to first describe the experimental procedures we employed and the criteria established whereby we determined the utility of the present nitrided materials. Certainly all of this could be written as a series of examples (and should be considered as such) but for purposes of brevity we will present the data in tabular form.

We would first point out that all percentages in the present specification and claims are by weight.

In our experimental work a series of alloys were melted under an argon 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 that generally weighed about 70 grams.

The processed alloys were cut into specimens approximately ⅜ x ⅜ x ⅛ in. and reacted in molecular nitrogen at atmospheric pressure unless otherwise described. The resulting structure, thickness, and microhardness of the various reaction zones or layers were determined using standard metallographic techniques. A variety of 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 on tool inserts the same size as the aforesaid specimens having an 0.030" nose radius which was used as a section of the cutting surface. Such radii were ground on the specimens prior to nitriding.

The alloys as thus prepared were subsequently nitrided. For nitriding we used a cold wall furnace employing a molybdenum heating element and radiation shields which furnace was evacuated to 5 microns pressure and flushed with nitrogen prior to heating. Temperatures were measured with an optical pyrometer, namely, a Leeds and Northrup optical pyrometer, Catalogue No. 862, sighting on an unnitrided molybdenum heating element which completely surrounded the specimen. Accordingly, all temperatures given herein are optically measured, uncorrected.

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 (Rc) 43 to 45. A feed rate of 0.005 in./rev. and depth of cut of 0.050 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.

For reasons set out below our principal criterion in determining whether the present nitrided materials pass or fail and thus whether or not they are included or excluded from the scope hereof is the ability to cut a required volume of the 4340 steel at speeds of both 100 and 750 s.f.m. Our invention covers, among others, all nitrided compositions listed in Table I which pass such criteria.

In the experimental discussions of this specification the following conditions apply unless otherwise specified:

(1) all nitriding was carried out in molecular nitrogen at atmospheric pressure;
(2) the specimens were of the size as set forth above; and
(3) initial testing involved the removal of 2 cubic inches of the 4340 steel.

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 passes the cutter.)

For a comparison of the typical cutting capability of a few of our materials with one of the best sintered carbides (C6 grade) presently available we would note that at 750 s.f.m. the carbide had more than 0.030 in. tool wear in about 3 minutes whereas one of our nitrided columbium-tungsten zirconium alloys wore much less even after cutting for the same length of time.

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 750 and 100 s.f.m. and 2 cu. in. removal, there is a uniform wearland of less than 0.025 in. These are the materials which are included within the scope of this invention. 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.

Development of an acceptable test criterion at this lower speed requires a somewhat more detailed comment. Materials that cut the required 2 cu. in. in the screening test at the speed with little wear and no chipping obviously pass. Those materials which exhibit gross chipping and high wear of the frontal cutting edge or the nose of the tool we have rated as failing. A number of materials have been shown to satisfactorily cut the 2 cu. in. and have serious nose chipping and our testing has shown that these materials get progressively worse; therefore, such materials are also rated as failures. Other materials show no chipping or high wear of the cutting edge, but some limited micro-chipping or scoring of the nose occurs as soon as 0.5 cu. in. of metal is removed. However, the toughness of the material is sufficient that this initial accentuated nose wear does not propagate. We have removed 6 cu. in. of metal by cutting and found little further change in cutting edge wear or the accentuated nose wear in some of these materials. We have rated the performance of these as preferred or pass depending upon the amount of the accentuated nose wear.

Table I presents cutting test results of some of our materials and others for the removal of 2 cu. in. of hardened steel at 750 and 100 s.f.m. All of such alloys were nitrided in molecular nitrogen at the temperatures indicated (as measured by the aforesaid optical pyrometer) for the times shown.

TABLE I

Alloy composition	Nitriding treatment ° F.	Nitriding treatment hrs.	Cutting test result at speed— 750 s.f.m.	Cutting test result at speed— 100 s.f.m.
Cb-2Mo-30Zr	3,200	2	P*	P
Cb-5Mo-45Zr	3,000	2	F	P
Cb-5Mo-45Zr	3,000	4	F	P
Cb-5Mo-45Zr	3,200	4	F	P
Cb-5Mo-45Zr	3,600	2	F	P*
Cb-5Mo-37Zr	3,200	4	P*	P*
Cb-5Mo-25Zr	3,200	4	P*	P*
Cb-5Mo-25Zr	3,600	2	F	F
Cb-5Mo-5Zr	3,000	2	F	P
Cb-5Mo-5Zr	3,200	2	P*	F
Cb-10Mo-30Zr	3,200	4	P*	P*
Cb-10Mo-30Zr	3,400	2	P*	P
Cb-10Mo-30Zr	3,600	2	P*	P
Cb-10Mo-10Zr	3,600	2	P*	P
Cb-15Mo-15Zr	3,200	2	P*	P*
Cb-20Mo-20Zr	3,200	4	P*	P*
Cb-20Mo-25Zr	3,000	2	P*	P*
Cb-20Mo-25Zr	3,200	4	P*	P*
Cb-20Mo-32Zr	3,200	2	P*	P*
Cb-20Mo-45Zr	3,200	4	P*	P*
Cb-30Mo-30Zr	3,200	2	P*	P*
Cb-40Mo-5Zr	3,400	2	P*	P*
Cb-40Mo-15Zr	3,000	2	P*	P*
Cb-40Mo-15Zr	3,400	2	P*	P*
Cb-30Mo-15Zr	3,400	2	P*	P*
Cb-30Mo-2Zr	3,200	2	P*	P*
Cb-55Mo-10Zr	3,400	2	P*	P*
Cb-15Mo-65Zr	3,000	2	F	X
Cb-2W-25Zr	3,200	2	F	X
Cb-2W-25Zr	3,200	4	P*	P
Cb-5W-5Zr	3,200	2	P	F
Cb-5W-5Zr	3,200	4	P*	F

Alloy composition	Nitriding treatment ° F.	Nitriding treatment hrs.	Cutting test result at speed— 750 s.f.m.	Cutting test result at speed— 100 s.f.m.
Cb-10W-10Zr	3,200	2	P*	P
Cb-10W-30Zr	3,200	2	P*	P*
Cb-15W-60Zr	3,200	4	F	F
Cb-15W-45Zr	3,200	2	P*	P
Cb-15W-45Zr	3,200	4	P*	P*
Cb-20W-20Zr	3,200	2	P*	P*
Cb-20W-32Zr	3,200	4	P*	P*
Cb-35W-15Zr	3,200	4	P*	P*
Cb-40W-24Zr	3,400	2	P*	P*
Cb-60W-15Zr	3,400	2	P*	P*
Cb-25W-2Zr	3,200	2	P*	P*
Ta-10Mo-10Zr	3,200	2	P*	P
Ta-5Mo-35Zr	3,400	2	P	P
Ta-10Mo-30Zr	3,400	2	P*	P
Ta-20Mo-20Zr	3,200	4	F	X
Ta-20Mo-20Zr	3,400	2.5	P	P
Ta-50Mo-8Zr	3,400	2	P	P
Ta-10Mo-50Zr	3,400	2.5	F	X
Ta-10Mo-50Zr	3,400	6.5	F	X
Ta-10Mo-70Zr	3,400	2	F	X
Ta-10W-10Zr	3,200	2	P	P
Ta-20W-10Zr	3,400	2	P	P
Ta-30W-15Zr	3,400	2	P*	P*
Ta-10W-30Zr	3,400	2	P*	P*
Ta-60W-8Zr	3,600	2	P	P
Ta-10W-70Zr	3,200	2	F	X
V-7.5Mo-7.5Zr	2,800	2	F	X
V-15Mo-15Zr	2,800	2	P	P
V-5Mo-30Zr	2,800	2	F	X
V-20Mo-25Zr	2,600	2	F	X
V-20Mo-25Zr	2,800	2	P	P
V-35Mo-25Zr	2,800	2	P*	P*
V-70Mo-8Zr	2,600	2	P	P
V-10Mo-70Zr	2,600	2	F	X
V-10Mo-70Zr	2,600	4	F	X
V-10Mo-70Zr	2,800	2	F	X
V-7.5W-7.5Zr	2,700	2	F	X
V-5W-30Zr	2,800	2	F	X
V-20W-25Zr	2,800	2	P	P
V-40W-20Zr	2,800	2	P*	P*

NOTE: P*=Pass, preferred.
P=Pass.
F=Fail.
X=Not tested.

Although the foregoing examples are directed to the reaction of various alloy compositions in molecular nitrogen at atmospheric pressure, sources of nitrogen other than the diatomic gas may be employed to produce the present nitrided composite materials or the nitrogen may be present as a relatively minor constituent in a gaseous mixture.

DESCRIPTION OF THE INVENTION AND DISCUSSION OF THE PREFERRED EMBODIMENTS

We next wish to turn to additional disclosure and discussion of the various nitrided compositions falling within the teachings hereof and of the general concepts underlying our invention.

We would first note that because of the wide variations in alloy compositions, within certain limits as hereinafter set forth, nitriding at different temperatures and times is required to develop the present high performance materials. In general, microhardness, metallography, hardness and weight gain are employed to guide the selection of useful nitriding treatments.

Furthermore, in order to produce useful, nitrided composite materials of the present alloy systems, i.e., those falling within the scope hereof, we find that the nitrogen pick-up must be at least 1 mg./cm.^{2} of surface area, although an even higher amount is preferred, the surface microhardness should be more than 1000 diamond pyramid numerals (DPN) and the reaction depth to which such hardness is developed is at least 0.5 mil.

Another important aspect to consider in understanding our invention relates to the relative nitrideability of the metallic constituents of our various alloy systems. Such background must be taken into consideration in order to intelligently practice the teachings of our invention. Thus, in terms of nitride reaction with the metals used herein molybdenum and tungsten are relatively inert, columbium, tantalum or vanadium readily nitride and zirconium and titanium are most reactive with nitrogen. Upon nitriding we find a partitioning of nitrogen depending upon the reactivity of the substrate matter. Because of this and as

shown in our experimental results the amount of zirconium (and titanium when it is used herein) used should be limited, as compared with the other constituents and furthermore if the molybdenum or tungsten content is increased the nitriding reaction in general proportionately decreases.

Thus, it should be borne in mind in considering the present invention and experimental results recited herein that the required nitriding temperatures and times are related to the composition being treated. This specification presents considerable data as to these variables but we would note that the general principles of the invention should be taken into consideration in nitriding compositions falling within the scope hereof but not shown as an example herein.

Still another important aspect of the present alloy systems is the fact that the original shape of a machined part is retained during the high temperature nitriding. When treated as herein taught dimensional growth of less than 1 percent is usually obtained; however, in many of our compositions this growth is significantly less and in a number of compositions we have noted a slight shrinkage. Thus, the nitriding of the present materials can be based upon achieving desired properties rather than minimizing the reaction to avoid possible piece distortion.

Many of our compositions can be nitrided to form a composite structure throughout thus forming a more homogenous, but still graded, composite with good toughness. However, the reaction can generally be limited to the outer region without much hardening of the core or substrate. The minimum reaction depth depends upon the intended use, but it has been shown that the amount of reaction required for severe applications such as the cutting test described herein is quite small.

The thickness of the alloy body will also influence nitriding kinetics and the amount of nitrogen absorption required to develop adequate hardness and grading for useful abrasion resistance and metal cutting capability. We find that as the alloy becomes thinner effective hardening can be accomplished at lower nitriding temperature or shorter time. This will apply whether the material is a free standing body or a clad or coating on another substrate.

The amount of nitrogen absorption required to obtain high performance is dependent upon alloy composition as well as sample thickness. For example, all of the following alloys and treatments thereof resulted in good cutting performance as ⅜ x ⅜ x ⅛ inch samples.

Composition	Nitriding treatment		Weight change (mg./cm.²)
	° F.	Hr.	
Cb-5Mo-25Zr	3,200	4	13.5
Cb-15Mo-15Zr	3,200	2	7
Cb-40Mo-15Zr	3,000	2	4.7
V-70Mo-8Zr	2,600	2	3

If the alloys requiring less nitrogen pick-up are employed as thin specimens, the required nitrogen absorption would be significantly reduced.

In the ternary phase diagrams appended as figures hereto the legend of "Preferred," "Pass" and "Fail" is applied. We wish to point out what is meant by this.

"Preferred," denoted by the solid black circles, means the test sample cuts at both 750 and 100 s.f.m. with little wear.

"Pass," denoted by the half-blackened circles, means the test sample cuts at both speeds but higher wear is noted at one speed. In most cases, this higher wear is observed at 100 s.f.m. and is caused by micro-chipping. Both the "Preferred" and "Pass" compositions are included in our invention.

"Fail," denoted by X, means the test sample fails by high wear at either 750 or 100 s.f.m. These materials are excluded from the scope of our invention.

We turn next to some of the specific alloy systems which are representative of and fall within the scope of our invention.

COLUMBIUM-MOLYBDENUM-ZIRCONIUM SYSTEM

A number of ternary alloys of the system Cb-Mo-Zr were reacted with nitrogen at elevated temperatures. The treatment conditions and cutting test results are set forth in Table I and the cutting test results are graphically shown in FIG. 1.

Compositions falling within the boundaries of the polygon formed by lines ABCDEFA of FIG. 1 cover all of our columbium-molybdenum-zirconium nitrided materials which pass the criteria set forth above, satisfactory cutting at both 750 and 100 s.f.m., and also our preferred materials which pass these tests with very low wear.

From FIG. 1 it can be seen that in such nitrided ternary system the following compositional ranges pass our test criteria:

from 23% to 85% columbium;
from 1% to 66% molybdenum; and
from 1% to 50% zirconium

and wherein:

the Cb/Zr ratio must be greater than 0.7;
the Mo/Cb ratio must be less than 2;
the Zr/Mo ratio must be less than 17.5; and
in alloys containing more than 37% zirconium the molybdenum content must be greater than that given by the difference of (percent Zr)—35.

Within such broad range of useful materials we find that alloys which contain as a minimum 1% zirconium and a maximum of 75% columbium and a minimum of 2% molybdenum and wherein:

the Cb/Zr ratio is greater than 0.7;
the Mo/Cb ratio is less than 2;
the Zr/Mo ratio is less than 10; and in alloys containing more than 39% zirconium the molybdenum content must be greater than that given by the difference of (percent Zr)—35

are preferred in that they show extremely low wear as cutting tool matrials at 100 and 750 s.f.m. Such preferred compositions for Cb-Zr-Mo nitrided alloys fall within the inner polygon formed by lines ABGHIFA of FIG. 1 and it is noted that all such materials are preferred as regards the 100 and 750 s.f.m criteria set out herein when nitrided as herein taught.

The alloy Cb-20Mo-20Zr represents one of the preferred ternary compositions that can be nitrided to develop useful nitrided material of our invention. When nitrided at 3200° F. for four hours there is developed a multiphase structure—that is, a structure consisting of two or more phases—usually differing in nitrogen content as well as metallic content, which are discernable when observed in cross-section under a microscope using typical metallographic techniques. The nitrided metallographically-observed reaction depth of the multiphase structure is readily seen. Some hardening can occur below the metallographically observed reaction zone. In this Cb-20Mo-20Zr sample, the reaction zone is 10 mils deep.

We would also note, to avoid any misunderstanding that the term "phase" as used herein means a physically homogeneous and distinct portion of a materials system and that "multiphase" means two or more of such phases.

Upon such treatment the Cb-20Mo-20Zr sample has a high surface hardness which grades to a reasonable depth.

Tool inserts prepared from Cb-20Mo-20Zr treated as noted above, gave the following cutting test results on the 4340 steel test piece at 750 s.f.m.

Vol. of material removed (cubic inches):	Tool wear (inch)
2.25	0.006
4.95	0.010

This of course, is a very low rate for this test condition. One of the best grades of sintered tungsten carbide (C6)[1] is totally worn and unsuitable for further cutting after removing this amount of material at this speed.

Cutting tests were also run at 100 s.f.m. After removing 2.0 cu. in. of material the tool showed only 0.006 in. of uniform nose wear and there was no evidence of chipping.

The alloy composition may be somewhat reduced in both molybdenum and zirconium content and useful cutting materials are produced upon nitriding. For example, the alloy Cb-15Mo-15Zr nitrided at 3200° F. for 2 hours, cut the test steel satisfactorily at both 100 and 750 s.f.m. At the high speed a cutting tool thus treated showed only 0.004 in. wear after removing 2.4 cu. in. of test steel.

If the alloy composition is modified by substituting additional molybdenum for columbium, while maintaining the zirconium content at 15% we found that similarly useful composites are produced upon subsequent nitriding. Thus alloys of composition Cb-30Mo-15Zr and Cb-40Mo-15Zr, nitrided for two hours at 3400° F., show useful cutting properties at both 750 and 100 s.f.m. Furthermore, such alloys display a high degree of latitude with regard to the amount of nitriding that yields these useful cutting properties. For example, a cutter of alloy Cb-40Mo-15Zr was nitrided at 3000° F. for two hours and passed our cutting test at both speeds. The nitrogen weight gain for this specimen was only 4.7 mg./cm.^{2} compared to 13 mg./cm.^{2} for the specimen treated at 3400° F. for two hours.

The zirconium content of the nitrided alloys can be increased to relatively high levels provided that sufficient molybdenum is present. For example, as shown in Table I alloys of the compositions Cb-20Mo-32Zr, Cb-30Mo-45Zr have been successfully nitrided to produce useful cutting tools meeting our test.

When the zirconium content becomes too high and/or the molybdenum content too low, and are outside of the scope of our teachings and claims, successful cutting tools cannot be produced by nitriding. This has been observed for the alloy Cb-5Mo-45Zr and Cb-15Mo-65Zr. Thus, the ratios set forth above must be followed in making cutting materials from this alloy system which meet our 750 and 100 s.f.m cutting criteria.

In treating materials of this Cb-Mo-Zr system we find that nitriding at from 3200° to 3400° F. for from 2 to 4 hours produces cutting tools which pass our test criteria.

COLUMBIUM-TUNGSTEN-ZIRCONIUM SYSTEM

The system Cb-W-Zr upon nitriding as herein taught is quite comparable to the system Cb-Mo-Zr with the principal differences being that in the latter the columbium range is slightly smaller (24% to 85% as compared with 15% to 85%) and the maximum amount of molybdenum permitted is somewhat less than that of tungsten (60% Mo as compared with 79% W). Except for these slight compositional differences the two alloy systems for purposes of this invention are essentially the same, and the resulting properties and capability of meeting our test criteria for utility are comparable. In fact, as is set out below, within certain compositional limits the tungsten and molybdenum contents are substitutable one for the other or both said metals may be included in the same base alloy.

Various examples of this alloy system with nitriding temperatures and times are presented in Table I and the cutting test results are graphically shown in FIG. 2.

[1] As defined in "Metals Handbook," 8th ed., vol. 1, p. 660 (1961).

Compositions falling within the boundary of the polygon formed by lines ABCDEFA of FIG. 2 cover all of our columbium-tungsten-zirconium nitrided materials which pass the criteria set forth above, satisfactory cutting at both 750 and 100 s.f.m., and also our preferred materials which pass these tests with very low wear.

From FIG. 2 it can be seen that in such nitrided ternary system the following compositional ranges are useful:

from 15% to 85% columbium;
from 1% to 79% tungsten; and
from 1% to 50% zirconium

and wherein:

the Cb/Zr ratio must be greater than 0.7;
the W/Cb ratio must be less than 4;
the Zr/W ratio must be less than 17.5; and
in alloys containing less than 37% zirconium the tungsten content must be greater than that given by the difference of (percent Zr)—35.

With such broad range of useful materials we find that alloys meeting the above criteria and which contain as a minimum 1% zirconium and a maximum of 75% columbium and a minimum of 2% tungsten and wherein:

the Cb/Zr ratio is greater than 0.7;
the W/Cb ratio is less than 4;
the Zr/W ratio is less than 10; and
in alloys containing more than 39% zirconium the tungsten content must be greater than that given by the difference of (percent Zr)—35,

are preferred in that they serve as cutting tool materials at 100 and 750 s.f.m. with very low wear when nitrided as herein taught. Such preferred compositions for Cb-Zr-W nitrided alloys fall within the inner polygon formed by lines ABGHIFA of FIG. 2 and it is noted that all such materials are preferred as regards the 100 and 750 s.f.m. criteria set out herein.

An example of one of our preferred materials of this system is the composition Cb-20W-32Zr. A most satisfactory cutter prepared from this alloy, nitrided at 3200° F. for 4 hours gained 10 mg./cm.^{2} of nitrogen during this treatment and had a visible nitrided reaction zone extruding to a depth of seven mils. Cutting tests were run at 750 s.f.m. with the following results.

Volume of material removed (cubic inches):	Tool wear (inch)
2.25	0.002
4.60	0.003

This, again, is an exceptionally low tool wear rate for this test condition.

Cutting tests were also run with such nitrided alloy at 100 s.f.m. After removing 2.4 cu. in. of the test steel the tool showed only 0.008 in. of nose wear.

An alloy, having the same tungsten content, but a higher Cb/Zr ratio, i.e. Cb-20W-20Zr, when nitrided at 3200° F., for two hours had a visible reaction depth of 6 mils and cut the test steel very effectively at both 100 and 750 s.f.m.

When the columbium content is increased to 80%, such as in the alloy Cb-10W-10Zr we find that nitrided tools retain their effective cutting capability with very low wear at 750 s.f.m. However, a tendency toward nose chipping leading to slightly more rapid wear is noted at 100 s.f.m. Such material passes our test criteria and is included within the scope hereof but is not one of our preferred compositions.

Very useful cutting tools are produced by nitriding these alloys containing rather large quantities of tungsten. We have produced materials that cut very effectively at both 100 and 750 s.f.m. by nitriding the alloys Cb-5Zr-35W, Cb-15Zr-35W, Cb-40W-24Zr, Cb-60W-15Zr and Cb-75W-

5Zr. The following data were obtained for the alloy Cb-40W-24Zr, nitrided at 3400° F. for two hours.

Volume of material removed (cubic inches):	Tool wear (inch)
2.65	0.003
5.00	0.004

When tested at 100 s.f.m. the following data were obtained.

Volume of material removed (cubic inches):	Tool wear (inch)
1.85	0.002
2.75	0.003
3.35	0.004

The nitrided cutter in the above examples had a visible reaction depth of 5 mils.

We find that the nitrided alloys in this system do not produce effective cutting tools and are thus excluded from the scope hereof where the zirconium content is too high, i.e., about 50%.

Thus the alloy Cb-15W-60Zr when nitrided at 3200° F. for two or four hours will not cut effectively at either 100 or 750 s.f.m.

In treating materials of this Cb-W-Zr system we find that nitriding at from 3200° to 3400° F. for from two to four hours produces cutting tools which pass our test criteria.

TANTALUM-MOLYBDENUM-ZIRCONIUM SYSTEM

Cutting test results on various nitride compositions of this alloy system are given in Table I. The results are similar to those for the columbium containing system. Nitrided ternary alloys, falling within the following compositional range and relationships satisfactorily cut the hardened steel test piece at both 100 and 750 s.f.m. and are included within the scope hereof:

from 27% to 88% tantalum;
from 1% to 66% molybdenum; and
from 1% to 39% zirconium

and wherein:

the Ta/Zr ratio must be greater than 1.5;
the Mo/Ta ratio must be less than 2;
the Zr/Mo ratio must be less than 17.5; and
in alloys containing more than 37% zirconium the molybdenum content must be greater than the difference of (percent Zr) −35.

In treating materials of this Ta-Mo-Zr system we find that nitriding at from 3200° to 3400° F. for two hours produces cutting tools which pass our test criteria.

Upon nitriding for 2.5 hours at 3400° F. with a pick-up of 6.3 mg./cm.², the material Ta-20Mo-20Zr passes at both 750 and 100 s.f.m., but incipient melting of the alloy is observed. Similarly, the composition Ta-10Mo-30Zr passes the cutting test criteria when nitrided at 3400° F. for two hours, but melting is observed upon nitriding at 3600° F.

TANTALUM-TUNGSTEN-ZIRCONIUM SYSTEM

Cutting tests results on various nitride compositions of this alloy system are also given in Table I. Nitrided ternary alloys falling within the following compositional range satisfactorily cut the hardened steel test piece at both 100 and 750 s.f.m. and are included within the scope hereof:

from 17% to 88% tantalum;
from 1% to 79% tungsten; and
from 1% to 39% zirconium

and wherein:

the Ta/Zr ratio must be greater than 1.5;
the W/Ta ratio must be less than 4;
the Zr/W ratio must be less than 17.5; and
in alloys containing more than 37% zirconium the molybdenum content must be greater than the difference of (percent Zr) −35.

A number of examples of nitrided Ta-W-Zr alloys is given in Table I. Most of the compositions, particularly those in the middle of the composition range, were nitrided at 3400° F. for two hours. With such treatment, the reacted alloy Ta-30W-15Zr picked up 5.3 mg./cm.² and showed a very low tool wear of 0.005 in. after cutting at either 750 or 100 s.f.m. Because of the high tungsten content, the alloy 32Ta-60W-8Zr was nitrided at 3600° for two hours resulting in a weight pick-up of 3.7 mg./cm.² and this material passed our test criterion.

In treating materials of this Ta-W-Zr system we find that nitriding at from 3200° to 3600° F. for two hours produces cutting tools which pass our test criteria.

VANADIUM-MOLYBDENUM-ZIRCONIUM SYSTEM

Cutting test results on various nitrided compositions of this alloy system are also given in Table I. Nitrided ternary alloys falling within the following compositional range satisfactorily cut the hardened steel test piece at both 100 and 750 s.f.m. and are included within the scope hereof:

from 15% to 75% vanadium;
from 6% to 79% molybdenum; and
from 1% to 50% zirconium

and wherein:

the V/Zr ratio must be greater than 0.7;
the Mo/V ratio must be less than 4; and
the Zr/Mo ratio must be less than 3.

The alloys within these systems shown in Table I passing the test criteria of cutting at both speeds were nitrided for two hours at 2600° or 2800° F. and such conditions are preferably used. Upon nitriding at 2800° F. for two hours, the alloy V-35Mo-25Zr cut with a tool wear of 0.005 inch at both speeds. With the same treatment, V-20Mo-25Zr passed the test criteria but showed higher wear (0.020 in.) at 750 s.f.m. and a propensity towards nose chipping at 1000 s.f.m. Other nitrided materials passing our test criteria include a higher vanadium content composition V-15Mo-15Zr and a higher molybdenum content composition V-70Mo-8Zr. However, the zirconium-rich nitride alloy V-10Mo-70Zr failed immediately upon testing at 750 s.f.m.

VANADIUM-TUNGSTEN-ZIRCONIUM SYSTEM

Cutting test results on various nitrided compositions of this alloy system are also given in Table I. Nitrided ternary alloys falling within the following compositional range satisfactorily cut the hardened steel test piece at both 100 and 750 s.f.m. and are included within the scope hereof:

from 15% to 75% vanadium;
from 6% to 79% tungsten; and
from 1% to 50% zirconium

and wherein:

the V/Zr ratio must be greater than 0.7;
the W/V ratio must be less than 4; and
the Zr/W ratio must be less than 3.

Excellent cutting results were observed with V-40W-20Zr. After nitriding at 2800° F. for two hours, the tool wear at 750 and 100 s.f.m. was 0.005 and 0.004 inch, respectively. Somewhat higher wear was found with V-20W-25Zr, but this nitride alloy also passed the test criteria.

In this alloy system nitriding at from 2600° to 2800° F. for two hours produces materials which fall within the scope hereof.

HIGHER ALLOYED SYSTEMS

Representative examples of higher alloyed nitrided materials, some of which fall within the scope hereof, along with nitriding conditions and cutting test results are set forth in Table II. Again, as with the ternary systems previously described, only those materials which pass both the 750 and 100 s.f.m. test are included within the scope of this invention.

TABLE II

Alloy composition (weight percent)	Nitriding treatment		Cutting test results at speed	
	° F.	Hrs	750 s.f.m.	100 s.f.m.
47Cb-19Mo-21Ti-13Zr	3,600	2	P*	P*
47Cb-19Mo-21Ti-13Zr	3,400	2	P*	P*
60Cb-20Mo-8Ti-12Zr	3,200	2	P*	P*
60Cb-25W-5Ti-10Zr	3,200	2	P	P
40V-40W-10Ti-10Zr	2,800	2	P*	P*
58V-10Mo-26Ti-6Zr	2,600+2,800	6	P	P
20Ta-10Mo-35Ti-35Zr	3,200	2	F	X
20Cb-10W-35Ti-35Zr	3,200	2	F	X
60Ta-15W-10Ti-15Zr	3,400	2	P*	P*
30Cb-30Ta-20Mo-20Zr	3,400	2	P*	P*
30Cb-30Ta-20W-20Zr	3,400	2	P*	P*
30Cb-30Ta-10Mo-10W-20Zr	3,400	2	P*	P
30Cb-30Ta-10V-5Mo-5W-20Zr	3,200	4	P*	P
30Cb-30Ta-10V-5Mo-5W-10Ti-10Zr	3,200	4	P	P

In the foregoing Table II the same legend is employed as in Table I.

When one wishes to make use of the higher alloyed systems of our invention including quaternary alloys having both zirconium and titanium, certain compositional relationships and formulae must be employed in some cases to determine whether the material will meet our cutting test criterion.

Zirconium-containing alloys containing up to six components may be prepared of the type:

(Cb, Ta, V)-(Mo, W)-Zr

We have found that such nitrided composites pass our cutting test criteria when the relationships specified previously for the ternary systems are applied to the groupings (Cb, Ta, V) and (Mo, W). These constituents all readily alloy and when the resulting complex alloys are nitrided a similar weight pick-up is observed. For example, one of the representative examples from Table II, 30Cb-30Ta-20Mo-20Zr was nitrided at 3400° F. for two hours with weight pick-up of 7.7 mg./cm.^{2}, and satisfactorily cut the test steel at 750 and 100 s.f.m. with a tool wear of 0.005 and 0.004 inch, respectively.

The more complex alloy 30Cb-30Ta-10Mo-10W-20Zr, similarly nitrided, well passed our criterion of cutting with low wear at both 750 and 10 s.f.m.

The further complexed composition 30Cb-30Ta-10V-5Mo-5W-20Zr, nitrided at 3200° F. for four hours cut very effectively at 750 s.f.m. showing a uniform nose wear of 0.006 in. and well meets our test criteria at 100 s.f.m.

Table II also shows a number of compositions wherein various proportions of the zirconium content have been replaced by titanium. Such alloys can contain up to seven constituents consisting:

(Cb, Ta, V)-(Mo, W)-(Zr, Ti)

We find that the titanium can readily be alloyed with the other constituents and the material can be nitrided with results similar to when titanium is absent. A number of examples containing zirconium and titanium showing good cutting performance at both 750 and 100 s.f.m. are given in Table II.

Similar to all of the individual ternary systems described previously, we find that the nitrided materials will not pass our test criterion when the combined Zr and Ti content is above 50%.

The utility of one of these higher alloyed, nitrided composites may be seen from the following data for the composition Cb-19Mo-13Zr-21Ti.

Nitriding treatment		Weight gain (mg./cu.in.)	Uniform tool wear			
			100 s.f.m.		750 s.f.m.	
° F.	Hr.		Volume removed (cu.in.)	Wear (in.)	Volume removed (cu.in.)	Wear (in.)
3,400	2	17.7	2	0.003	2	0.003
3,600	2	27.7	1.3	0.003	2	0.004
			6	0.004	7	0.006

In addition to these low tool wear rates, no chipping was noted; therefore such material has excellent cutting utility.

We also note that the complex alloys 60Cb-20Mo-8Ti-12Zr and 60Cb-25W-5Ti-10Zr, nitrided at 3200° F. for two hours cut the hardened test steel at both speeds.

Complex alloys of vanadium containing both titanium and zirconium pass our test criteria when nitrided as herein taught as may be noted from Table II.

The complex alloy, 30Cb-30Ta-10V-5Mo-5W-10Ti-10Zr, nitrided at 3200° F. for four hours shows tool wear of 0.006 and 0.007 in. after cutting the required test steel at 100 and 750 s.f.m. respectively. Obviously, such alloy clearly falls within the scope hereof.

COMPOSITIONAL RANGES

The compositional limitations for each of the six zirconium-containing ternary systems are presented above. These compositional limits and relationships define a compositional polygon ABCDEFA in FIG. 1, for Cb-Mo-Zr. As previously noted such compositions are not the same for all six ternary systems but they overlay over certain ranges. In view of this an alloy containing 60(Cb, Ta, V)-20(Mo, W)-20Zr would be within the allowable range for any combination of Cb, Ta, or V at the 60% level and any combination of Mo or W at the 20% level. It is also apparent that many compositions fall outside the allowable alloy range regardless of the combination of Cb, Ta, or V or Mo or W. For example, all compositions containing more than 50% zirconim are outside our range.

Additionally, in materials in which up to 97% of the zirconium has been replaced by titanium the compositional limits are further modified. For example, when the aggregate of titanium and zirconium present in the alloy is in the proportion 97% Ti-3Zr and is used in conjunction with the Group I and Group III metals the relationships set forth below are found to apply. In the compositions and ratios thus set out as regards this particular quaternary group of materials the letter M stands for the constituent in which the titanium and zirconium are present in this specific proportion, 97–3.

In the columbium-molybdenum-zirconium system when 97% of the zirconium is replaced by titanium the compositional range and relationships are as follows:

from 25% to 85% columbium;
from 1% to 66% molybdenum; and
from 1% to 45% M (i.e. the 1% corresponds to a constituent of 0.97% Ti and 0.03% Zr and the 45% corresponds to a constituent of 43.65% Ti and 1.35% Zr.)

and wherein:

the Cb/M ratio must be greater than 1;
the Mo/Cb ratio must be less than 2;
the M/Mo ratio must be less than 17.5; and
in alloys containing more than 37% M content, the Mo content must be greater than (percent M)—35.

In the Cb-W-Zr-Ti system of this group of materials the compositional range and relationships are as follows:

from 17% to 85% columbium;
from 1% to 79% tungsten; and
from 1% to 45% M

and wherein:

the ratio of Cb/M must be greater than 1;
the W/Cb ratio must be less than 4;
the M/W ratio must be less than 17.5; and
in alloys containing more than 37% M the W content must be greater than that given by the difference of (percent M)—35.

In the Ta-Mo-Zr-Ti system of this group of materials (97Ti-3Zr) the compositional range and relationships are as follows:

from 37% to 88% tantalum;
from 1% to 49% molybdenum; and
from 1% to 39% M

and wherein:

the ratio of Ta/M must be greater than 1.5;
the Mo/Ta ratio must be less than 1;
M/Mo ratio must be less than 17.5; and
in alloys containing more than 37% M the Mo content must be greater than that given by the difference of (percent M)—35.

In the Ta-W-Zr-Ti system of this group of materials (97Ti-3Zr) the compositional range and relationships are as follows:

from 17% to 88% tantalum;
from 1% to 79% tungsten; and
from 1% to 39% M

and wherein:

the ratio of Ta/M must be greater than 1.5;
the W/Ta ratio must be less than 4;
the M/W ratio must be less than 17.5;
in alloys containing more than 37% M the W content must be greater than that given by the difference of (percent M)—35.

In the V-Mo-Zr-Ti system of this group of materials (97Ti-3Zr) the compositional range and relationships are as follows:

from 23% to 90% vanadium;
from 1% to 66% molybdenum; and
from 1% to 50% M

and wherein:

the ratio of V/M must be greater than 0.7;
and Mo/V ratio must be greater than 2; and
the M/Mo ratio must be less than 17.5.

In the V-W-Zr-Ti system of this group of materials (97Ti-3Zr) compositional range and relationships are as follows:

from 15% to 90% vanadium;
from 1% to 79% tungsten; and
from 1% to 50% M

and wherein:

the ratio of V/M must be greater than 0.7;
the W/V ratio must be less than 4;
the M/W ratio must be less than 17.5; and
in alloys containing more than 37% M the W content must be greater than that given by the difference of (percent M)—35.

We find certain compositional relationships whereby one can determine whether or not a particular alloy containing 4 to 7 constituents of the group (Cb, Ta, V)-(Mo, W)-(Zr, Ti) will fall within our useful ranges. Such alloys when nitrided as herein taught, pass our test criteria. These formulae are based upon the ranges for the 6 ternary systems containing only zirconium and the 6 systems containing titanium and zirconium in the proportion 97Ti-3Zr as the constituent (M). These 12 systems represent boundary conditions and have been used to develop formulae presented below that cover a range of titanium contents from 0 to 97% substituted for zirconium. Such formulae represent linear proportionate amounts based upon weight percentages.

These factors have been briefly noted before but now they should be considered in some detail to fully understand the teachings hereof. A modest mathematical statement is required.

In the present specification and claims the following ratios shall have the following meanings:

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

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

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

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

$$D=\frac{Ti}{Ti+Zr}$$

$$E=\frac{Zr}{Ti+Zr}$$

$$F=\frac{Mo}{Mo+W}$$

$$G=\frac{W}{Mo+W}$$

In making the various alloyed, nitrided systems of this invention—that is, alloys consisting of one or more metal of Group I, titanium and zirconium, and one or both Group III metals—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 replaceable 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:

$$\frac{Zr+Ti}{Mo+W}$$

is equal to or less than $17.5(A+B)+C(3E+17.5D)$;

(4) The relationship of total molybdenum and tungsten content to total columbian, tantalum and vanadium is given by the expression:

$$\frac{Mo+W}{Cb+Ta+V}\leq A(2F+4G)+C[4G+2F(D+2E)]+B[4G+F(D+2E)]$$

(5) The relationship of columbium, tantalum and vanadium to titanium and zirconium is given by the expression:

$$\frac{Cb+Ta+V}{Ti+Zr}\geqq E(0.7A+1.5B+0.7C)+D[A+1.5B+0.7C[$$

and

(6) When Ti+Zr content is greater than 37%, Group III content must be greater than

(Percent Group II)—35

In the foregoing formulae it will be apparent that Cb+Ta+V could be replaced by the term "Group I"; Zr+Ti by the term "Group II" and W+Mo by the term "Group III."

With some of our nitrided materials cutting tests were run at 1250 s.f.m. to demonstrate the high speed cutting capability. In particular, we note that alloys containing moderate to high levels of columbium display very effective cutting capability under these conditions as shown by the following data:

Alloy composition	Nitriding treatment		Volume of material removed (cu. in.)	Tool wear (in.) at 1,250 s.f.m.
	° E	Hrs.		
Cb-15Mo-15Zr	3,200	2	1.18	0.012
Cb-5Mo-25Zr	3,200	4	1.06	0.006
Cb-20Mo-20Zr	3,200	4	0.95	0.007

We would further note that many of the alloys which are nitrided as herein taught, in addition to being readily fabricated in the form of solid stock, may likewise be fabricated by standard powder techniques, as well as cladding or coating processes.

The usefulness of these nitrided composites as high speed cutting tool materials for hardened steel has been described. In addition, cutting of other difficult-to-machine materials has been demonstrated. For example, many of our nitrided composites will cut 2 cu. in. from a cobalt base alloy (Haynes 25) at 400 s.f.m. with low tool wear whereas sintered carbide will fail under these conditions. Our testing has shown that our materials exhibit excellent abrasion resistance as well. The nitrided materials are resistant to a variety of strong acids.

Thus, applications involving both corrosion and abrasion can be considered.

More particularly, the present nitrided materials find utility, among others, for use in rotary files and burrs, taps, drills, dies, rotary seals, nozzles and tube liners.

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. A graded nitrided material having a nitrogen pickup of at least 1 milligram per square centimeter of surface area having excellent cutting and abrasion resistance properties 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 consists of 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) there is from 1% and up to 50% Group II present;

(b) maximum Group I content is equal to or less than

$$C(90D+75E)+88B+85A$$

(c) Group II/Group III content is equal to or less than

$$17.5(A+B)+C(3E+17.5D)$$

(d) Group III/Group I is equal to or less than

$$A(2F+4G)+C[4G+2F(D+2E)]+B[4G+F(D+2E)]$$

(e) Group I/Group II is equal to or greater than

$$E(0.7A+1.5B+0.7C)+D(A+1.5B+0.7C)$$

and

(f) when Group II content is greater than 37%, Group III content must be greater than

(Percent Group II)—35

and wherein, in the foregoing in weight percent concentrations

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

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

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

$$D=\frac{Ti}{Ti+Zr}$$

$$E=\frac{Zr}{Ti+Zr}$$

$$F=\frac{Mo}{Mo+W}$$

$$G=\frac{W}{Mo+W}$$

2. The material as defined in claim 1 wherein the surface microhardness thereof is at least 1000 diamond pyramid numerals and the reaction depth to which such hardness is developed is at least 0.5 mil.

3. The material as defined in claim 1 consisting essentially of columbium, molybdenum and zirconium and the ranges for such metals are as follows:

from about 23% to 85% columbium;
from about 1% to 66% molybdenum; and
from about 1% to 50% zirconium.

4. The material as defined in claim 1 consisting essentially of columbium, tungsten and zirconium and the ranges for such metals are as follows:

from about 15% to 85% columbium;
from about 1% to 79% tungsten; and
from about 1% to 50% zirconium.

5. The material as defined in claim 1 consisting essentially of tantalum, molybdenum and zirconium and the ranges for such metals are as follows:

from about 27% to 88% tantalum;
from about 1% to 66% molybdenum; and
from about 1% to 39% zirconium.

6. The material as defined in claim 1 consisting essentially of tantalum, tungsten and zirconium and the ranges for such metals are as follows:

from about 17% to 88% tantalum;
from about 1% to 79% tungsten; and
from about 1% to 39% zirconium.

7. The material as defined in claim 1 consisting essentially of vanadium, zirconium and a metal selected from the group consisting of molybdenum and tungsten and combinations thereof and the ranges for such metals are as follows:

from about 15% to 75% vanadium;
from about 1% to 50% zirconium; and
from about 6% to 79% of a metal selected from the group consisting of molybdenum and tungsten and combinations thereof.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

148—20.3, 39, 133

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,549,429

DATED : December 22, 1970

INVENTOR(S) : John J. Rausch and Ray J. Van Thyne

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 16, "zinconium" should read -- zirconium --;

Column 1, line 49, "commerical" should read -- commercial --;

Column 9, line 42, delete "45Zr" and insert -- 30Zr and Cb-20Mo-45

Column 11, line 21 "about" should read -- above --;

Column 11, line 32, "nitride" should read -- nitrided --;

Column 11, line 62, "nitride" should read -- nitrided --;

Column 12, line 44, "1000" should read -- 100 --;

Column 12, line 47, "nitride" should read -- nitrided --;

Column 12, line 71, "nitride" should read -- nitrided --;

Column 13, Table II, the sixth entry (58V-10Mo-26Ti-6Zr) should be 2600 for 6 hours plus 2800 for 2 hours;

Column 14, line 12, under the heading "Weight gain", "(mg/cu. in)" should read -- (mg/Cm^2) --;

Column 14, line 40, "overlay" should read -- overlap --;

Column 14, line 48, "zirconim" should read -- zirconium --;

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,549,429
DATED : December 22, 1970
INVENTOR(S) : John J. Rausch and Ray J. Van Thyne

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

Column 16, line 59, "columbian" should read -- columbium --;

Column 17, in the Table at line 16, "^{o}E" should read -- ^{o}F --;

Signed and Sealed th

Eighth Day of March 1

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Traden