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METHOD OF PRODUCING HIGH
TEMPERATURE ALLOYS

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This invention relates to molybdenum-base alloys and tungsten-base alloys and, more particularly, to a method for preparing alloys of molybdenum and alloys of tungsten containing small quantities of carbon and certain of the metals of Group IV of the Periodic Table, namely metals of the group consisting of titanium, zirconium, hafnium or thorium.

Although molybdenum and tungsten have been known for some time as excellent materials for high temperature applications, recent technological developments, particularly in the fields of missiles and space vehicles, have created a need for metals having mechanical properties at elevated temperatures which are not attainable by pure molybdenum or tungsten. Alloys of molybdenum or tungsten with small quantities of carbon and one or more of the above-mentioned Group IV metals, which have been developed in an effort to meet this need have been produced recently by a method involving pressing and sintering of the powdered ingredients, and including the familiar arc casting operation. Although these arc cast alloys have afforded materials of substantially better high temperature properties than pure molybdenum or tungsten they are expensive to produce, primarily because of the arc casting step which heretofore has been considered necessary to bring the ingredients into proper association. Furthermore, because of the inherently large grain structure of the arc cast alloys, they must be extended to break down the grain size before the material can be fabricated by other forms of mechanical working.

It is, therefore, an object of this invention to provide a process for making alloys of a metal selected from the group consisting of molybdenum and tungsten with carbon and a metal selected from the group consisting of titanium, zirconium, hafnium and thorium which obviates the need for arc casting to bring the ingredients of the alloys into proper association.

It is a further object to provide a simple process for producing alloys of the aforesaid description having improved high-temperature mechanical properties.

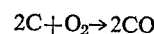
The method of the present invention involves operations of the general type employed in the familiar powder metallurgical procedures. More particularly, the starting materials are consolidated by pressing and sintering operations, and the resulting sintered billets are then subjected to a succession of fabrication steps, e.g., forging, rolling and extruding, and heat treatment steps to obtain sheet material of the ultimate desired properties. However, within these broad principles and operations characteristic of the powder metallurgical procedure, the present invention involves the application of specific unique steps and conditions which are set out in detail below.

For the sake of simplicity of explanation and clarity of understanding, the method of the invention is described below in terms of its application to the preparation of alloys of molybdenum, titanium and carbon. Within the broad scope of the invention, the conditions for carrying out the method with tungsten in lieu of molybdenum as the major constituent of the alloy, and employing one of the Group IV metals other than titanium, may differ in detail from the conditions of operation set forth below with respect to the alloys of molybdenum, titanium and carbon. Where these differences are significant to a

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full understanding of the invention particular reference to them will be made. It will be further understood that for purposes of the method hereinafter described the same procedures are used and the same results are realized regardless of whether the elemental metal or the hydride of the metal is employed in the starting powder mixture. Accordingly, it will be understood that when reference is made to the above-mentioned Group IV metals in the following specification and claims, the corresponding hydride is also contemplated.

For purposes of illustration, alloys of molybdenum, titanium and carbon are produced by first thoroughly mixing the ingredients in powder form. Alloys of this type which are particularly amenable to production by the method of this invention are those in which the primary element is molybdenum, the amounts of titanium and carbon being present, respectively, in amounts, by weight, in the ranges of about 0.40% to 0.60% and about 0.02% to 0.06%. A portion of the carbon included in the initial mix is lost during the sintering process by combination, at the sintering temperature, with oxygen present either in free or combined form with the initial powdered ingredients or in the sintering environment. Accordingly, an excess of powdered carbon must be incorporated in the starting mixture prior to pressing it into compacts in order to insure a final carbon content within the above-mentioned range of 0.02% to 0.06%. The carbon reacts with the oxygen present primarily in accordance with the equation



so that the necessary initial excess of carbon may readily be determined by those skilled in the art employing this invention, from an analysis of the starting materials for oxygen and a knowledge of the oxygen in the sintering environment.

After the component powders have been thoroughly mixed, the mixture is pressed into a compact of any desired size. This pressing or compacting operation normally is accomplished at room temperature. Sufficient pressure is employed in pressing the powdered mixture to obtain a compact of sufficient strength to facilitate the subsequent sintering step. It has been found that the desired compact density and strength is best obtained if the powder charge is compressed at pressure of the order of 30,000 pounds per square inch. However, it should be understood that lower or higher pressures may be employed depending on factors such as billet size, and the particle size and configuration of the particles.

The compacts are next subjected to a sintering operation which involves heating in a vacuum, hydrogen, or other protective atmosphere. In this step, the sintering is carried out at a temperature above 1800° C., the melting point of titanium, but below the melting point of molybdenum. Higher temperatures in this range may be used in order to accelerate the sintering operation, and temperatures of about 2300° C. have been found to be particularly suitable for rapid sintering. Depending on the size of the billet being sintered, and the temperature employed, the length of time it is necessary to maintain the billet at sintering temperature may be widely varied. Thus, satisfactory results have been achieved by maintaining the billet at a temperature of 2300° C. for only about 0.5 hour. On the other hand, good results have been obtained by sintering billets at about 1850° C. for times up to 22 hours.

Although, as indicated above, considerable latitude is permitted in the selection of the conditions for carrying out the sintering operation, it is essential that the sintering temperature and the time of sintering be sufficient to cause melting of the titanium and complete solution of the titanium and carbon in the molybdenum. At the re-

quired temperatures, titanium in the molten condition disappears during the operation as it dissolves in the solid molybdenum. During the balance of the sintering period the titanium and the carbon diffuse uniformly throughout the molybdenum. The density of the billet increases as a result of the sintering. It has been found that for optimum results in the subsequent fabrication steps, the billet should have a minimum density of 92% of theoretical. This same criterion for the sintering operation, that is, heating above the melting point of the Group IV metal, is applicable generally to the other molybdenum and tungsten base alloys defined above. Thus for those compositions containing zirconium (M.P. 1852° C.) sintering temperatures of about 1900° C. are preferred. Similarly, alloys containing either thorium or hafnium must be sintered at temperatures of at least 1750° C. or 2222° C., the melting points of the respective metals. In those cases in which the alloy contains more than one of the Group IV metals, the temperature of the higher melting metal is determinative of the minimum temperature at which the green billet must be sintered.

It is to be noted that the sintering operation described above departs from the usual concepts of sintering prevalent in the powder metallurgy field. More particularly, the generally accepted procedure for preparing alloys in which one metal is soluble in another is to maintain the sintering temperature below the melting point of all of the ingredients of the starting powder mixture. Temperatures above the melting point of any element of the mixture normally are employed only in those cases where the metals are substantially insoluble in each other, and it is desired to obtain maximum densities by melting an element of lower melting point to fill the interstices between the particles of a higher melting element.

In view of the solubility of titanium and carbon in molybdenum, attempts were made to follow the usual powder metallurgy technique referred to above by sintering at temperatures at and below the melting points of all of the components, i.e., at and below 1800° C., the melting point of titanium. However, it was found that the ultimate tensile strengths of sheets fabricated from billets sintered at these lower temperatures was substantially lower than the ultimate tensile strengths of sheets fabricated from billets sintered at temperatures above the melting point of titanium. Tensile test results at 1200° C. on 40-mil thick sheets fabricated from billets sintered at various temperatures from 1700° C. to 2300° C. are listed in Table I, below. The ultimate tensile strengths are expressed in terms of thousands of pounds per square inch (K s.i.).

Table I

Sintering temperature (° C.):	1200° C. UTS (K s.i.)
1700	34
1800	40
1850	54
1900	52
1950	56
2000	56
2150	54
2300	56

The sintered billets prepared as described above may be fabricated by forging, extruding, swaging or rolling, or by a combination of two or more of these operations, into forms for ultimate use. One of the features of the method of the present invention is in a unique schedule of mechanical working and heat treatment adapted to produce sheet material of the alloy herein described, which is characterized by substantially higher ultimate tensile strength at elevated temperatures than sheet fabricated by conventional processes from similar arc cast alloys.

In the preparation of sheet material, the sintered billet first is mechanically worked as by forging, rolling or ex-

truding into an intermediate "sheet bar" or "plate" at a temperature in the range of from about 1350° C. to about 1500° C. The precise amount of working may be varied depending on the type of working employed and the extent to which the sheet bar or plate is to be further reduced in the manufacture of sheet. Typically, if rolling is employed the billet may be reduced to plate of about one fourth to about three-fourths of the billet thickness. In any event, the working is sufficient at the temperature employed to cause a substantial degree of strain-induced precipitation of titanium carbide from solution in the molybdenum. It has been found that if temperatures below about 1300° C. are used in this first stage of mechanical working of the molybdenum-titanium-carbon alloys, the plate tends to split in subsequent rolling steps. It will be understood that different temperature ranges for this mechanical working will be found preferable for other alloys of the types contemplated by the present method. In general, the working temperature should be sufficiently high to permit fabrication of the billet, but less than the melting point of the Group IV metal.

In order to further reduce the sheet bar or plate to relatively thin plate in accordance with the method of this invention, the plate is next subjected to heat treatment at temperatures above about 1650° C. In this heat treatment higher temperatures may be employed to reduce the time of heating required, but otherwise there is no particular advantage in employing a temperature in excess of 2150° C. Table II, below, shows the effect of various heat treatment temperatures of 400-mil thick plate. The ultimate tensile strengths at 1200° C. tabulated were made on 40-mil thick sheets rolled from the plates heat treated at the indicated temperatures.

Table II

Heat Treatment Temp. (° C.)	Time at Temp. (Hr.)	1,200° C. UTS (K s.i.)
2,150	0.5	69
1,900	1.0	67
1,700	2.0	67
None (Control)		56
1,550	7.5	50
1,350	18.0	48

It will be noted from the results of the first three tests recorded in Table II that the ultimate tensile strengths at 1200° C. of the 40-mil sheets rolled from plate heat treated at temperatures above about 1650° C. are considerably higher than the ultimate tensile strength (56 K s.i.) of sheet rolled from the control plate which received no heat treatment. Furthermore, it is surprisingly evident from Table II that heat treatment of the plate at lower temperatures, i.e., 1350° C. and 1550° C. afforded lower strength sheet material than that obtained from the control plate.

The apparently critical response of the alloy to the heat treatment of the plate would appear to be indicative of strengthening by strain-induced precipitation. Strengths higher than that of the control apparently are attributable to dissolution of the titanium carbide segregated in the structure during rolling of the plate from the sintered billet, followed by precipitation of the TiC during the subsequent lower temperature deformation of the plate into sheet as will hereinafter be described. Strengths lower than that of the control apparently resulted because the TiC is chemically stable in the dispersed phase below 1650° C. and did not dissolve in the molybdenum matrix at 1350° C. and 1550° C. but, instead, coalesced in such a manner as to detract from the strengthening effect of the TiC dispersion in the structure.

The reduction of the plate or sheet bar to the alloy sheet material is accomplished at temperatures below the temperatures used in the sintering and intermediate plate heat treatments described above. This is for the reason

that the strain-induced precipitation of the TiC is desired incidental to the rolling to final thickness. At temperatures above 1650° C. the TiC is chemically unstable and tends to remain in solution in the molybdenum. Therefore the temperatures employed in the final rolling stages must be substantially below 1650° C. to insure the desired TiC precipitation. Temperatures as high as 1400° C. can be used in the final rolling stages, but optimum ultimate tensile strengths at 1200° C. are obtained at rolling temperatures of about 1100° C. for most of the reduction from plate to sheet thickness. Lower temperatures may be employed for the last stages of the rolling which do not involve a high degree of working.

As previously mentioned in this specification, tungsten as well as molybdenum may be used as the base metal when alloyed with the Group IV metals referred to above, and carbon, in accordance with the technique of the present invention. Table III, below, shows the results of tensile tests at 1650° C. made on various alloys of tungsten with hafnium, zirconium and titanium. All of the alloys referred to in the table were sintered at 2350° C. and were reduced to sheet form following the general procedure for working and heat treating set forth above.

Table III

Composition (weight percent):	1650° C. UTS (K s.i.)
W—.03 Hf—.013 C	62
W—.5 Hf—.017 C	73
W—1.0 Hf—.037 C	69
W—.02 Zr—.017 C	64
W—.29 Zr—.018 C	63
W—.45 Zr—.036 C	70
W—.24 Ti—.027 C	59

In order that those skilled in the art better may understand the method of the present invention, the following example is given of the preparation of a molybdenum alloy sheet material containing about 0.50% titanium and 0.026% carbon.

A mixture of molybdenum, titanium and carbon powders was first prepared, the mixture containing 0.50% titanium and 0.087% carbon, the balance being molybdenum. The titanium and carbon and a portion of the molybdenum were first mixed by tumbling for about one-half hour, and this mixture was then mixed with the balance of the molybdenum powder for three hours in a blender.

About 2.8 kilograms of the powder mixture was loaded into a long pliable mold of 2½" by 2½" cross section. The filled mold was then sealed and immersed in water in a hydrostatic press and subjected to a pressure of about 30,000 pounds per square inch. The resulting unsintered or "green" compact was then removed from the mold and the corners were removed or rounded so that the maximum cross-sectional diagonal was 2 inches.

The compact then was loaded into a 2-inch diameter tungsten susceptor in a 50 kilowatt induction furnace. The furnace was closed and flushed with dry hydrogen, and the compact was inductively heated to 2300° C. in about 75 minutes. After the compact was maintained at this temperature for an additional 90 minutes, it was cooled in the furnace while flushing with dry hydrogen. The resulting sintered billet has the approximate dimensions 1.5 inches by 1.5 inches by 6.5 inches and had a density of about 94% of theoretical.

The sintered billet next was subjected to a breakdown rolling operation at temperatures in the range of 1400° C. to 1430° C. In this step of the method, the billet was first rolled longitudinally in five reductions, each of about 17%, from the original thickness of about 1.5 inches to 590 mils thickness. The billet was heated at the above temperature for eight minutes prior to the first reduction and was reheated for three minutes after each reduction. Next the billet was cross-rolled from 590 mils to 400

mils in the same temperature range of 1400° C. to 1430° C. Five cross-rolling reductions, each of about 7.5% were used. The material was reheated for three minutes after all but the last reduction.

The 400-mil thick plate or sheet bar fabricated as described just above was next cleaned in molten caustic, and about one-half inch was trimmed from the ends. The cleaned and trimmed plate then was heat treated for two hours at 1700° C. In this heat treatment, the titanium carbide, which was precipitated in the structure of the metal by the strains introduced during the breakdown rolling, was redistributed by dissolution in the molybdenum.

The heat treated plate was further rolled at 1100° C. to 60 mils thickness. In this operation the plate first was reduced to about 150 mils by cross-rolling in seven reductions of about 15% each, followed by eight reductions of about 12% each to 60 mils. The sheet was reheated at 1100° C. for about three minutes after each rolling stage except the last. The 60 mil thick sheet then was cleaned in molten caustic, acid-etched in a mixture of hydrofluoric and nitric acids to about 55 mils and finish straight-rolled to 40 mils at room temperature in a series of reductions, each of 5% or less. The final sheet, after trimming, measured 0.040 inch by six feet seven inches by thirty inches. Specimens cut from this sheet exhibited an average ultimate tensile strength at 1200° C. of about 67,000 pounds per square inch.

What is claimed is:

1. The method of producing alloys having high strength at elevated temperatures which comprises the steps of heating a compact of a powder mixture of carbon, a first metal selected from the group consisting of molybdenum and tungsten and a second metal selected from the group consisting of titanium, zirconium, hafnium and thorium to a temperature above the melting point of said second metal and below the melting point of said first metal to form a sintered billet containing the second metal and carbon, respectively, in the amounts of from about 0.40% to about 0.60% and from about 0.02% to about 0.06%, the balance being said first metal, mechanically working said billet at a temperature in the range of between about 1350° C. and about 1500° C. to form a plate of lesser thickness than said billet and thereby causing precipitation of a carbide of said second metal from said first metal, reheating said plate at a temperature between about 1650° C. and about 2150° C. to redissolve the precipitated carbide, and thereafter mechanically working said plate at a temperature below about 1400° C. to an alloy body of desired dimensions.

2. The method of producing an alloy having high strength at elevated temperatures which comprises the steps of

heating a compact of a powder mixture of carbon, molybdenum and a second metal selected from the group consisting of titanium, zirconium, hafnium and thorium to a temperature above the melting point of said second metal and below the melting point of molybdenum to form a sintered billet containing the second metal and carbon, respectively, in the amounts of from about 0.40% to about 0.60% and from about 0.02% to about 0.06%, the balance being molybdenum.

mechanically working said billet at a temperature in the range of between about 1350° C. and about 1500° C. to form a plate of lesser thickness than the billet,

reheating said plate to a temperature between about 1650° C. and about 2150° C. to redissolve particles of carbides of said metal precipitated by the afore-said mechanical working,

and thereafter mechanically working said plate at a temperature below about 1400° C. to an alloy body of desired dimensions.

3. The method according to claim 2 in which said second metal is titanium.

4. The method according to claim 2 in which said second metal is zirconium.

5. The method according to claim 2 in which said second metal is hafnium.

6. The method according to claim 2 in which said second metal is thorium.

7. The method of producing an alloy of molybdenum, titanium and carbon in sheet form which comprises the steps of

thoroughly mixing molybdenum, titanium and carbon powders, the titanium and carbon in the resulting mixture being present, respectively, in the amounts of from about 0.40% to about 0.60% and from about 0.02% to about 0.06%, and the balance of the mixture being molybdenum,

pressing a quantity of said powder mixture to form a compact,

heating said compact to a temperature above 1800° C. to form a sintered billet from the compact and to

cause the titanium and carbon to diffuse into the molybdenum,

mechanically working said billet by rolling at a temperature in the range of from about 1350° C. to about 1500° C. to form a plate of between about one-fourth and about three-fourths the thickness of the billet,

heating said plate at a temperature between about 1650° C. and about 2150° C. to redissolve titanium carbide precipitated from solution in the molybdenum by the rolling of the sintered billet,

and thereafter reducing the plate to sheet by rolling at a temperature below about 1400° C.

References Cited

UNITED STATES PATENTS

2,839,819	6/1958	Platte	75—214 X
3,103,435	9/1963	Iredell	75—214 X
3,194,697	7/1965	Chang	75—176 X
3,243,291	3/1966	Dickenson et al.	75—176

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