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MOLYBDENUM-VANADIUM ALLOYS

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This invention relates to alloys of molybdenum and vanadium, and more specifically to large, sound, cast molybdenum-vanadium alloy ingots, which are capable of being worked at elevated temperatures by forging, pressing, rolling, extrusion and other similar methods. The invention is also concerned with molybdenum-vanadium alloys containing minor amounts of other elements and to such alloys in which a part of the molybdenum has been replaced by tungsten. Such alloys are useful in applications requiring metals of high strength or hardness at both room and elevated temperatures and more specifically in such applications as piercing points for forming seamless steel tubing, electrodes for heating molten glass, die-casting dies for brass and other metals, etc. This application is a continuation-in-part of applicants' copending application, Serial No. 218,522, filed March 30, 1951, now abandoned.

The principal object of this invention is to provide improved cast alloys of molybdenum which are capable of being worked at elevated temperatures.

A further object of this invention is to provide improved molybdenum-base alloys which are characterized by improved hardness and strength both at room and elevated temperatures, and have increased resistance to oxidation at elevated temperatures.

Another object of this invention is to provide cast molybdenum-base alloys in which the intergranular cohesion of the grains is improved and the grain size reduced by the addition of the alloying element.

This invention has as another of its objects the provision of molybdenum-base alloys which are of lower specific gravity than pure molybdenum and which for that reason have particular utility as gas turbine blades.

The terms "casting" and "cast" as used in this application are intended to designate the product resulting from the melting of metal and solidifying the same in a mold, whether or not the metal has been subjected to subsequent working or machining. The term "casting" is also used to designate any process or method which involves melting metal and solidifying the same in a mold.

In accordance with this invention, it is found that the addition of vanadium increases the strength and hardness of cast molybdenum and molybdenum-base alloys.

Cast alloys of molybdenum and vanadium can be hot-worked only when the vanadium is pres-

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ent within certain limits and oxide and carbide impurities are present in amounts less than certain maximum quantities.

It has previously been established that the presence of minute amounts of oxygen in a casting of molybdenum or a molybdenum-base alloy seriously impairs or destroys the capacity of the casting to be worked at elevated temperatures if the oxygen is segregated at the grain boundaries in the form of certain metallic oxides. The detrimental oxide is visible on microscopic examination of intergranular fractures and is believed to consist largely of MoO_2 . However, the oxides of certain other metals, if present, are also detrimental. In any event, when examined microscopically, castings which can be worked at elevated temperatures have no visible oxide segregations at the grain boundaries which are similar to the manifestations of MoO_2 . Cast molybdenum containing less than about .001% oxygen does not contain a detrimental quantity of grain boundary oxides and can be worked at elevated temperatures, but it is very difficult in the production of cast ingots of molybdenum and its alloys to reduce the oxygen content of the metal to such a low value.

As set forth in the patent to Frederick P. Bens et al., No. 2,580,273, the detrimental oxide segregation is not found in molybdenum castings containing not more than .005% oxygen if small amounts of carbon are present. Such castings can be worked at elevated temperatures.

It is now found that the detrimental oxides may also be eliminated by incorporating in the casting certain metals which have a stronger affinity for oxygen than does molybdenum and form oxides that either do not segregate at the grain boundaries or, if segregated at the boundaries, provide greater intergranular cohesion than does the oxide of molybdenum. Aluminum and beryllium have been found to fulfill these requirements, and forgeable castings of molybdenum and molybdenum-base alloys containing up to a maximum of .05% oxygen have been produced by incorporating small quantities of aluminum or beryllium or both in the casting. Carbon may also be present, if desired, and small quantities of carbon or aluminum are particularly beneficial in molybdenum-base alloys containing beryllium.

The effect of oxygen on the molybdenum-vanadium alloy castings of the present invention is similar to its effect in other molybdenum-base alloy castings, and consequently it is necessary to eliminate segregations of molybdenum

oxide at the grain boundaries if the casting is to be worked at elevated temperatures. This is preferably done by incorporating carbon, aluminum or beryllium in the alloy, either singly or in combination. This critical effect of oxygen on the capacity of the alloy to be worked at elevated temperatures is peculiar to cast alloys as distinguished from those produced by sintering metal powders.

If carbon is present in amounts between .01% and .04% and no aluminum or beryllium is present, the maximum oxygen content which can be tolerated in a casting that must be worked at elevated temperatures is about .005%. The minimum quantity of residual carbon should, preferably, increase within these limits as the residual oxygen content approaches .005%. Larger amounts of carbon up to a maximum of about .25% may be present in a casting that must be worked at elevated temperatures, but the resulting additional carbides increase the difficulty of working the cast alloy without imparting other advantages and, therefore, it is preferred that the carbon not exceed about .07%.

If aluminum or beryllium is present in adequate quantities, the maximum oxygen content which can be tolerated in a casting that must be worked at elevated temperatures is about .05%. The quantity of aluminum or beryllium must be at least sufficient to stoichiometrically react with the oxygen present in the final alloy to form Al_2O_3 or BeO , and is preferably three times that quantity in the case of aluminum. Thus, aluminum in the range of .003% to .4% or beryllium in the range of .001% to .03% may be present. In actual practice, aluminum is preferred to beryllium for this purpose and, if beryllium is used, it is preferred to use small quantities of aluminum or carbon with the beryllium. When aluminum is present within the ranges stated, residual carbon is preferably omitted altogether or does not exceed .02%. However, cast molybdenum-vanadium alloys containing aluminum and as high as .06% carbon can be worked at elevated temperatures. When beryllium is used, it is preferred that the carbon not exceed .06%.

Excellent results are achieved in the working of molybdenum-vanadium castings containing carbon in the range of .02% to .05% and oxygen less than .003%; or aluminum from .003% to .2% and oxygen less than .02%; or beryllium from .001% to .02% and oxygen less than .02%. Quantities of aluminum and beryllium above the minimum required to react with the oxygen have other beneficial effects and hence aluminum may be present up to a maximum of about 2.5% or beryllium up to a maximum of about .25%. However, as set forth hereinafter, the amount of vanadium present must be reduced below its maximum if the aluminum exceeds about .4% or the beryllium exceeds about .03% and the alloy is to be worked at elevated temperatures.

Molybdenum-base alloys containing aluminum or beryllium and the herein-disclosed process of producing such alloys are more fully disclosed and claimed in applicants' copending applications, Serial No. 250,202, on "Molybdenum-Tungsten-Aluminum Alloys," and Serial No. 250,201, on "Cast Alloys and Method for Heat-Treating the Same," both filed concurrently herewith.

The addition of vanadium to cast molybdenum results in the following changes in properties: (1) the as-cast room temperature hardness is increased; (2) the hardness and strength at elevated temperatures are increased; (3) the oxidation resistance is slightly increased; (4) the grain

size is refined; (5) the grain boundary strength is increased; and (6) the specific gravity is decreased. All of the above changes in properties have been noted in some degree in cast molybdenum alloys containing vanadium in percentages ranging between .25% and 7%. The presence of less than .25% vanadium in molybdenum alloys was not found to be particularly beneficial. Grain refinement has been observed to increase with increasing vanadium content, and the same observation may be made in relation to hardness and strength at elevated temperatures. Cast molybdenum alloys containing .25% to 7% vanadium may be worked at elevated temperatures to a beneficial degree, but it has been found exceedingly difficult to work molybdenum castings containing more than about 7% vanadium. The difficulty of working increases as the oxygen and vanadium contents increase. The preferred range of vanadium content is .5% to 5%. Alloys containing .25% to 7% vanadium in molybdenum are solid solutions at room temperature.

If desired, tungsten may be present in an amount not exceeding the molybdenum present. The substitution of tungsten for molybdenum has the effect of increasing the hardness of the alloy but to a lesser degree than that caused by the addition of vanadium. If the maximum percentage of tungsten is employed in a cast alloy containing the maximum percentage of vanadium, the resulting alloy cannot be successfully worked at elevated temperatures. However, cast alloys containing tungsten which are capable of being worked at elevated temperatures are obtained if the vanadium percentage is proportionately decreased toward the minimum of .25% as the tungsten percentage is increased toward its maximum of about 50%. It is to be understood that the relationship between the tungsten and vanadium contents relates only to the maximum allowable vanadium which may be present for a given tungsten percentage without interfering with working at elevated temperatures, and that alloys containing less vanadium and tungsten than the maximums fall within the scope of this invention. Actually, it is preferred to use no tungsten or amounts less than 10%. Working of molybdenum-vanadium castings is facilitated if the oxygen content is decreased toward the practical minimum of about .001% as the amounts of vanadium or tungsten increase.

Minor quantities of other elements may also be present. Thus, certain hereinafter-listed transition elements produce advantageous effects when added to the molybdenum-vanadium alloys of the present invention. However, to produce a cast alloy which can be worked at elevated temperatures to a beneficial degree, the amounts of tungsten, other transition elements, aluminum and beryllium must be limited; the preferred alloys contain at least 85% molybdenum. Thus, even in pure binary alloys of molybdenum, the following beneficial transition elements should not be present in amounts exceeding the following percentages if the alloy is to be worked at elevated temperatures;

	Percent
Titanium	14.0
Zirconium	2.0
Chromium	2.0
Iron	1.3
Cobalt	.9
Nickel	.4
Columbium	10.0
Tantalum	9.0

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Beryllium in amounts in excess of .03% and up to a maximum of about .25% and aluminum in amounts in excess of .4% and up to a maximum of 2.5% have an effect on workability similar to that of the above transition elements. They all produce a proportionate increase in hardness at 1600° F. as their quantities increase toward the above maximums. The maximum amounts given for beryllium, aluminum and each of the transition elements other than tungsten correspond roughly to those quantities of each element which, when added alone to molybdenum, will produce a hardness at 1600° F. of 200 V. P. N. (Vickers Pyramid Numeral) in an annealed casting. It has not been possible with normal working techniques to achieve a worthwhile percentage of recovery from the working of metals and alloys having greater hot-hardness, but a beneficial working, at temperatures substantially above 1600° F., may be performed on the alloys of the present invention, provided the hardness at 1600° F. does not exceed about 200 V. P. N. in an annealed casting. The effects of all of the above-mentioned metals, also vanadium and tungsten, on hot-hardness are additive and, therefore, when two are present the maximum permissible amount of one should be proportionately reduced from its maximum given to the extent that the other approaches its maximum if the alloy is to be capable of being worked at elevated temperatures to a beneficial degree. Still further reductions on the same basis must be made if more than two are present, and in all cases less than those maximums gives the best results. From the standpoint of high strength and hardness at elevated temperatures in a molybdenum-vanadium alloy casting that is well adapted to working, the preferred alloying transition elements are titanium, zirconium, columbium and tantalum.

Molybdenum-base alloys characterized primarily by the beneficial effects of zirconium, columbium, titanium and tantalum, respectively, are more fully disclosed and claimed in applicants' copending applications filed concurrently herewith, as follows: Serial No. 250,206, "Molybdenum-Zirconium Alloys"; Serial No. 250,207, "Molybdenum-Columbium Alloys"; Serial No. 250,204, "Molybdenum-Titanium Alloys"; Serial No. 250,205, "Molybdenum-Tantalum Alloys."

It has been noted that additions of .01% to .5% thorium to cast molybdenum or tungsten increase the temperature to which the worked metals may be heated without excessive grain coarsening and without becoming embrittled. Thus, thorium within the range stated may be present in the alloys of this invention.

Therefore, the expression "balance consisting essentially of molybdenum" occurring in the following claims, means that the alloys called for are those whose primary characteristics result from the presence of vanadium, but that the alloys may also contain quantities of unspecified elements, such as the above-mentioned transition elements, which do not appreciably impair the beneficial effects of vanadium or destroy the capacity of the alloy to be worked at elevated temperatures to a beneficial degree.

By way of example, the following alloys may be mentioned as illustrative of specific alloys

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which may be cast, worked at elevated temperatures and used in accordance with this invention:

Example 1

	Per cent
Vanadium -----	.96
Carbon -----	.012
Oxygen -----	less than .005
Molybdenum -----	balance

Example 2

	Per cent
Vanadium -----	3.74
Carbon -----	.027
Oxygen -----	less than .005
Molybdenum -----	balance

Example 3

	Per cent
Vanadium -----	4.6
Aluminum -----	.25
Oxygen -----	.03
Molybdenum -----	balance

Example 4

	Per cent
Vanadium -----	5
Tungsten -----	5
Carbon -----	.02
Oxygen -----	less than .002
Molybdenum -----	balance

Example 5

	Per cent
Vanadium -----	2.4
Carbon -----	.01
Oxygen -----	.02
Beryllium -----	.015
Molybdenum -----	balance

The alloys of this invention may be made by a variety of procedures, but cast alloys containing carbon are preferably made by the process which consists in the steps of (1) mixing molybdenum, vanadium, carbon and any other desired elements in the form of powders, in the desired proportions; (2) pressing the mixture into successive pellets to form a continuous rod; (3) sintering the rod to impart sufficient strength to the same to render it self-supporting; and (4) arc-melting the sintered rod as a consumable electrode in a vacuum and collecting the metal directly into a water-cooled copper mold.

The starting materials used in the process are commercially pure molybdenum powder, preferably containing not more than about .05% oxygen, and commercially available carbon and vanadium powders as well as powders of any other elements employed. Metals in the form of small chips or granules may comprise part of the charge. The starting materials are analyzed for carbon and oxygen, and the amount of carbon required to stoichiometrically react with the oxygen present to form carbon monoxide and to provide a residual carbon content of at least .01% but less than .25% is employed.

The powder charge is fed into an extrusion die positioned beneath the ram of a reciprocating press wherein successive pellets of the powder material are pressed continuously on top of preceding pellets to form a continuous rod of pressed metal powders. Pressing is accomplished within a vacuum-tight container, and pelleting pressures of approximately 10,000 p. s. i. to 20,000 p. s. i. have been used, with 14,000 p. s. i. normally being adequate.

Sufficient strength to make the pressed metal rod self-supporting is imparted by sintering the

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rod in vacuum at a temperature of approximately 2400° F. to 2900° F. for approximately a quarter of a minute to several minutes. Sintering may be accomplished by any well-known method of heating. Electrical resistance heating has been employed successfully.

The sintered rod is then used as a consumable electrode in a vacuum arc furnace. Melting is started by striking an arc between the rod and a starting electrode comprising a pile of chips of the same or similar alloy placed on a disc of molybdenum at the bottom of the casting mold. A water-cooled copper mold has been successfully used for receiving the molten molybdenum alloy without contaminating the alloy with copper. Molten alloy striking the water-cooled copper mold quickly solidifies, forming a protective coating on the surface of the mold. Thereafter, the liquid alloy becomes the lower electrode and the upper, consumable electrode is mechanically fed toward the lower, liquid electrode to maintain continuous melting with the proper arc spacing.

For steps 2, 3 and 4, the pressure within the container should be as low as possible and should not exceed a maximum of 500 microns, and preferably should be below 100 microns. All three of these steps may be carried out in the same container.

If aluminum or beryllium or any other relatively volatile element is employed in the alloy, the above-described process cannot be practiced under the degree of vacuum set forth above and hence it is necessary to employ an inert atmosphere of higher pressure in the melting chamber. An argon or helium atmosphere at or slightly above atmospheric pressure has been found suitable for this purpose. Except for the change from vacuum to an inert atmosphere at higher pressure, the process previously described may be used. The desired quantities of aluminum or beryllium are added to the mixture of metal powders which are sintered to produce the consumable electrode.

Inasmuch as extremely minute quantities of oxygen impair the capacity of the alloy casting to be worked at elevated temperatures, the starting materials should be as low in oxygen as possible and it is necessary to avoid the introduction of significant amounts of oxygen as a contaminant in the inert atmosphere. The inert atmosphere may be purified by circulating it through a commercial drying tower before introduction into the casting container. The gas may be re-circulated or re-used after passing over a bed of titanium metal maintained at approximately 1500° F. and a bed of magnesium metal maintained at approximately 1100° F. Because of the relatively high volatility of aluminum and beryllium at the arc temperature, the pressure of the inert atmosphere within the casting container is preferably maintained at substantially atmospheric pressure or slightly above, for example, up to about 15.5 pounds per square inch. The casting container is first evacuated and then flushed with the inert gas; and, during operation, the inert gas is bled into the casting container to maintain atmospheric pressure or slightly above.

If carbon is employed in addition to aluminum or beryllium, the partial pressure of carbon monoxide in the melting chamber should be maintained below about 100 microns. In some cases, this may require a flow of the purified inert gas through the chamber.

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One suitable form of apparatus for use in forming, sintering and melting the powder rod is disclosed in the copending application of Edgar K. Leavenworth, Serial No. 787,797, filed November 24, 1947, now Patent No. 2,651,952, issued September 15, 1953.

All of the proportions given herein are proportions by weight in the final alloy.

What is claimed is:

1. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures and its high strength in a worked condition at elevated temperatures, said alloy containing from .25% to 7% vanadium, from .003% to .4% aluminum, from zero to .02% carbon, oxygen less than .02%, and the balance consisting of molybdenum.

2. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures, said alloy containing from .25% to 7% vanadium; from .003% to .4% aluminum; from zero to .02% carbon; oxygen less than .02%; metal from the group consisting of the transition elements titanium from zero to 14%, chromium from zero to 2%, iron from zero to 1.3%, cobalt from zero to .9%, nickel from zero to .4%, zirconium from zero to 2%, columbium from zero to 10%, tantalum from zero to 9%, and tungsten from zero to 10%, the total amount of metal from said group of transition elements being further limited to an amount within the range from none to the amount which will increase the hardness of the annealed casting to a value not exceeding 200 V. P. N. at 1600° F.; and the balance consisting of molybdenum.

3. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures, said alloy containing from .25% to 7% vanadium; at least one element from the group consisting of carbon from .01% to .25%, aluminum from .003% to 2.5% and beryllium from .001% to .25%; metal from the group consisting of the transition elements titanium from zero to 14%, chromium from zero to 2%, iron from zero to 1.3%, cobalt from zero to .9%, nickel from zero to .4%, zirconium from zero to 2%, columbium from zero to 10%, tantalum from zero to 9%, and tungsten from zero to 10%, the total amount of metal from said group of transition elements being further limited to an amount within the range from none to the amount which will increase the hardness of the annealed casting to a value not exceeding 200 V. P. N. at 1600° F.; and the balance consisting of molybdenum.

4. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, carbon from .01% to .25%, oxygen not more than .005%, and the balance consisting of molybdenum.

5. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, oxygen not more than .05%, aluminum in an amount at least sufficient to react with all of the oxygen present and not more than 2.5%, the maximum amount of aluminum within the range stated being reduced toward .4% as the amount of vanadium approaches its upper limit, and the balance consisting of molybdenum.

6. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium,

oxygen not more than .05%, beryllium in an amount at least sufficient to react with all of the oxygen present and not more than .25%, the maximum amount of beryllium within range stated being reduced toward .03% as the amount of vanadium approaches its upper limit, and the balance consisting of molybdenum.

7. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures, said alloy casting containing from .25 to 7% vanadium, carbon from .01% to .25%, oxygen not more than .005%, metal from the group consisting of the transition elements titanium from zero to 14%, chromium from zero to 2%, iron from zero to 1.3%, cobalt from zero to .9%, nickel from zero to .4%, zirconium from zero to 2%, columbium from zero to 10%, tantalum from zero to 9%, and tungsten from zero to 10%, the total amount of metal from said group of transition elements being further limited to an amount within the range from none to the amount which will increase the hardness of the annealed casting to a value not exceeding 200 V. P. N. at 1600° F., and the balance consisting of molybdenum.

8. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, oxygen not more than .05%, aluminum in an amount at least sufficient to react with all of the oxygen present and not more than 2.5%, the maximum amount of aluminum within the range stated being reduced toward .04% as the amount of vanadium approaches its upper limit, metal from the group consisting of the transition elements titanium from zero to 14%, chromium from zero to 2%, iron from zero to 1.3%, cobalt from zero to .9%, nickel from zero to .4%, zirconium from zero to 2%, columbium from zero to 10%, tantalum from zero to 9%, and tungsten from zero to 10%, the total amount of metal from said group of transition elements being further limited to an amount within the range from none to the amount which will increase the hardness of the annealed casting to a value not exceeding 200 V. P. N. at 1600° F., and the balance consisting of molybdenum.

9. A cast alloy consisting of at least 85% molybdenum and characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, oxygen not more than .05%, beryllium in an amount at least sufficient to react with all of the oxygen present and not more than .25%, the maximum amount of beryllium within the range stated being reduced toward .03% as the amount of vanadium approaches its upper limit, metal from the group consisting of the transition ele-

ments titanium from zero to 14%, chromium from zero to 2%, iron from zero to 1.3%, cobalt from zero to .9%, nickel from zero to .4%, zirconium from zero to 2%, columbium from zero to 10%, tantalum from zero to 9%, and tungsten from zero to 10%, the total amount of metal from said group of transition elements being further limited to an amount within the range from none to the amount which will increase the hardness of the annealed casting to a value not exceeding 200 V. P. N. at 1600° F., and the balance consisting of molybdenum.

10. A cast, molybdenum-base alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, carbon from .01% to .07%, oxygen not more than .003%, and the balance consisting of molybdenum.

11. A cast, molybdenum-base alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, aluminum from .003% to .4%, carbon not more than .06%, oxygen not more than .05%, the minimum amount of aluminum within the range stated being that required to combine with all of the oxygen in the alloy to form aluminum oxide, and the balance consisting of molybdenum.

12. A cast, molybdenum-base alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting comprising from .25% to 7% vanadium, beryllium from .001% to .03%, carbon not more than .06%, oxygen not more than .05%, the minimum amount of beryllium within the range stated being that required to combine with all of the oxygen in the alloy to form beryllium oxide, and the balance consisting of molybdenum.

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