

1

2,960,403

**MOLYBDENUM-BASE ALLOYS**

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The present invention relates to cast molybdenum-base alloys; and this application is a continuation in part of copending application, Serial No. 551,227, filed December 6, 1955, now abandoned.

It is the object of the present invention to provide cast molybdenum-base alloys of great strength at elevated temperatures and which are easier to work at elevated temperatures than previously known alloys having comparable resistance to creep under stress in the temperature range of 1800° F. to 2000° F. or have even higher strengths or creep resistance in the temperature range of 1600° F. to 2000° F. The invention is limited to alloys which may be hot worked and are produced by casting, i.e., melting the metal and allowing it to solidify in a mold. In general, cast molybdenum-base alloys, after working, are known to have properties distinctly different from wrought alloys of similar composition produced by sintering powdered materials.

It has been known that the addition of relatively small amounts of a number of alloying elements to molybdenum increases its hardness and strength, the effect being due to a solution hardness which increases up to some limit with the amount of the element added. Among elements having this effect are: zirconium, titanium, niobium, vanadium and cobalt. However, when these elements are added to molybdenum castings, the resulting alloy becomes increasingly more difficult to work as the amount of the addition increases; and this difficulty places practical limits on the amount which may be added. Conversely, the solution hardness and added strength decrease as the amount of added element is reduced until the minimum amounts which in the past have been considered beneficial are approximately .1% zirconium, .25% titanium, .25% niobium or .25% vanadium; see United States Patents Nos. 2,678,268, 2,678,269, 2,678,271, and 2,678,272. Molybdenum-base alloys containing certain of these elements, particularly zirconium and titanium, in amounts at or above the stated minimums, have evidenced remarkable tensile strength and resistance to creep under stress at temperatures of 1600° F. or higher, but it has hitherto been supposed that these high temperature properties were related to solution hardness and would increase with increasing alloy additions.

In accordance with the present invention, it has been discovered that exceptional high temperature properties may be imparted to molybdenum by the addition of

2

amounts of zirconium substantially less than those hitherto thought to be the minimum useful amount. It has been found also that very small amounts of titanium, cobalt, niobium or vanadium will, when combined with the zirconium addition, effect a further improvement in the high temperature properties. Moreover, these new cast alloys are more easily worked at elevated temperatures than other alloys of comparable strength at temperatures in the range of 1600° F. to 2000° F. or have higher strength in that temperature range than previously known materials.

The molybdenum-base alloys of the present invention contain from about .01% to .08% zirconium and preferably contain small quantities of carbon. They are produced by arc casting in vacuum, preferably using a furnace of the type disclosed in United States Patent No. 2,656,743. Carbon may be added to the extent necessary to control the oxygen content of the final casting plus a sufficient excess to leave a small residual carbon content. While the casting may contain as much as .005% oxygen and as much as .25% carbon, the preferred alloys contain not more than .0015% oxygen and from about .01% to about .04% carbon. The specific alloys referred to hereinafter were prepared by mixing powdered molybdenum and zirconium sponge with carbon and other specified elements and arc melting the mixture at an absolute pressure of about 20 to 30 microns of mercury. The molybdenum powder should contain not more than .05% oxygen and preferably less than .03%. The specific alloys referred to herein were made from molybdenum powder which ranged in oxygen content from .012% to .029%, while the zirconium sponge contained less than .2% oxygen.

The present invention contemplates two classes of alloys: first, those in which the sole alloying metal addition is zirconium, the balance of the alloy being molybdenum and minute and unavoidable amounts of impurities; and, second, those in which small amounts of other metals are added to enhance or supplement the effect of zirconium.

Specific examples of the improved cast alloys in which zirconium is the sole metal added to the molybdenum include the following:

	A	B	C	D	E
Zirconium.....	Percent .013	Percent .027	Percent .03	Percent .054	Percent .08
Oxygen.....	.001	.001	.001	.001	.001
(Added).....	.033	.026	.033	.027	.036
Carbon.....					
(Retained).....	.024	.009	.020	.018	.019
Molybdenum.....	balance	balance	balance	balance	balance

The unexpected properties of the above class of alloys can be shown by the following comparison of the properties of Examples A, B and D above, with a similar molybdenum-base alloy containing about .09% zirconium (just below the previously considered minimum useful amount) and unalloyed molybdenum.

	Alloy A .013% Zirconium	Alloy B .027% Zirconium	Alloy D .054% Zirconium	.09% Zirconium	Unalloyed Molybdenum
Room temp. hardness as cast, V.P.N.	180	172	168	187	180
Room temp. tensile-wrought, #/sq. in.	108,900	119,400	126,400	125,900	97,200
Short time tensile strength at 1,600° F., #/sq. in.	71,500	82,100	74,700	79,000	52,400
Stress required to rupture in 100 hrs. at 1,800° F., #/sq. in.	47,000	58,000	62,000	56,000	22,000
Stress required to rupture in 100 hrs. at 2,000° F., #/sq. in.	30,000	34,000	30,000	39,000	13,000
Yield of sound stock, percent	66.5	69.4	49.4	36.2	59
Tensile transition temperature range, ° F.	-54 to -20	-46 to -25	+10 to +15		+20 to +32
Recrystallization temperature, ° F.	2,450	2,500	2,520	2,700	2,150

3

The above data on stress rupture were obtained by creep-rupture tests of  $\frac{1}{2}$ " and  $\frac{3}{8}$ " bars in vacuum. The castings were initially machined to cylinders ranging in diameter from 4" to 6 $\frac{1}{2}$ " and then extruded at 2300° F. or 2600° F. to effect a substantial reduction in diameter. The extruded sections were fully recrystallized and then rolled at 2250° F.-2400° F. until reduced to the  $\frac{1}{2}$ " or  $\frac{3}{8}$ " diameter bars. This treatment imparted considerable work hardness and the tensile strengths, stress rupture data and transition temperature data given above were obtained on the rolled bars after they had been stress relieved by holding them for one hour at 2000° F. (1800° F. for alloy D, the .09% zirconium, and the unalloyed molybdenum). The working treatment results in considerable loss due to the necessity of cropping end bursts, etc., and an important advantage of alloys A and B over the .09% zirconium alloy resided in the fact that they yielded a much higher percentage of recovery of sound stock. The work hardness is retained during the creep-rupture test due to the high recrystallization temperature.

A further important advantage of the alloys which contain zirconium in amounts near the lower limit of the range given is that they have a lower tensile transition temperature range. This is the temperature range below which the alloys are brittle.

The fact that alloys A and B, containing only .013% and .027% zirconium, were about as strong as the .09% zirconium alloy in short time tensile at 1600° F. and were comparable in stress rupture properties at 1800° F. and 2000° F. is quite surprising. In addition, they yielded much better recovery on forging, and had a markedly lower transition temperature range.

The best results have been attained when the castings of the present invention contain small amounts of carbon. Increases in the carbon content appear to increase the recrystallization temperature and reduce the yield on working. Accordingly, the carbon content may range from about .01% to .25% but preferably falls between about .01% and about .04%.

The above alloys of the first class fall in two groups, those containing from about .01% to about .03% zirconium, which are notable for their high yields on working and which have excellent high temperature properties, and those containing from .03% to .08% zirconium which have greater strength in a worked condition but are more difficult to work.

In addition to the above alloys, it is found that at a sacrifice of forging recovery even greater strength may be obtained by combining, with from .01% to .08% zirconium, any one of the following alloying metals: titanium from .1% to .22%; cobalt from .02% to .2%; niobium from .25% to 1%; and vanadium from .25% to 1%. The following are specific examples of such alloys:

	F	G	H	I	J	K	L	M
Zirconium.....percent.....	.05	.08	.07	.04	.06	.08	.04	.06
Titanium.....do.....	.18	.22						
Cobalt.....do.....			.06	.15				
Niobium.....do.....					.50	.25		
Vanadium.....do.....							.75	.50
Carbon.....do.....	.015	.024	.027	.022	.024	.025	.03	.02
Molybdenum.....do.....	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

The above alloys must also contain less than .005% oxygen and preferably less than .0015%. The carbon content should range between about .01% and .25% and is preferably between about .01% and about .04%.

4

The following representative data indicate the properties of certain of the above alloys:

Alloy	Short time tensile strength, #/sq. in. at 1,600° F.	Stress in #/sq. in. to rupture in 100 hrs. at—	
		1,800° F.	2,000° F.
G.....	86,100	66,000	50,000
H.....	92,600	60,000	34,000
J.....	85,300	63,000	40,000

So far as applicants can ascertain, alloy G has exceptional 100-hour strength at both 1800° F. and 2000° F., and alloy H is one of the strongest known materials for short time use at 1600° F., and alloys A, B and C yield a greater percentage of recovery of sound stock on hot working than any alloy which so nearly approaches the 100-hour strength at 1800° F. of alloy G. The data given above are the result of tests in vacuum of stress relieved specimens prepared and worked in the manner previously described.

What is claimed is:

1. A cast molybdenum-base alloy containing from about .01% to .08% zirconium, not more than .005% oxygen, not more than .25% carbon, and a metal from the group consisting of titanium up to a maximum of .22%, cobalt up to a maximum of .2%, niobium up to a maximum of 1% and vanadium up to a maximum of 1%, the balance consisting essentially of molybdenum.
2. A cast molybdenum-base alloy containing from about .01% to .08% zirconium, not more than .005% oxygen, from about .01% to about .25% carbon, and a metal from the group consisting of titanium from .1% to .22%, cobalt from .02% to .2%, niobium from .25% to 1%, and vanadium from .25% to 1%, the balance consisting essentially of molybdenum.
3. A cast molybdenum-base alloy containing from about .01% to .08% zirconium, from .01% to .25% carbon, not more than .005% oxygen, and the balance consisting essentially of molybdenum.
4. A cast molybdenum-base alloy containing from about .03% to .08% zirconium, not more than .005% oxygen, not more than .04% carbon, and a metal from the group consisting of titanium from .1% to .22%, cobalt from .02% to .2%, niobium from .25% to 1%, and vanadium from .25% to 1%, the balance consisting essentially of molybdenum.
5. A cast molybdenum-base alloy containing from about .03% to .08% zirconium, not more than .25% carbon, and the balance consisting essentially of molybdenum.
6. A cast molybdenum-base alloy containing from about .03% to .08% zirconium, from about .01% to about .25% carbon, not more than .005% oxygen, and the balance consisting essentially of molybdenum.
7. A cast molybdenum-base alloy containing from

about .01% to about .03% zirconium, not more than .005% oxygen, from about .01% to about .04% carbon, and a metal from the group consisting of titanium from .1% to .22%, cobalt from .02% to .2%, niobium from

5

.25% to 1%, and vanadium from .25% to 1%, the balance consisting essentially of molybdenum.

8. A cast molybdenum-base alloy containing from about .01 to about .03% zirconium, not more than .25% carbon, and the balance consisting essentially of molybdenum.

9. A cast molybdenum-base alloy containing from about .01% to about .03% zirconium, from about .01% to about .04% carbon, and the balance consisting essentially of molybdenum.

5

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10

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6

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