

1

3,177,076

FORGEABLE HIGH TEMPERATURE CAST ALLOYS
George A. Timmons, Ferndale, and Marion Semchyszen,
Dearborn, Mich., assignors to American Metal Climax,
Inc., New York, N.Y., a corporation of New York
No Drawing. Filed June 12, 1961, Ser. No. 116,251
8 Claims. (Cl. 75-176)

This application is a continuation-in-part of application Serial No. 30,773, filed May 23, 1960, and now abandoned.

The present invention relates to molybdenum and/or tungsten base alloy castings which are capable of being worked at elevated temperatures and methods of making same.

In the past, the preferred method of making forgeable castings of molybdenum and tungsten has involved the addition of small quantities of carbon and the melting of the material in vacuum. For some purposes, carbon additions may be undesirable and the present invention resides in the discovery that boron may be substituted for carbon with similar results. Moreover, while vacuum melting is preferred, it is not essential when boron is used in lieu of carbon. Finally, it has been found that alloys containing more than 50% tungsten are more easily worked and provide larger percentages of sound stock recovery on working than similar alloys containing carbon in lieu of boron.

The alloy castings of the present invention comprise alloys consisting primarily of molybdenum or tungsten or combinations of the two in any desired proportions. In accordance with the present invention, the castings are made by melting powders, chips or particles of the metals in combination with small quantities of boron in vacuum or an inert atmosphere such as argon.

The preferred method involves melting the metal in a vacuum preferably at an absolute pressure less than 100 microns of mercury. The boron is believed to combine with any oxygen present in the metal to form B₂O₃, which is gaseous at the melting temperatures. Therefore, it is extracted from the melting and melted material at a higher rate in a vacuum than would be the case if an inert atmosphere at a higher absolute pressure were employed. One of the most effective methods of achieving such a melting operation is in a consumable electrode arc furnace, one such furnace suitable for the purpose being disclosed in United States Patent 2,656,743. When this type of equipment is used the electrode is formed by sintering the powder or chips of metal constituting the charge. Another method which may be employed is to melt the material by an electron beam in a very high vacuum. In either case the molten material is collected in a water-cooled copper mold.

The molybdenum or tungsten powder, chips or particles should contain as little oxygen as possible and preferably include not more than .05% oxygen, including oxygen which is both combined and adsorbed. Sufficient boron is added to combine with all of the combined oxygen and leave some residual excess in the final product. For this purpose, the final product should contain from .005% to .50% boron and preferably not more than .005% oxygen.

It is known that the properties of molybdenum and tungsten castings may be improved by the addition of small quantities of other transition elements, and therefore the present invention is applicable also to molybdenum or tungsten alloys which contain such additions. Thus, the alloys of the present invention may contain

2

minor quantities of one or more of the elements titanium, zirconium, tantalum, vanadium, columbium, chromium, iron, cobalt, nickel and hafnium. However, these elements increase the hardness of the alloy and therefore may be used, but in amounts not exceeding the following percentages if the alloy is to be worked:

	Percent
Titanium -----	14
Zirconium -----	2
Tantalum -----	9
Vanadium -----	7
Columbium -----	10
Chromium -----	2
Iron -----	1.3
Cobalt -----	.9
Nickel -----	.4
Hafnium -----	12

The effect of all of the above listed elements on hot hardness is additive and, therefore, when two are present the maximum quantity of one is preferably reduced from the maximum given in the above list in proportion to the extent that the other approaches its maximum. Still further reductions on the same basis are preferably made if more than two are present. In all cases, less than the maximum values thus determined is preferred where it is important to achieve a high percentage of recovery of sound stock on working.

In the absence of carbon, a minimum residual quantity of about .005% boron is required to obtain a workable alloy. For this purpose, it should be noted that at the level of .005% boron, the methods of analysis employed by applicants are subject to a possible error of plus or minus .002%, and therefore the useful minimum may be as low as .003% boron. Larger quantities in the range of .02% to .50% have a significant grain-refining effect and may be employed for that purpose, if desired. When hafnium, zirconium or titanium are present, maximum strength is obtained if the residual boron is about one-tenth by weight of the total of those three elements present and therefore where strength is a major consideration the quantity of residual boron may be increased to that value. If no hafnium, zirconium or titanium is present it is preferred to keep the boron content below .05% because the advantage of grain refinement obtained with larger quantities is for most purposes offset by an increase in the brittle to ductile transition temperature.

A particularly valuable class of alloys coming within the scope of the present invention is tungsten base alloys containing boron within the limits stated and from about 2½% to 35% molybdenum. These are particularly useful for applications in which an alloy is required which will evidence great strength at temperatures in the range of 2400° F. to 4000° F. As compared with similar alloys prepared with carbon in place of boron, this class of alloys is more readily worked. This class of tungsten base, molybdenum-containing alloys has finer grain, greater strength and hardness at 2400° F. than tungsten-boron alloys of the present invention which contain no molybdenum but are otherwise similar, and when the molybdenum content exceeds about 10%, they are easier to machine and have higher recrystallization temperatures. The hardness and strength of this class of alloys at elevated temperatures may be further increased by one or more of the elements hafnium, zirconium, tantalum and columbium.

In the case of alloys containing about 65% or more tungsten, it is preferred to keep the boron content in the

range of .005% to .015%, except where hafnium or zirconium are present in which event the boron may be increased up to about one-tenth by weight of the total of those two elements. Larger quantities of boron may be employed but they increase the brittle to ductile transition temperature which may be objectionable for some purposes. While grain refinement is obtained with larger quantities of boron, it is usually preferable to employ molybdenum for grain refinement where the tungsten content exceeds 65%.

Therefore, special advantages at very high temperatures are achieved with a class of alloys ranging from 2½% to 35% molybdenum, about .004% to .05% boron, and the balance consisting essentially of tungsten. If desired and to increase high temperature strength, there may be added one or more elements from the group consisting of hafnium, zirconium, tantalum and columbium, in which event the amount of boron may be increased to a value as high as one-tenth the total weight of hafnium and zirconium. For this purpose, the amount of each of the elements in the above group may range up to the maximum quantities given in the foregoing table, but where ease of working is important, it is preferred that the amounts fall within the range of .10% to 2% hafnium, .01% to .50% zirconium, .10% to 1.50% tantalum, and .10% to 2% columbium.

Another class of alloys having excellent high temperature strength characteristics, but at slightly lower temperatures than the first class, are those containing from zero to 35% tungsten, .004% to .50% boron, and the balance consisting essentially of molybdenum. In this class, the boron in excess of about .02% performs a desirable grain-refining function. If desired, and to increase high temperature strength, there may be added to this second class of alloys one or more elements from the group consisting of titanium, zirconium, tantalum, vanadium, columbium, chromium, iron, cobalt, nickel and hafnium in amounts not exceeding those given in the foregoing table. If hafnium, titanium or zirconium are present, maximum strength is obtained if the quantity of boron is increased up to about one-tenth by weight of the total of those three elements present. To facilitate working, the preferred alloying elements from the last mentioned group and the maximum permissible quantity of each are: hafnium from .10% to 2%; titanium from .15% to 3%; zirconium from .01% to .50%; tantalum from .10% to 2%; and columbium from .10% to 2%.

Examples of alloys coming within the scope of the present invention include the following:

Example No.	Molybdenum, percent	Tungsten, percent	Boron, percent	Carbon, percent	Other Elements, percent
1	Bal.		.010		
2	Bal.		.300		
3	Bal.		.030	.001	1.18 Ti
4	Bal.		.074	.001	1.43 Ti
5	Bal.		.180	.011	1.28 Ti
6	Bal.		.140	.130	1.28 Ti
7	Bal.		.050	.063	1.25 Ti
8	Bal.		.025	.002	.05 Zr
9	66.2	Bal.	.004	.001	.043 Zr
10	66.4	Bal.	.020	.001	.43 Ti
11	Bal.	50.0	.013	.001	
12	Bal.	50.0	.020		
13	Bal.	50.0	.015	.003	
14	31.1	Bal.	.010	.001	
15	Bal.	67.0	.016	.010	.055 Zr
16	30.3	Bal.	.020	.004	.14 Ti
17	15.2	Bal.	.010	.004	
18	14.2	Bal.	.010	.006	.039 Zr
19	15.1	Bal.	.010	.004	.43 Cb
20	Bal.	74.0	.100		1.00 Hf
21	Bal.	84.7	.030		.30 Zr
22	Bal.	78.4	.600		6.00 Ta
23	Bal.	74.0	1.00		10.00 Cb
24	Bal.	90.0	.01		
25	Bal.	97.0	.01		
26		Bal.	.012	.001	
27		Bal.	.01		.50 Ti
28		Bal.	.015	.009	.05 Zr
29		Bal.	.015	.007	.25 Hf
30		Bal.	.03		.30 Hf

The high tensile strength of representative examples of the above alloys at 2400° F. may be seen from the following table:

Example	Tensile Strength, Lbs./Sq. In.	
	Stress Relieved	Recrystallized
4	24,400	
9	53,900	27,000
14	59,300	31,000
16	48,400	28,400
19	53,300	35,600

The advantage which results from increasing the boron content when titanium is present is indicated by the fact that the alloys of Examples 3, 4 and 5 had the following short-time tensile strength in pounds per square inch at 1600° F. in a fully recrystallized condition.

Example:	Tensile strength
3	28,700
4	42,200
5	53,000

This shows that as the boron content approaches about one-tenth the titanium content, the high temperature strength increases. In a stress relieved condition, these alloys are stronger and the same relationship prevails. Thus, Example 5 had a tensile strength at 1600° F. in a stress relieved condition of 82,100 pounds per square inch, as compared with 45,300 pounds per square inch for Example 3 under the same conditions.

While, as previously indicated, the presence of about .004% residual boron or more makes it unnecessary to employ the .01% or more of carbon which would otherwise be required to obtain a workable alloy, it will be appreciated that traces of carbon in the order of .005% or less are often found in these metals and that such quantities may be present without deleterious effects. While it is preferred that the alloys of the present invention contain less than .01% carbon, larger quantities may be present without loss of some of the advantages of the invention, and this is particularly so in the case of alloys containing hafnium, zirconium or titanium.

Alloys made in accordance with the foregoing may be worked by extrusion, hammering and rolling. The critical stage in working is the initial breakdown which is preferably done by extrusion at temperature in the range of 2300° F. to 3400° F. At the higher temperatures, alloy steel extrusion dies lined with aluminum oxide or zirconium oxide have proven useful. After initial breakdown, further working to bars, rods or sheets presents less difficulty.

What is claimed is:

1. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting containing from .005% to .50% boron, at least one metal from the group consisting of titanium up to 14%, zirconium up to 2%, tantalum up to 9%, columbium up to 10%, and hafnium up to 12%, and the balance consisting essentially of metal from the group consisting of molybdenum and tungsten and mixtures thereof.

2. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting containing from .005% to .50% boron, at least one metal from the group consisting of titanium up to 14%, zirconium up to 2%, tantalum up to 9%, columbium up to 10%, and hafnium up to 12%, and the balance consisting essentially of molybdenum.

3. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy casting containing at least one metal from the group consisting of titanium up to 14%, zirconium up to 2%, tantalum up to 9%, hafnium up to 12%, columbium up to 10%, said casting also including boron within the range from about

.005% to the larger of the values .50% and about one-tenth of the total quantity of titanium, zirconium and hafnium present, and the balance consisting essentially of at least one metal from the group consisting of molybdenum and tungsten.

4. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy containing from 2½% to 35% molybdenum, about .005% to .05% boron, and the balance consisting essentially of tungsten.

5. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy containing from 2½% to 35% molybdenum, at least one metal from the group consisting of hafnium up to 12%, titanium up to 14%, zirconium up to 2%, tantalum up to 9%, columbium up to 10%, said casting also containing boron in an amount between about .005% and the larger of the values .50% and one-tenth of the total quantity of titanium, hafnium and zirconium present, and the balance consisting essentially of tungsten.

6. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy containing from 2½% to 35% molybdenum, at least one metal from the group consisting of hafnium from .10% to 2%, titanium from .15% to 3%, zirconium from .01% to .50%, tantalum from .10% to 1.50%, columbium from .10% to 2%, said casting also containing boron in an amount between about .005% and the larger of the values .05% and one-tenth of the total quantity of titanium, hafnium and zirconium present, and the balance consisting essentially of tungsten.

7. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy containing at least one metal from the group consisting of hafnium from .10% to 2%, titanium from .15% to 3%, zirconium from .01% to .50%, tantalum from .10% to 2%, columbium from .10% to 2%, said casting also containing boron in an amount between about .005% and the larger of the values .50% and one-tenth of the total quantity of hafnium, titanium and zirconium present, and the bal-

ance of said casting consisting essentially of molybdenum.

8. A cast alloy characterized by its capacity to be worked at elevated temperatures, said alloy containing at least one metal from the group consisting of hafnium from .10% to 2%, titanium from .15% to 3%, zirconium from .01% to .50%, tantalum from .10% to 2%, columbium from .10% to 2%, said casting also containing boron in an amount between about .005% and the larger of the values .50% and one-tenth of the total quantity of hafnium, titanium and zirconium present, and the balance of said casting consisting of molybdenum and tungsten with the tungsten content not exceeding 35%.

References Cited by the Examiner

UNITED STATES PATENTS

1,774,849	9/30	Schroter	75—176
2,163,354	6/39	Schmidt et al.	75—176
2,188,405	1/40	Hensel et al.	75—176
2,234,969	3/41	Hensel et al.	75—176 X
2,253,533	8/41	Ruben	75—176 X
2,580,273	12/51	Bens et al.	75—176
2,678,269	5/54	Ham et al.	75—176

FOREIGN PATENTS

408,662	4/34	Great Britain.
584,289	1/47	Great Britain.

OTHER REFERENCES

Institute of Metals, Journal, vol. 82, Bulletin No. 2, September 1953—August 1954 (pages 361—373).

Arc-Cast Molybdenum Base Alloys, Project No. O31—331, First Annual Report, April 1, 1950, by Climax Molybdenum Co. of Michigan, pages 28—30.

DAVID L. RECK, *Primary Examiner.*

MARCUS U. LYONS, WINSTON A. DOUGLAS,
Examiners.