

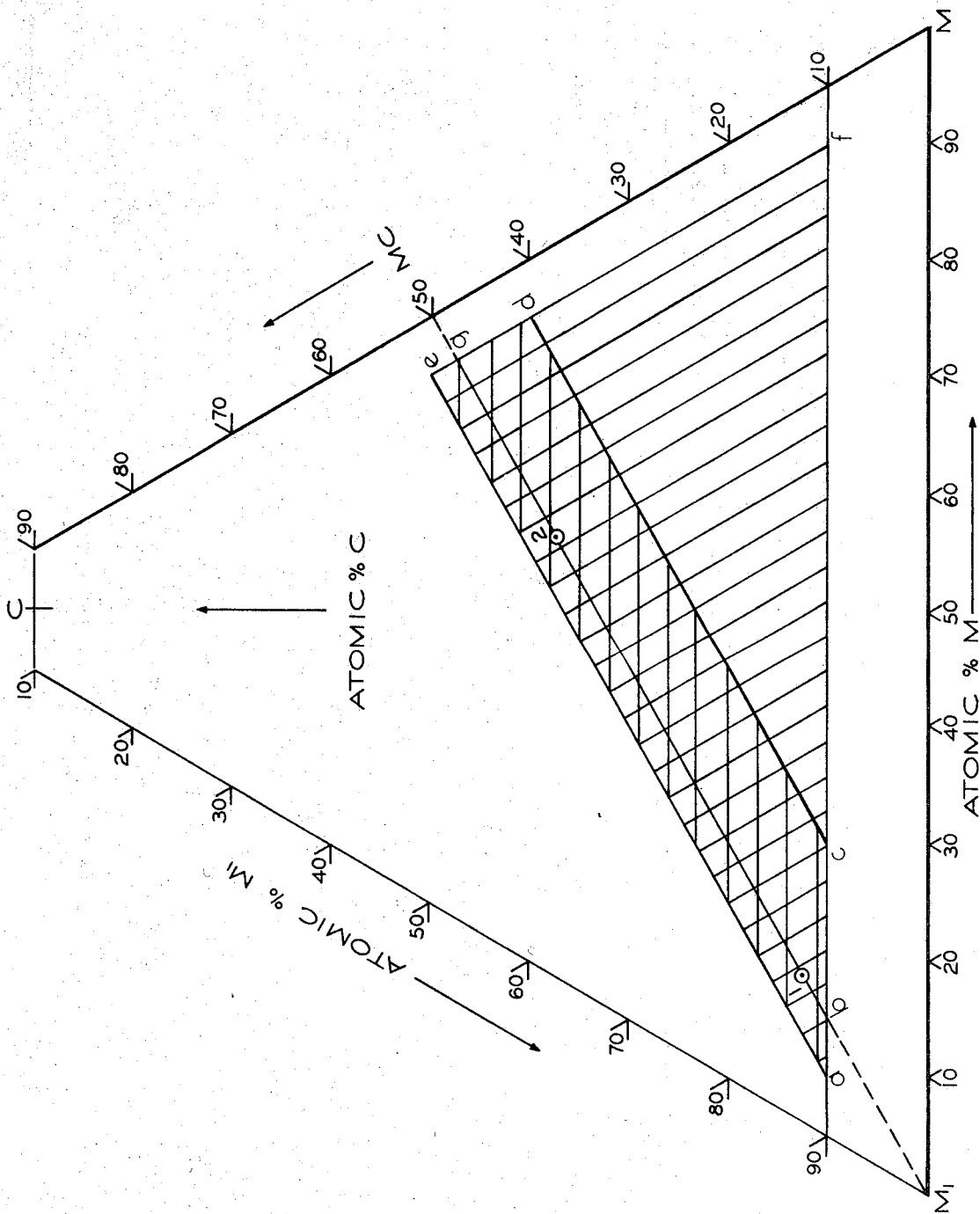
Jan. 12, 1971

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3,554,737

CAST REFRACTORY ALLOY

Filed May 21, 1968



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CAST REFRACTORY ALLOY

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Continuation-in-part of application Ser. No. 503,759, Oct. 22, 1965. This application May 21, 1968, Ser. No. 730,690

Int. Cl. C22c 15/00, 27/00

U.S. Cl. 75—134

15 Claims

ABSTRACT OF THE DISCLOSURE

Cast refractory alloys of at least one metal selected from the group of tungsten, molybdenum, chromium, and rhenium, at least one metal selected from the group titanium, hafnium and tantalum, and carbon, the W, Mo, Cr, or Re being present in amounts of from about 5 to about 85 atomic percent, the Ti, Hf, and Ta being present in amounts of from about 5 to about 85 atomic percent and the carbon being present in amounts of from about 10 to about 50.0 atomic percent have been found to form eutectic structures that provide surprisingly high strength properties at elevated temperatures. Alloys consisting essentially of at least one metal selected from the group tungsten, chromium and rhenium, zirconium and carbon within corresponding ranges also have been found to have unexpected high temperature strength properties.

PARENT APPLICATIONS

This application is a continuation-in-part patent application to application Ser. No. 503,759, filed Oct. 22, 1965, now abandoned, entitled "Cast Refractory Alloy," Ellis L. Foster et al.

BACKGROUND

This invention relates to the discovery of new and novel cast refractory alloys comprising at least one metal selected from the group tungsten, molybdenum, chromium, and rhenium, at least one metal selected from the group titanium, hafnium and tantalum, and carbon. Additional new alloys having corresponding properties comprise at least one metal selected from the group tungsten, chromium and rhenium, carbon, and zirconium.

The Group VIa metals and Group IVa metals (which include all of the metals of the present alloys with the exception of rhenium and tantalum) are well known for their refractory properties (melting points greater than 3000° F.). As a result, they have been used widely in applications where materials are placed in high-temperature environments. Heretofore the elevated temperature properties of the above-mentioned refractory metals have been further improved by alloying with another metal or by dispersion strengthening. Although notable in providing improved properties, alloying generally results in a lowering of the melting point of the metal and thus limits the upper limit of temperature to which it may be used. Dispersion strengthening overcomes the limitation of lowered melting point inherent in alloying. By this latter method, a uniform dispersed phase such as a refractory oxide or carbide is provided throughout the matrix of refractory metal. To make a dispersion strengthened alloy, it has hitherto been necessary to use complex fabrication procedures to: (1) obtain a uniform mixture of dispersoid in the matrix; (2) retain small particle size of the dispersoid and; (3) achieve adequate densification of the product.

Although a sacrifice in melting point can be eliminated upon using a dispersion strengthened material, the same is not amenable to the simpler melting and casting pro-

cedures used for materials strengthened by alloying. As the need for improved refractory metals in aircraft, turbines, rockets, furnaces, and the like continues, further attempts have been made to obviate the above-mentioned and related difficulties attendant upon the prior art but none have been entirely successful.

Although the dispersion strengthened materials possess unusually high resistance to stress at elevated temperatures, such properties in these compositions tend to deteriorate after long time exposure to such high temperatures. In many of the aforementioned applications the metals and alloys must be capable of repeated or indefinite exposure to stress at elevated temperatures. In these instances the highest reliable resistance to stress consists of the lowest resistance offered by the materials after extended exposure to elevated temperatures. Thus, although many of the dispersion strengthened materials exhibit high initial resistance to stress and some retain such properties for relatively extended periods of time at such elevated temperatures, they fail in many instances to provide the desired or required long time high temperature resistance to externally applied stress.

THE INVENTION

We have found that cast refractory alloys comprising from about 5 to 85 atomic percent tungsten, molybdenum, chromium, rhenium, or combinations thereof, about 5 to 85 atomic percent titanium, hafnium, and tantalum, and about 10 to 50.0 atomic percent carbon provide stress resistance properties at elevated temperatures that are substantially equivalent to the high initial elevated temperature stress resistance qualities of the dispersion strengthened alloys but which retain these high temperature properties for either an indefinite period of time or for a period of time exceeding that expected of dispersion strengthened alloys. We have also found that equivalent stress resistance properties are demonstrated by alloys comprising tungsten, chromium, rhenium, and combinations thereof, in the range above specified, from about 5 to 85 atomic percent zirconium and carbon in the range above specified.

We have found that cast compositions falling within the area *a*, *e*, *f*, of the diagram of the drawing possess a generally eutectic structure. It is our contention that not only does this eutectic structure provide unexpected high temperature resistance to compressive stress that is substantially equivalent to the dispersion strengthened materials but also that it is surprisingly stable so as to provide the high resistance to compressive stress at elevated temperatures over extended periods of time.

Our new alloys may be employed as test blocks for elevated temperature compressive tests. Testing is effected by applying a high compressive force to the specimen pushing it against the block. Long time high temperature tests have showed the blocks to be unusually resistant to any deformation.

For example, we have found W-Re-Zr-C blocks (15 Re, 20 Zr, 20 C, bal. W atomic percent) to be particularly useful as test blocks for testing high temperature resistant materials.

Accordingly, it is an object of the present invention to provide a novel refractory alloy.

It is a further object of this invention to provide a cast refractory alloy having high temperature stress resistance properties characteristic of the initial high temperature stress resistance properties of dispersion strengthened alloys but being capable of retaining these properties for extended periods of time.

It is a still further object of this invention to provide a cast refractory alloy characterized by a structure containing a eutectic phase.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which:

The single figure of the drawing is a graph illustrating the proportions of components that may be used to successfully practice the instant invention.

The cast refractory alloy composition of this invention includes within its scope about 5 to about 85 atomic percent of one or more of the above-enumerated metals selected from the Group VIA metals or rhenium or alloys thereof, about 5 to about 85 atomic percent of one or more of the above-enumerated metals selected from Group IVA metals or tantalum and about 10 to about 50.0 atomic percent of carbon. Generally, the ratio in atomic percent of the aforesaid Group IVA metals or tantalum to atomic percent of carbon should be about 0.95 or greater. The alloys of the invention described herein are especially adaptable for use at elevated temperature when the combination of retention of strength, and resistance to oxidation and thermal shock is important.

Reference is made to the figure of the drawing representing the relationship of the various elements that comprise the composition of this invention. In the ternary compositional relationship of the figure: M_1 represents one or more of the Group VIA metals, rhenium or combinations thereof; M represents one or more of the Group IVA metals, tantalum or combinations thereof; C represents carbon; and MC represents a monocarbide of the Group IVA metals or tantalum. When M, M_1 , C, and MC are hereinafter described in connection with the figure, it is intended that these symbols refer to the aforementioned description of elements and compounds that they represent.

It has been found that when alloys of a composition falling generally on the line running from M_1 to MC are rendered molten, a eutectic reaction occurs upon cooling the aforesaid molten metal to the solid state. For practical purposes, significant amounts of eutectic can be produced from compositions falling within the band represented by a, c, d, e of the figure. The exact composition will depend to some extent on the specific composition and intended use of the alloy. This is readily accomplished by those skilled in the art applying routine techniques well known to the art. It is believed that the eutectic that is formed within the described compositional area comprises an intimate finely divided mixture of metal phase plus metal carbide phase. It is postulated that the metal phase of the eutectic comprises the metals of the group corresponding to M_1 while the metal of the metal carbide phase of the eutectic comprises the metals of the group corresponding to M. From the figure, it can be seen that compositions on the line running from M_1 to MC or in close proximity thereto contain approximately equal atomic percentages of carbon (C) and M metal (ratio of $M/C=1$). For example, the alloy represented at point 1 contains 75 atomic percent of M_1 and 12.5 atomic percent of M and C, respectively. At point 2, the alloy contains 25 atomic percent of M_1 and 37.5 atomic percent of C and M. Alloys containing less than about 10 atomic percent of carbon (C), are found to form typical carbide dispersion strengthened alloys. It follows that alloys containing less than about 5 atomic percent of M or alloys within the range of 85 to 100 atomic percent of M_1 or 0 to 5 atomic percent of M_1 plus M higher than 85 percent or C higher than 50.0 percent can also be excluded. The alloys rich in M_1 will consist essentially of M_1 phase while the alloys rich in M and C will consist essentially of metal carbide. Alloys within the triangular band represented by d, c, f (ratio of M/C substantially greater than 1) will be satisfactory for some applications. These alloys will contain the favorable eutectic and a metal phase that may consist largely of an alloy of M and M_1 . Alloy compositions lying above the line a, e (ratio of M/C substantially less than 0.95)

are less than desirable in that their structure is characterized by the presence of carbides of M_1 and C.

The compositions of the present invention are preferably prepared by arc-melting in a manner well known to those skilled in the art of melting. For example, compositions of this invention listed below have been produced by arc-melting using a carbon electrode and employing a partial atmosphere of helium.

Example	Composition atomic percent					Structure
	W	Re	Hf	Ta	C	
1	25	37.5	37.5			HfC dendrites and eutectic.
2	50	25	25			Do.
3	75	12.5	12.5			W dendrites and eutectic.
4	25	37.5	37.5			TaC dendrites and eutectic.
5	50	25	25			Do.
6	75	12.5	12.5			W dendrites and eutectic.
7	56	19	12.5	12.5		Small amount of W+Re dendrites and eutectic.

The alloy of Example 7 was subjected to extreme temperature conditions and was found to display resistance to thermal shock and oxidation superior to that of other conventional alloys under test. It was also observed that the eutectic structure remained stable at temperatures approaching the melting point of the alloy. From the structures observed and outlined above, a structure comprising substantially all eutectic would exist for the listed alloys at a level of 50 to 75 atomic percent of tungsten or combined tungsten and rhenium plus 25 to 50 atomic percent of equal amount of tantalum or hafnium and carbon. Variations from the eutectic can be used to provide varying structures having varying properties.

The examples show that alloys of metals selected from the enumerated group of Group VIA metals and rhenium may be used in the practice of this invention. The tungsten of Example 7 is shown partially replaced by rhenium. As a further example where the metal selected from the enumerated group of Group VIA metals and rhenium is molybdenum, it may be partially or wholly replaced by tungsten where the Group IVA metal is titanium or hafnium (or tantalum).

Additional alloys of the present invention were prepared as follows:

Example	Composition atomic percent					C
	Cr	Mo	Ti	Zr	Hf	
1	75	12.5				12.5
2	75		12.5			12.5
3	75			12.5		12.5
4		75	12.5			12.5
5		75			12.5	12.5

The alloy of Example 1 displayed a microstructure characterized by the presence of chromium and eutectic. In the remaining alloys, eutectic existed in the microstructure together with a carbide of titanium, zirconium, or hafnium.

The above examples are intended to be illustrative of the new and useful alloys that have been provided but are not intended to be limiting thereof. The examples described hereinabove do illustrate an alloy composition characterized by the presence of a fine stable eutectic structure produced upon casting to provide, in effect, a dispersion strengthened alloy wherein the dispersion is produced in situ.

What is claimed is:

1. A cast refractory alloy comprising:

- From about 85 to 5 atomic percent of at least one metal selected from the group consisting of titanium, hafnium, and tantalum;
- Where from 85 to 5 atomic percent of tantalum alone is present, from 5 to 85 atomic percent of at least one metal selected from the group consisting of chromium and rhenium;
- Where from 85 to 5 atomic percent of at least one metal selected from the group consisting of ti-

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tanium and hafnium are present, from 5 to 85 atomic percent of at least one metal selected from the group of molybdenum, tungsten, chromium, and rhenium;

(d) From about 50.0 to about 10.0 atomic percent of carbon; and

(e) The proportional relationship between said metals being such that a point representing the composition of said alloy lies substantially within the area *a, f, e* set forth in the figure of the accompanying drawing and the ratio of percent of said metal selected from the group consisting of titanium, hafnium, and tantalum to percent of said carbon is at least about 0.95.

2. The cast refractory alloy of claim 1 wherein said metal selected from the group consisting of molybdenum, tungsten, chromium and rhenium is tungsten.

3. The cast refractory alloy of claim 2 wherein said metal selected from the group consisting of titanium, hafnium and tantalum is hafnium.

4. The cast refractory alloy of claim 2 wherein said metal selected from the groups consisting of chromium and rhenium and molybdenum, tungsten, chromium and rhenium is an alloy of tungsten and rhenium.

5. The cast refractory alloy of claim 1 wherein said metal selected from the groups consisting of chromium and rhenium and molybdenum, tungsten, chromium and rhenium is chromium.

6. The cast refractory alloy of claim 5 wherein said metal selected from the group consisting of titanium, hafnium and tantalum is titanium.

7. The cast refractory alloy of claim 5 wherein said metal selected from the group consisting of titanium, hafnium and tantalum is hafnium.

8. The cast refractory alloy of claim 1 wherein said metal selected from the group consisting of molybdenum, tungsten, chromium and rhenium is molybdenum.

9. The cast refractory alloy of claim 8 wherein said metal selected from the group consisting of titanium, hafnium and tantalum is titanium.

10. The cast refractory alloy of claim 8 wherein said metal selected from the group consisting of titanium, hafnium and tantalum is hafnium.

11. The cast refractory alloy of claim 1 wherein said metal selected from the groups of chromium and rhenium and molybdenum, tungsten, chromium and rhenium and said metal from the group titanium, hafnium and

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tantalum is within the range of 5 to 55 percent so that said alloy falls within the area *a, c, d, e* of the figure of the accompanying drawing.

12. The cast refractory alloy of claim 1 wherein said metal selected from the group consisting of titanium, hafnium and tantalum comprises about 47.5 to about 5 percent of the alloy composition, the proportional relationship between said metals being such that a point representing the composition of said alloy lies substantially along the line *g, b* set forth in the figure of the accompanying drawing and the ratio of percent of said metal selected from the group consisting of titanium, hafnium and tantalum to percent of said carbon is at least 1.0.

13. A cast refractory alloy comprising, by atom percent, about 5 to about 85 percent of at least one metal selected from the group tungsten, chromium and rhenium, about 85 to about 5 percent zirconium and about 50.0 to about 10 percent of carbon, the proportional relationship between said metals being such that a point representing the composition of said alloy lies substantially within the area *a, f, e* set forth in the figure of the accompanying drawing and the ratio of percent of zirconium to percent of said carbon is at least 0.95.

14. The cast refractory alloy of claim 13 wherein said metal selected from the group tungsten, chromium and rhenium is chromium.

15. The cast refractory alloy of claim 13 wherein said zirconium comprises about 47.5 to 5 percent of the alloy composition, the proportional relationship between said metals being such that a point representing the composition of said alloy lies substantially along the line *g, b* set forth in the figure of the accompanying drawing and the ratio of percent of said zirconium to percent of said carbon is at least 1.0.

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U.S. Cl. X.R.

75-174, 175.5, 176