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## HIGH TEMPERATURE CHROMIUM-MOLYBDENUM ALLOY

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This invention relates to a chromium-molybdenum alloy having exceptionally high oxidation resistance at elevated temperatures. It pertains particularly to a refractory metal alloy of this type which is designed for buckets and vanes of gas turbine engines in which metal temperatures reach 2000° F.

The nickel base alloy and cobalt base alloy blades commonly used today in gas turbine engines for aircraft normally have maximum service temperatures of approximately 1800° F. to 1900° F. This limitation necessarily restricts the performance and efficiency of these engines. Refractory metals, such as niobium, tungsten, molybdenum and chromium, have satisfactory high melting temperatures and sufficient potential availability to warrant investigation as high temperature turbine blade materials. However, each of these metals exhibits poor oxidation resistance at temperatures of 2000° F. or above. Therefore, such metals are unsatisfactory for use in turbine blades which necessarily are exposed to extremely hot oxidizing gases. During recent years attempts have been made to correct this deficiency by adding small amounts of various alloying elements to these refractory base metals. However, these attempts have been unsuccessful since the resultant products still did not possess adequate oxidation resistance at the very high temperatures under consideration.

Accordingly, a principal object of the present invention is to provide a refractory alloy which can be employed as a turbine blade material at temperatures up to 2000° F. because of its outstanding oxidation resistance at such temperatures, coupled with good hot strength and other necessary physical properties. Such an alloy should possess adequate fabricability and a melting point of at least 3000° F. It is preferable that turbine blades formed of this alloy have an oxide scale thickness of not more than 0.005 inch after 100 hours exposure in air at a temperature of 2000° F.

In accordance with the present invention, I have found that an alloy comprising about 45% to 70% chromium and 30% to 55% molybdenum satisfies the foregoing requirements to a greater extent than the refractory alloys heretofore known. A chromium content of 50% to 61% appears to provide most advantageous results, particularly with respect to the combination of oxidation resistance and hot strength. For example, an alloy composed solely of 60% chromium and 40% molybdenum produces an oxide coating having a thickness of 0.01 inch after 100 hours exposure at a temperature of 2000° F.

Small but effective amounts of certain readily oxidizable elements and alloys, such as silicon, aluminum, titanium, calcium, arsenic and mischmetal, may be added to the binary alloy to further improve its extreme high temperature properties. In general, the maximum quantities of these addition agents which should be used to obtain optimum physical properties are approximately 3% silicon,

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0.5% aluminum, 0.5% titanium, 0.3% calcium, 0.08% arsenic and 0.15% mischmetal.

With a silicon-containing chromium-molybdenum alloy having a chromium content measurably less than 60%, it is desirable to include at least 0.1% silicon and preferably 0.2% silicon to achieve adequate resistance to high temperature oxidation. The latter amount of silicon is required for best results if other minor constituents are not added. However, as little as 0.01% silicon has been found to appreciably improve the oxidation resistance of the higher chromium content alloys. Likewise some improvement in this property is produced with only 0.02% calcium.

Small amounts of various elements can be tolerated in the chromium-molybdenum alloy without detriment to its physical properties. For example, if arsenic, manganese, aluminum, titanium, tantalum and thorium or boron is present in the binary alloy as the only minor constituent, less than 1% of such an element does not significantly affect the high temperature oxidation resistance of the alloy. However, combination additions of small quantities of silicon plus aluminum, silicon plus aluminum and titanium, calcium plus mischmetal, and calcium plus arsenic and mischmetal prevent the average thickness of the oxide scale formed on the chromium-molybdenum alloy from exceeding 0.005 inch after 100 hours cyclic exposure to air at a temperature of about 2000° F.

When non-metallic inclusions are present in the grain boundaries of the alloy of this invention, deoxidizing additions may be beneficially made. These intergranular impurities appear to be reduced to the greatest extent by the addition of 0.05% titanium and 0.1% to 0.3% calcium.

Sound extrusions may be obtained with the chromium-molybdenum alloy by first hot pressing it to approximately 10% reduction in thickness at a temperature of 3150° F. Initial hot working produces a wrought recrystallized structure which enables the alloy to be further hot worked, such as by extrusion. Prior to the present invention, it had been thought that a molybdenum alloy containing more than about 25% chromium lacked suitable high temperature oxidation resistance and could not be worked without cracking. As indicated above, however, the alloy described herein has excellent oxidation resistance and can be suitably hot worked.

My tests have shown that silicon additions in amounts up to 3% greatly enhance the oxidation resistance of a 50% chromium-50% molybdenum alloy, and substantial improvement was obtained with an addition of only 0.2% silicon. The oxidation resistance of such an alloy was further benefited with the inclusion of 0.2% aluminum. For example, a 50% chromium-50% molybdenum alloy containing 0.2% silicon and 0.2% aluminum had an oxide layer thickness of 0.003 inch after 100 hours exposure at a temperature of 2000° F.

In general, I found that a 60% chromium-40% molybdenum alloy is more resistant to oxidation at 2000° F. than a 50% chromium-50% molybdenum alloy. Oxidation resistance of this higher chromium content alloy is further improved by the addition of 0.3% silicon plus 0.1% titanium and 0.1% aluminum. A 60% chromium-40% molybdenum alloy containing 0.02% calcium, 0.08% arsenic and 0.15% mischmetal also had excellent high temperature oxidation resistance. In each instance the thickness of the oxide scale on the alloy containing

these addition agents was not greater than 0.001 inch after 100 hours exposure at a temperature of 2000° F.

The following table lists the approximate chemical compositions of specific examples of the chromium-molybdenum alloy of this invention and shows the thickness of the total oxide scale formed by heating in air at 2000° F. for the number of hours indicated in parentheses:

Base Alloy (percent)		Elements Added (percent)						Total Oxide Thickness Formed in Air at 2,000° F. (inches)
Cr	Mo	Si	Al	Ti	Ca	As	MM	
50.4	49.2	0.2	0.2					0.003 (72 hrs.)
51.2	48.1	0.5	0.2					0.003 (100 hrs.)
50.2	48.8	0.5	0.5					0.003 (96 hrs.)
50.0	47.0	3.0						0.002 (100 hrs.)
60.0	40.0							0.010 (115 hrs.)
59.2	40.6				0.02	0.08	0.15	0.001 (96 hrs.)
60.0	39.8	0.2						0.0007 (118 hrs.)
59.3	40.3	0.2	0.2					0.002 (100 hrs.)
61.4	38.1	0.3	0.1	0.1				0.0005 (118 hrs.)
60.0	39.3	0.2	0.5					0.005 (115 hrs.)
68.0	31.8	0.2	0.03					0.004 (115 hrs.)

Normally it would be expected that of these various alloys, those having the higher chromium contents would have lower melting points than the alloys in which the amounts of chromium and molybdenum are approximately equal. However, the minor constituents, such as silicon and aluminum, have very significant effects on melting temperature. For example, the alloy composed of 50.2% chromium, 48.8% molybdenum, 0.5% silicon and 0.5% aluminum and the alloy containing 50% chromium, 47% molybdenum and 3% silicon were found to have melting points between 3200° F. and 3300° F. On the other hand, the alloy consisting of 68% chromium, 31.8% molybdenum, 0.2% silicon and 0.03% aluminum melted between 3300° F. and 3400° F.

The refractory alloys described herein all were prepared by non-consumable arc-melting in an inert atmosphere of argon plus helium. Raw materials of maximum available purity were used. The constituents of the alloys may be added either simultaneously or successively.

Stress-rupture tests were conducted on as-cast chromium-molybdenum alloy test bars in an argon atmosphere at a temperature of 2000° F. under a load of 15,000 p.s.i. For example, an alloy consisting of about 48.2% chromium, 51.57% molybdenum, 0.18% silicon and 0.05% aluminum had a stress-rupture life of 37.8 hours under these conditions. On the other hand, 50 hours passed before a tensile test bar formed of an alloy composed of approximately 62.4% chromium, 37.4% molybdenum, 0.17% silicon and 0.03% aluminum was ruptured under the same test conditions.

While my invention has been described by means of certain specific examples, it is to be understood that the scope of my invention is not to be limited thereby except as defined in the following claims.

I claim:

1. An alloy consisting essentially of about 45% to 70% chromium, 30% to 55% molybdenum, and a small amount effective to materially increase the high temperature oxidation resistance of said alloy of at least one readily oxidizable member selected from the group consisting of silicon, aluminum, titanium, calcium, arsenic and mischmetal.

2. A gas turbine blade characterized by outstanding oxidation resistance upon exposure to oxidizing gases at a temperature of 2000° F., said blade being formed of an alloy consisting essentially of about 50% to 61% chromi-

um, a small amount effective to materially increase the high-temperature oxidation resistance of said blade of at least one readily oxidizable member selected from the group consisting of silicon not in excess of 3%, aluminum not in excess of 0.5%, titanium not in excess of 0.5%, calcium not in excess of 0.3%, arsenic not in excess of 0.08% and mischmetal not in excess of 0.15%, and the balance substantially all molybdenum.

3. A chromium-molybdenum alloy having an oxide scale thickness of not in excess of about 0.005 inch after 100 hours exposure in air at a temperature of 2000° F., said alloy consisting essentially of about 45% to 70% chromium, 0.1% to 3% silicon and the balance substantially molybdenum.

4. An alloy characterized by high oxidation resistance at a temperature of 2000° F., said alloy consisting essentially of about 50% to 61% chromium, 39% to 50% molybdenum, silicon not in excess of 3%, and aluminum not in excess of 0.5%, the amount of silicon and aluminum present being sufficient to materially increase the oxidation resistance of said alloy at 2000° F.

5. An alloy having high oxidation resistance at elevated temperatures, said alloy consisting essentially of about 50% to 61% chromium, 39% to 50% molybdenum, silicon not in excess of 3%, aluminum not in excess of 0.5% and titanium not in excess of 0.5%, said silicon, aluminum and titanium being present in amounts sufficient to materially increase the oxidation resistance of said alloy at a temperature of 2000° F.

6. An oxidation-resistant alloy for use at extremely high temperatures, said alloy consisting essentially of 50% to 61% chromium, calcium not in excess of 0.3%, mischmetal not in excess of 0.15%, and the balance substantially molybdenum, said calcium and mischmetal being present in amounts sufficient to prevent the formation of an oxide scale on said alloy having an average thickness in excess of about 0.005 inch after 100 hours exposure to air at a temperature of 2000° F.

7. An alloy characterized by high oxidation resistance at a temperature of 2000° F., said alloy consisting essentially of 50% to 61% chromium, 39% to 50% molybdenum, calcium not in excess of 0.3%, arsenic not in excess of 0.08%, and mischmetal not in excess of 0.15%, said calcium, arsenic and mischmetal being present in amounts effective to prevent the oxide scale on said alloy from having an average thickness in excess of about 0.005 inch after 100 hours exposure to air at a temperature of 2000° F.

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