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## HIGH-TEMPERATURE ALLOYS

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This invention relates to a ternary base alloy containing tungsten, chromium and aluminum that is suitable for use at high temperatures.

The ever-increasing demands of industry for stronger and more heat resistant materials of construction have spurred research in the metals and alloys field. Recent developments in the fields of rocketry and gas turbine engines, for example, have provided designs for apparatus requiring exceptional performance characteristics in their structural components. The high strength-high temperature metals field has been called upon to provide metals and alloys suitable for use in these new devices. Old metals and alloys have been improved and new alloys are avidly being sought to provide materials capable of withstanding high stresses at ultra-high temperatures for extended periods of time.

The present high temperature alloys are the iron, nickel, and cobalt-base alloys. These alloys have excellent strength characteristics within specific temperature ranges but the use of these materials is severely limited at temperatures above 1800° F. and the alloys are wholly inadequate at the ultra-high temperatures of operation in the 2400° F. to 3500° F. range that is demanded today. The deficiencies are especially evident when the alloys are subjected to high stresses at ultra-high temperatures.

Tungsten has long been known as a possibly useful metal for high temperature application since tungsten possesses the highest melting point (3410° C.) of any metal in the periodic table. However, exploitation of tungsten or the other high melting point refractory metals, such as columbium and tantalum, has been seriously limited by their extremely poor resistance to oxidation at high temperatures. When exposed to air at 1040° C. for a period of 24 hours, a specimen of tungsten was oxidized almost completely—the actual weight gain due to oxidation was 1235 mg. per cm.<sup>2</sup>.

The primary object of the invention, therefore, is to provide a complex tungsten-based alloy which is characterized by superior oxidation resistance at ultra-high temperatures.

Another object of this invention is to provide a complex tungsten-based alloy which, in addition to having excellent oxidation resistance, also exhibits superior high-temperature properties and corrosion resistance.

A further object of this invention is to provide tungsten-base alloys possessing improved ductility and workability.

Other aims and advantages of the invention will be apparent from the following description and appended claims.

In accordance with the present invention a ternary-base alloy is provided containing from 45 to 94.5 percent by weight tungsten, from 5 to 45 percent by weight chromium and from 0.5 to 12.0 percent aluminum. To this ternary-base alloy may be added one or more modifying metals in the following ranges: from 0 to 49.5

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percent by weight in the aggregate of tantalum, titanium, vanadium, molybdenum, zirconium and hafnium, and from 0 to 40 percent by weight in the aggregate of iron, nickel, cobalt and manganese, and from 0 to 5 percent by weight in the aggregate of elements selected from the group consisting of the rare earth metals, yttrium, scandium, calcium, silicon and magnesium. The total amount of these modifying metals which may be added to the tungsten-chromium-aluminum base should not exceed 49.5 percent by weight.

In a preferred embodiment, the alloy contains at least 45 percent by weight tungsten, from 10 to 40 percent by weight chromium and from 1 to 12 percent by weight aluminum with the modifying metals present in the following ranges: from 0 to 40 percent by weight in the aggregate of tantalum, titanium, vanadium, molybdenum, zirconium and hafnium, and from 0 to 30 percent by weight in the aggregate of iron, nickel, cobalt and manganese, and from 0 to 5 percent in the aggregate of one or more elements selected from the group consisting of the rare earth metals, yttrium, scandium, calcium, silicon and magnesium. The total amount of these modifying metals which may be added to the tungsten-chromium-aluminum base should not exceed 44 percent by weight of this preferred embodiment of the alloy.

Carbon, oxygen and nitrogen may be present in a combined amount not exceeding 2 percent by weight, but superior results are obtained when they are limited to one percent maximum amounts.

By alloying tungsten with chromium and aluminum, alloys are formed which retain the inherent high strength of tungsten, and which have a much greater oxidation resistance than pure tungsten. For example, a ternary-base alloy containing by weight 60 percent tungsten, 35 percent chromium and 5 percent aluminum, yields a greater than 20 fold improvement in oxidation resistance over pure tungsten. Furthermore, sizeable additions of chromium and aluminum will greatly reduce the density of the alloy.

By adding to the tungsten-chromium-aluminum alloy one or more of the high-melting point reactive elements, tantalum, titanium, vanadium, molybdenum, zirconium and hafnium in the percentages specified, the alloy exhibits even greater oxidation resistance at temperatures above 1000° C.

The addition of one or more metals from the group consisting of iron, nickel, cobalt and manganese in the ranges specified gives greater oxidation resistance, high strength, and corrosion resistance to the tungsten base alloy. Additions of iron also serve to lower the density of the alloy.

Furthermore, the addition to the alloy of one or more elements from the group consisting of the rare earth metals and the elements yttrium, scandium, calcium, silicon and magnesium improves the oxidation resistance of the alloy. It has been found that addition of these metals will improve the mechanical properties of the alloy. For these reasons up to 5 percent by weight in the aggregate of these elements may be added to the alloy.

The total amount of these modifying elements added must be limited to 49.5 percent by weight of the tungsten-chromium-aluminum-base alloy, and 44 percent for the more specific embodiment, since additions of these metals in amounts exceeding these percentages reduced the amount of high strength primary metals present.

The overall properties of the alloy of the invention are dependent, to some degree, on the impurity content of the individual constituents since impurities may be transferred to the alloy. Therefore, it is recommended that high purity materials be employed to form the alloys. However, a total of up to one percent metallic impuri-

ties will not materially affect the properties of the alloys.

Carbon, oxygen, and nitrogen may be present in a combined amount not exceeding two percent by weight, but the best results, particularly with respect to workability, are obtained when the total amount of these impurities does not exceed one percent.

Alloys which fall within the compositions defined above may be prepared in an arc-melting furnace having consumable or non-consumable electrodes. These alloys may also be prepared by any powder metallurgical technique, as for instance, extruding, slip casting, or hot- or cold-pressing, by induction melting or by any other method provided some precaution may be exercised to protect the hot metal from contamination by air.

The superior oxidation resistance of the alloy of the invention was substantiated experimentally. An alloy containing 60 percent by weight tungsten, 35 percent by weight chromium and 5% by weight aluminum was prepared by melting together the required amounts of the two constituents in a non-consumable electrode, inert-gas-shielded, arc-melting furnace. Complete homogeneity of the alloy was ensured by repeatedly remelting the button until material suitable for testing was obtained. A specimen was machined from the cooled product of this operation and tested for resistance to oxidation. The specimen was weighed and then heated in a muffle furnace at a temperature of 1040° C. for a 24 hour period, after which it was weighed again to determine the weight gain due to oxidation.

Under these conditions the alloy showed a weight gain of 60.80 mg. per cm.<sup>2</sup>. Unalloyed tungsten tested under similar conditions showed a weight gain of 1235 mg. per cm.<sup>2</sup>. Comparison of these results shows a greater than 10-fold improvement in oxidation resistance by use of the tungsten-chromium-aluminum-base alloy of this invention. By the addition to the tungsten-chromium-aluminum base alloys of the heretofore described modifying metals, even greater oxidation resistance can be achieved. Table 1 shows the weight gain due to oxidation at a temperature of 1040° C. for a 24 hour period, for several alloy compositions. These alloys were produced and tested under the same conditions as the example given above.

Table 1

| Composition, Percent by Weight |      |     |           | Weight gain<br>due to<br>oxidation,<br>mg./cm. <sup>2</sup> |
|--------------------------------|------|-----|-----------|-------------------------------------------------------------|
| W                              | Cr   | Al  | Other     |                                                             |
| 100                            | ---  | --- | ---       | 1,235                                                       |
| 60                             | 35   | 5   | ---       | 60.8                                                        |
| 45                             | 15   | 5   | 15Fe-20Ti | 15.9                                                        |
| 45                             | 30   | 5   | 20Ti      | 5.92                                                        |
| 46                             | 20   | 4   | 30Ni      | 3.63                                                        |
| 55                             | 30   | 5   | 10Ti      | 9.43                                                        |
| 56                             | 30   | 4   | 10Fe      | 4.34                                                        |
| 56                             | 30   | 4   | 10Ni      | 9.40                                                        |
| 60                             | 22.5 | 3   | 14.5Ni    | 3.40                                                        |
| 46                             | 35   | 4   | 15Fe      | 2.30                                                        |
| 46                             | 30   | 4   | 20Fe      | 2.93                                                        |
| 46                             | 27   | 4   | 18Ni-5Mo  | 8.66                                                        |

By comparing the results obtained in the above examples with those obtained for pure tungsten, the vast improvement in oxidation resistance which characterizes the alloy of this invention is immediately evident.

It is seen, therefore, that the alloy of this invention constitutes an important advancement in high-temperature technology. Possessing the high strength and corrosion resistance inherent in tungsten, as well as increased oxidation resistance and workability, the alloys may be fabricated into useful forms suitable for service at ultra-high temperatures for extended periods of time.

What is claimed is:

1. An oxidation resistant alloy for use at high temperatures consisting essentially of at least 45 percent by weight tungsten, from 5 to 45 percent by weight chromium, from 0.5 to 12.0 percent by weight aluminum, up to 49.5 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of tantalum, titanium, vanadium, molybdenum, zirconium and hafnium, up to 40 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of iron, nickel, cobalt and manganese, up to 5 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of the rare earth metals, yttrium, scandium, calcium, silicon and magnesium, the maximum amount of said modifying metals being not more than 49.5 percent by weight.
2. An oxidation resistant alloy for use at high temperatures consisting essentially of at least 45 percent by weight tungsten, from 10 to 40 percent by weight chromium, from 1 to 12 percent by weight aluminum, up to 40 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of tantalum, titanium, vanadium, molybdenum, zirconium and hafnium, up to 30 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of iron, nickel, cobalt and manganese, up to 5 percent by weight in the aggregate of at least one modifying metal selected from the group consisting of the rare earth metals, yttrium, scandium, calcium, silicon and magnesium, the maximum amount of said modifying metals being limited to not more than 44 percent by weight.
3. An oxidation resistant alloy for use at high temperatures consisting essentially of from 5 to 45 percent by weight chromium, from 0.5 to 12.0 percent by weight aluminum, and the balance tungsten and incidental impurities.
4. An oxidation resistant alloy for use at high temperatures consisting essentially of about 35 percent by weight chromium, about 5 percent by weight aluminum, and the balance tungsten and incidental impurities.
5. An oxidation resistant alloy for use at high temperatures consisting essentially of about 30 percent by weight chromium, about 4 percent by weight aluminum, up to about 20 percent by weight iron, and the balance tungsten and incidental impurities.
6. An oxidation resistant alloy for use at high temperatures consisting essentially of about 30 percent by weight chromium, about 5 percent by weight aluminum, up to about 20 percent by weight titanium, and the balance tungsten and incidental impurities.

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