This invention relates to chromium base alloys and more particularly to a chromium base alloy of improved ductility and oxidation resistance as a result of a combination of reactive metal additions.

As propulsion apparatus is improved, there is an ever increasing need for higher temperature operating alloys. The cobalt base and nickel base alloys have been developed to a relatively high degree so that utility at temperatures up to about 2000°F. have been realized. Further development for high temperatures will be limited by melting points. Thus the refractory metals such as columbium, molybdenum, tantalum, tungsten and chromium, which have significantly higher melting points, have been studied.

The refractory metal alloys, with the exception of chromium, exhibit poor oxidation resistance at temperatures above about 1000°F, and require complex protective oxidation resistant coatings. Chromium, by virtue of its relatively high melting point and inherent oxidation resistance, possesses potential for application at temperatures above 2000°F. Furthermore, it is more readily worked than the other refractory metals: although it has a melting point of 600-800°F higher than iron, nickel and cobalt, its melting point is 1000-1300°F lower than columbium and molybdenum. Its strengthening potential appears to be equivalent to that of iron, columbium, molybdenum and tungsten. In addition, chromium possesses a favorably low density compared to the other refractory metals of interest. During oxidation, Cr₂O₃ is formed, which is relatively stable in comparison with other refractory metal oxides such as WO₃ and MoO₃.

In spite of the favorable basic properties of chromium base alloys, including the improved oxidation resistance reported in U.S. 3,011,889, they have not been developed to a point of extensive application. This is due, in part, to limitations in low temperature ductility and high temperature oxidation-nitridation resistance. Probably the single most important factor which has limited the application of chromium base alloys is the embrittlement which occurs during high temperature air exposure and which is caused by reaction with nitrogen. A layer of chromium nitride, due to inward diffusion of nitrogen, forms between the metal and oxide surface. Such a nitride layer is very hard and brittle and produces sharp increases in the ductile-to-brittle transition temperature.

It is a principal object of the present invention to provide an improved chromium base alloy which has improved high temperature oxidation-nitridation resistance. This and other objects and advantages will be more clearly understood from the following detailed description and examples which are meant to be typical of rather than a limitation on the scope of the present invention.

Briefly, the alloy of the present invention provides a chromium base alloy consisting essentially of, by weight, 0.1 to less than 0.5% Y, 0.03 to less than 0.7% Th, 0.1-0.3% Hf, with the balance chromium and incidental impurities. In one form, this alloy can include up to about 10 weight percent Re.

It has been found that additions of the reactive metals ytrium, thorium and hafnium in combination with interstitial impurities to significantly improve the oxidation-nitridation resistance of chromium alloys and hence improve ductility. The further addition of the solid solution strengthening element rhenium in combination with the reactive metal additions results in an alloy which has a combination of improved strength and oxidation-nitridation resistance. Combinations of the gettering additions Y, Th and Hf were found to be significantly more effective in preventing nitridation than any of these elements added alone or in other combinations. Thorium and Hafnium appear to getter the incoming nitrogen, preventing the nitride layer formation. This permits the formation of a relatively impervious oxide film. Also, the ytrium can then diffuse and enter into the surface reaction, possibly improving the properties of the surface oxide which is Cr₂O₃.

The following Table I shows alloy forms typical of those studied during the evaluation of the present invention.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Y (wt%)</th>
<th>Th (wt%)</th>
<th>Hf (wt%)</th>
<th>Re (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M100</td>
<td>0.17</td>
<td>0.08</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>M101</td>
<td>0.17</td>
<td>0.08</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>M102</td>
<td>0.24</td>
<td>0.7</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>M103</td>
<td>0.17</td>
<td>0.08</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>M104</td>
<td>0.27</td>
<td>0.7</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>M209</td>
<td>0.18</td>
<td>0.08</td>
<td>0.23</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The alloys in Table I were prepared as 12 pound induction-melted heats, extruded and reduced to sheet for evaluation. In the above Table I, alloys M191 and M214, typical of the alloy within the scope of this invention, include the element yttrium, which is a strong de-oxidizer in chromium, the element thorium, which is a strong nitride oxide and sulfide former, and the element hafnium which is a strong carbide former. It has been found, as will be shown in more detail later, that this combination results in unexpected improvement in resistance to oxidation-nitridation and an improvement in ductility sufficient to change the alloy from an academic study alloy to one useful as an article such as a vane, in jet engines.

It has been found that the retained yttrium content must be kept below the solubility limit of about 0.5 weight percent at 2260°F. because of eutectic melting. The yttrium level of about 0.3 weight percent is effective in improving oxidation behavior and therefore the optimum retained yttrium level in the alloy of the present invention is about 0.1-0.3 weight percent. From previous experience, it was determined that the preferred range of yttrium could be retained in the alloy if approximately 0.7 weight percent yttrium was added during melting. Therefore, in the melting of alloys in Table I, about 0.7 weight percent yttrium was added to the alloy to obtain the retained amount of yttrium shown in Table I. In that table, alloy M214 includes the solid solution strengtheners immediately to indicate that the alloy within the scope of the invention can be further strengthened by solid solution strengthening.

The following Table II gives the oxidation-nitridation data for 0.250" thick specimens tested for 100 hours in a cyclic test in which the specimen was cycled from the temperature indicated to room temperature each 25 hours.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Test Temp. (°F)</th>
<th>Hardness-DPH</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>M100</td>
<td>2,000</td>
<td>1,288</td>
<td>145</td>
</tr>
<tr>
<td>M101</td>
<td>2,000</td>
<td>154</td>
<td>115</td>
</tr>
<tr>
<td>M102</td>
<td>2,000</td>
<td>148</td>
<td>115</td>
</tr>
<tr>
<td>M305</td>
<td>2,000</td>
<td>200</td>
<td>190</td>
</tr>
<tr>
<td>M209</td>
<td>2,000</td>
<td>200</td>
<td>190</td>
</tr>
</tbody>
</table>

25 mill nitride layer,
No nitrided layer,
Completely nitrided,
Nitride layer >25 mils.
Completely nitrided,
No nitrided layer.
In the table under hardness, the term "DPH" means Diamond Pyramid Hardness at the 100 gram load indicated. The amount of oxidation-nitridation of the specimens was determined in several ways. One principal test was the DPH hardness performed (1) at the specimen edge subjected to oxidation-nitridation and (2) at a point 0.02" from the edge to measure any significant change in hardness indicating the presence of a nitride layer. In another test, photomicrographs of these specimens were studied to determine the extent of the nitride layer.

From the data shown in Table II, it is easily seen that alloys M191 and M214 within the scope of the present invention formed substantially no nitride layer as indicated by the relative uniformity in hardness data as well as from the photomicroscopic studies. On the other hand, alloy M190, which included both yttrium and thorium, but not hafnium, showed a 5 mil layer of nitride and significant change in hardness. Alloys M193 which included only yttrium and M208 which included yttrium and hafnium but no thorium were completely nitrided and Alloy M194, which included only thorium, had a 25 mil nitride layer. It is interesting to note that alloys M193 and M208, which were completely nitrided, were in that condition at tests conducted at 2300° F., 200° F. lower than the other tests indicating that even the presence of increased amounts of yttrium alone or in the presence of only one of the other two reactive metals thorium and hafnium does not inhibit the formation of the nitride layer which is detrimental to ductility.

For the metallographic examination of the specimens of Table II, the specimens were mounted in an epoxy resin which was cured at 200° F., after which the specimens were polished and electrolytically etched in 10% oxalic acid in the usual manner. The micro hardness evaluations were carried out at room temperature. The rate of loading of the Diamond Pyramid Indentor was held constant for approximately 30 seconds to apply the full load which was maintained for an additional 15 seconds.

With regard to ductility in chromium base alloys, chromium and other body-centered cubic metals undergo a rapid transition from ductile to brittle condition as the temperature is decreased. The temperature of this rapid transition is termed the ductile-to-brittle transition temperature. The ductile-to-brittle transition temperature in pure chromium under low strain rate tensile tests in the wrought condition is about 5° F. and in the recrystallized condition about 104° F. Low temperature brittleness in such body-centered cubic metals is usually attributed to interstitial impurities. Because the alloy of the present invention inhibits the effect of such impurities, the ductile-to-brittle transition temperature of chromium is significantly improved.

In order to evaluate the alloys of the type included in Table I, a bend test was performed on tensile machine equipment with a V-block having supports 1" apart and a plunger of a radius of curvature of 0.06". The specimens were 1¼" long by ⅜" wide by 0.02" thick. A resistance heated furnace was used for those tests above room temperature. Strain was measured by the vertical travel of the cross-head which was constant at approximately 0.02" per minute.

Alloys M190, 193, 194 and 208, were first oxidized for 100 hours at 2300° F. and tested according to the bend test at 600° F. to determine their brittle or ductile condition. All of these specimens broke in a brittle manner at 0° deflection at 600° F. On the other hand, alloy M191, within the scope of the present invention and treated in exactly the same manner, was successfully bent to a deflection of 90° at temperatures down to as low as 300° F. The specimen for alloy M191 broke at 200° F. indicating at least a 400° F. improvement in the ductile-to-brittle transition temperature of similar chromium base alloys including some but not all three of the reactive metals yttrium, thorium and hafnium.

From the dramatic improvement in ductile-to-brittle transition temperature and the resistance to the formation of a nitride layer on the alloys of the present invention, it can be readily seen that an unexpected and significant improvement has been achieved by combining the three elements yttrium, thorium and hafnium compared with combinations of one or two of these elements alone.

Although the present invention has been described in connection with specific examples, it will be understood by those skilled in the metallurgical art the variations and modifications of which the invention is capable, particularly with regard to the other strengthening mechanisms such as solid solution strengthening or precipitation strengthening which can be added to the alloys of the present invention.

What is claimed:

1. A chromium base alloy of improved ductility and resistance to oxidation-nitridation comprising, by weight, 0.1 to less than 0.5% Y; 0.03 to less than 0.7% Th, 0.1-0.3% Hf, with the balance chromium.

2. A chromium base alloy of improved ductility and resistance to oxidation-nitridation consisting essentially of by weight, 0.1-0.3% Y, 0.03 to less than 0.7% Th, 0.1-0.3% Hf, up to about 10% Re with the balance essentially chromium.

3. A chromium base alloy of improved ductility and resistance to oxidation-nitridation nominally consisting of, by weight, about 0.2% Y, 0.05% Th, 0.2% Hf, up to 10% Re with the balance chromium.

4. A chromium base alloy of improved ductility and resistance to oxidation-nitridation consisting essentially of, by weight, 0.17-0.18% Y, 0.03-0.08% Th, 0.19-0.23% Hf, up to about 10% Re with the balance chromium.

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