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METHOD OF ALUMINIZING CHROMIUM ALLOYS AND OXIDATION RESISTANT ARTICLE PRODUCED THEREBY

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This invention relates to oxidation resistant alloys. In particular, the invention relates to improvements in chromium containing steels and other chromium containing alloys which are designed for use at elevated temperatures, and the invention provides a means whereby the upper temperature limit of use of such alloys can be substantially extended.

Chromium steels and other alloys containing various alloying elements along with chromium have found wide use in applications where stress at elevated temperatures is experienced. For example, alloys containing chromium in amounts from 5 to 35% are known to have suitable strengths at extremely high temperatures and, therefore, these alloys have many applications in this area.

There is, however, a constant demand for materials which can withstand even higher temperatures while sustaining greater loads. Thus, in the production of aircraft, rockets, missiles, space vehicles and the like the greater speed, size and power demanded require materials which can efficiently cope with ever increasing stress-temperature combinations.

One of the major problems confronting the industry in passing beyond the present stress-temperature barriers relates to the corrosion of metals under extreme conditions. In the case of chromium containing alloys, good elevated temperature corrosion resistance is realized to a point, but oxidation of the alloys occurs at undesirably low temperature levels. As a result, the mechanical properties of the alloys quickly become inferior above these temperatures and, therefore, such alloys have not been employed beyond these limits.

It has been proposed that the chromium containing alloys could be surface treated in a manner such that their oxidation resistance would be increased and, accordingly, the strength of the alloys would be relatively stable at extreme temperatures. Siliconizing, chromizing and aluminizing have been attempted as surface treatments, but the results have not been entirely satisfactory. The surface layers produced by known techniques do not adequately withstand thermal shock such as experienced where the structures produced from the alloys are rapidly subjected to great temperature differentials. In the case of aluminizing, detrimental cracks have developed in the treated surface after preparation of the aluminized layers. If the cracks extend below the aluminized layer, as they often do, corrosion of the chromium alloy can proceed as if there were no protective layer. Accordingly, the prior art surface treating techniques have not been suitable for producing chromium alloys capable of withstanding more extreme conditions.

It is, therefore, an object of this invention to provide a method for improving the oxidation resistance and other elevated temperature characteristics of alloys, including steels, containing chromium with or without other alloying elements.

It is an additional object of this invention to provide chromium alloy products which have improved oxidation resistance characteristics and which are adapted to cope with extreme stress and temperature combinations.

It is a more specific object of this invention to provide a technique for improving the elevated temperature characteristics of chromium alloys wherein oxidation resistant surfaces are provided on the products whereby the products will withstand severe stress and temperature conditions.

These and other objects of this invention will appear hereinafter, and it will be understood that the specific embodiments hereinafter set forth are provided for purposes of illustration and not by way of limitation.

In providing improvements in chromium alloys, various techniques have been developed in accordance with this invention. Each of the techniques to be described enables the production of chromium alloys which are unique in various respects. Furthermore, it will become apparent that the various techniques which have been devised are capable of use in combination whereby particular valuable products can be achieved.

In accordance with the concepts of this invention, chromium containing articles are provided with an oxidation resistant surface by means of an aluminizing technique. In order to achieve a satisfactory aluminized layer capable of withstanding temperature and stress extremes, it has been found necessary to provide aluminum contents in the surface layer in excess of the amount of chromium contained in the basic alloy. More specifically, amounts of aluminum of from 1.5 to 2.0 times the amount of chromium in the alloy will provide an ideal oxidation resistant surface. The application of an aluminized layer of this type to alloys containing from 5 to 35% chromium, with or without other major alloying ingredients, will produce products which will be stable at temperatures beyond those now considered to be the upper limits of chromium alloys.

It has been found that, contrary to present aluminizing techniques, the alloys should be aluminized at temperatures in excess of 1,000° C. In a further technique developed, components which are aluminized in accordance with this invention are rapidly chilled immediately after completion of the aluminizing step. The rapid chilling is preferably accomplished by water quenching the aluminized components.

In accordance with an additional development, it has been found that the aluminum content sought in the surface layer should extend to a depth between 20 microns (.0007874 inch) and 30 microns (.0011811 inch). It has further been determined that the minimum aluminizing temperature can become critical insofar as the performance of the aluminized components is concerned. Specifically, it has been found that where the components are to be subjected to a particular maximum temperature, the aluminizing should be carried out at temperatures in excess of this maximum temperature.

As indicated, the various developments of this invention can be incorporated into a single process for producing ideal components. In such a process the maximum temperature to which the components are to be subjected in use is first determined. If this temperature is in excess of 1,000° C., the aluminizing is carried out at temperatures above this maximum temperature. In any event, in accordance with this invention the aluminizing is carried out above 1,000° C.

The amount of aluminum provided in the surface layer in accordance with the preferred method will be from 1.5 to 2.0 times the amount of chromium in the base alloy. Furthermore, the layer of this composition will be provided to penetrate to a depth between 20 to 30 microns. After completion of the aluminizing, the articles are rapidly chilled to room temperature preferably by means of water quenching.

Various advantageous results are realized when aluminizing the chromium containing alloys in the manner described. The provision of aluminum in the diffusion layer in an amount in excess of the chromium content in the base metal markedly improves the oxidation resistance

and, accordingly, increases the temperature at which the metal can be used. Therefore, the strength of the aluminized components will be maintained over long periods, even at extreme temperatures.

By providing the amount of aluminum in the diffusion layer in the range of 1.5 to 2.0 times the chromium content, a particularly suitable product results. In a 5% chromium steel, an amount of aluminum of about 10% in the diffusion layer will successfully provide the desired results.

The quick chilling technique employed, which is advantageously carried out by quenching the steel in water immediately after the aluminizing, avoids detrimental cracks in the final product. The relatively large cracks which have been experienced in the past and which have led to oxidation of aluminized chromium alloys are avoided by the instant method. In their place, the chilling technique of this invention produced numerous tightly meshed, hairline cracks in the extreme outside area of the diffusion zone. Such cracks do not penetrate to the base alloy and, therefore, corrosion will not proceed in the manner experienced in the past.

As noted, it has been found preferable to carry out diffusion of the aluminum at temperatures in excess of 1,000° C., although prior art techniques have resorted to lower temperatures. An additional temperature limitation is also employed where the components to be manufactured from the chromium alloys are to be subjected to temperatures in excess of 1,000° C. In such a case, the minimum temperature for aluminizing should be the greatest temperature to which the components are to be subjected in use. When employing this minimum temperature, the aluminized components can more efficiently cope with the temperature extremes corresponding to this temperature. A component aluminized at a minimum temperature of 1,100° C. has been found to perform more satisfactorily at 1,100° C. than a component aluminized at a temperature below 1,100° C. The upper limit of aluminizing temperatures will depend upon the proposed maximum temperature of use.

The thickness of the aluminized coating is an important factor in the quality of the final product. As noted, prior aluminizing techniques have resulted in cracks which defeated the purpose of the anti-oxidation coating. To avoid the detrimental results of such cracks, diffusion layers of a thickness greater than 80 microns (.0031496 inch) were resorted to and, in some cases, this procedure succeeded. It is obvious, however, that thicker layers require longer diffusion times and are, accordingly, more expensive. Furthermore, cracks were found to initiate in thick diffusion layers when the aluminized components were subjected to severe thermal shock.

The provision by this invention of an aluminized layer having a thickness between 20 and 30 microns avoids the problems inherent in prior art techniques. It has been found that a relatively thin layer within this range is less susceptible to occurrence of detrimental cracks. It would appear that the thin surface layer has a pronounced elasticity and can therefore more readily respond to thermal shock and other conditions without cracking.

The particular method of diffusing the aluminum into the chromium alloys does not form a part of this invention. Among the known procedures which can be employed is the packing of the components in powders consisting of about 50% aluminum along with aluminum oxide and a small proportion of aluminum chloride. This

procedure, or any equivalent technique which is adapted for use at the temperatures and under the other conditions of this invention, will be suitable.

There have been described techniques for producing chromium steel and other chromium containing alloys having heretofore unobtainable oxidation resistance. The products of this invention are eminently suitable for aircraft, missile, rocketry and space applications, as well as in other areas demanding strength and stability at extreme temperatures. Although the invention is particularly useful in connection with alloys containing from 5 to 35% chromium, it will be apparent that other chromium containing alloys can be treated in accordance with the disclosed techniques. Reference is made to "High-Temperature Alloys," Claude L. Clark, London, 1953, Sir Isaac Pitman & Sons Ltd., and ASTM Special Technical Publication No. 170–A, "Compilation of Chemical Compositions and Rupture Strengths of Super Strength Alloys," for compilations of the nature of alloys contemplated.

It will be understood that various modifications may be made in the above described techniques which provide the characteristics of this invention without departing from the spirit thereof, particularly as defined in the following claims.

We claim:

1. A method for the production of articles from alloys containing from 5 to 35% chromium and having an oxidation resistant surface comprising the steps of aluminizing said articles at a temperature in excess of 1000° C. to achieve an aluminum content in said surface consisting of from 1.5 to 2.0 times the amount of chromium contained in said alloy, said aluminum content extending to a depth into said articles from between 20 to 30 microns, and rapidly chilling said articles after completion of the aluminizing step.

2. An article of manufacture consisting of an alloy containing from 5 to 35% chromium and having an oxidation resistant surface, said surface comprising an aluminized layer extending to the depth of between 20 and 30 microns and containing aluminum in an amount of from 1.5 to 2.0 times the amount of chromium contained in said alloy.

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