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ARTICLE OF MANUFACTURE HAVING A CHROMIUM ALLOY BASE AND A VAPOR DIFFUSED ALUMINIZED SURFACE

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This invention relates to the provision of materials which are capable of resisting the effects of high temperature. In particular, the invention provides for the production of alloys which are not subject to scaling at high temperatures and which will not corrode at high temperatures even when exposed to such atmospheres as those comprising hot combustion gases.

The concepts of this invention are applicable to various alloys which are employed for use under extreme conditions. Chromium containing alloys have met with particular favor where high temperatures are to be encountered and where corrosive atmospheres are prevalent. A number of iron, nickel or cobalt base alloys containing chromium have been formulated, and the following list will serve as a non-limiting illustration of the type of alloys with which this invention is concerned:

	Percent
Cr, up to	5.0–35.0
Ni and/or Co, up to	80.0
Mo, up to	5.0
W, up to	10.0
V, up to	3.0
Ti, up to	5.0
Ta/Nb, up to	5.0
Al, up to	8.0
Si, up to	2.0
Mn, up to	2.0
B, up to	0.5
Zr, up to	0.5
Fe, up to	50.0

Alloys containing chromium in the range of 5 to 35% and other high temperature alloys are known to have suitable strengths at extremely high temperatures and, therefore, these alloys have many applications in this area. However, there is a constant demand for materials which can withstand even higher temperatures while sustaining greater loads. In the production of rockets, missiles, space vehicles and other aircraft, for example, greater speed, size and power demands have resulted in the need for materials which can efficiently cope with extreme stress and temperature combinations.

The tendency for materials to corrode, particularly in the presence of hot combustion gases, is well known and has provided a major barrier in the production of more suitable materials. In the case of chromium containing alloys, oxidation of the alloys occurs at undesirably low temperature levels and as a result the mechanical properties of the alloys quickly become inferior.

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 the strength of the alloys would be relatively stable at extreme temperatures. Siliconizing, chromizing and aluminizing techniques have been employed, however, the results have not been entirely satisfactory. The surface layers produced by these techniques have not adequately withstood thermal shock such as is experienced where the structures which have been surface treated are rapidly subjected to great temperature changes. In the case of aluminizing, detrimental cracks have developed in the treated surface after preparation of the aluminized layer. Where such

cracks extend beyond the aluminized layer, as they do in many cases, intergranular corrosion of the chromium containing alloys can proceed as if there were no protective layer. Accordingly, the prior art surface treating techniques have not proven satisfactory for producing high temperature alloys capable of withstanding conditions beyond the upper limit of use of the alloys themselves.

It is an object of this invention to provide a method for improving the surfaces of high temperature alloys whereby the oxidation resistance, corrosion resistance and other elevated temperature characteristics of the alloys will be improved.

It is an additional object of this invention to provide high temperature alloys, particularly chromium containing alloys, which will resist scaling at elevated temperatures and which will resist corrosive attack in atmospheres such as those containing hot combustion gases.

It is a more specific object of this invention to provide a technique for improving the elevated temperature characteristics of chromium containing alloys whereby oxidation resistant surfaces can be provided on the alloys which will enable the alloys to withstand stress and temperature conditions beyond their present limits.

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.

It has been previously found that high temperature alloys are strongly affected when subjected to temperatures above 700° C., particularly in atmospheres containing combustion gases. Examination of the alloys has shown that there has been corrosive attack along the grain boundaries of the alloys apart from the oxidation thereof. It has been suggested that the sulphur compounds contained in hot combustion gases may play a large part in the intergranular corrosion. However, other ingredients in the atmosphere likely contribute to this condition.

In accordance with this invention, in order to avoid detrimental corrosion, protective layers have been provided on high temperature materials which will resist oxidation and which will also prevent penetration of the atmosphere thereby avoiding corrosive attack. The surface treatment of this invention provides a surface layer which is not susceptible to chipping off when subjected to stress or to thermal shock and, therefore, the protective condition can be retained in the alloys indefinitely.

More specifically, the present invention provides a surface treating process wherein articles composed of high temperature alloys are subjected to an aluminizing treatment. The treatment comprises heating the articles to a temperature above 1000° C. in a powder mixture. In accordance with this invention, the said mixture includes metallic aluminum and inactive oxides and the particle size of the aluminum powder is retained below 5 microns, while the particle size of the inactive oxides is preferably maintained between 50 and 100 microns.

In accordance with a preferred practice of this invention, the aluminizing treatment is carried out to provide an aluminum content between 2 and 8% to a depth of about 10 microns. Furthermore, an important additional discovery has led to the processing of the surface of the high temperature alloys prior to the aluminizing treatment. This processing, which may involve well known machining, polishing or buffing techniques, provides for a surface roughness of less than 98 micro-inches and preferably less than 79 micro-inches in the parts to be aluminized. It has been surprisingly found that after these parts are aluminized, the surface roughness initially provided is maintained in the surface treated parts. The final products, particularly where alloys containing 5 to 35% chromium are employed, are characterized by extra-

ordinary resistance to scaling, intergranular corrosion and thermal shock. The parts of the high alloy materials which have been provided with the aluminized layer resist scale and corrosive attack without any difficulty at temperatures between 600° C. and 1200° C., even in atmospheres containing hot combustion gases. Such parts are obviously especially suited for use in the production of turbine vanes and other combustion chamber components. In addition, there are obviously various uses, for example, in installations where atmospheres of coke oven gases and similar corrosive atmospheres are prevalent.

The surface roughness referred to herein conforms to measurement and designation standards as defined in Kent's Mechanical Engineers' Handbook, Twelth Edition, on "Design and Production." The roughness values referred to relate to the minute irregularities which cover a surface, the figures in micro inches indicating the maximum allowable roughness height.

It will be appreciated that the concepts of this invention can operate independently to provide improvements in aluminized articles. Thus, it has been found that the use of an aluminizing mixture containing from 2 to 8% and, preferably, 5% aluminum along with aluminum oxide in a treating process provides clear benefits where the aluminized layer extends about 10 microns and contains from 2 to 8% aluminum. The use of higher aluminum contents in the layers, as suggested in the prior art, is specifically avoided and, surprisingly, improved layers are realized.

It has also been established that processing of the surface of the high temperature alloys to provide a surface roughness below the above mentioned values will provide extraordinary improvements insofar as the production of highly resistant components is concerned. This surface processing carried out before aluminizing is preferably employed in combination with the above mentioned control of the aluminizing mixture whereby particularly valuable aluminized components are obtained. Furthermore, each of the techniques employed in the practice of this invention have been found to jointly contribute to the production of heretofore unobtainable properties in high temperature alloys.

In the aluminizing step, the temperature should be maintained above 1000° C. and preferably at about 1100° C. Where the articles are packed in an aluminum containing mixture, a small amount of a halogen salt such as 0.3% of ammonium chloride can be added to the aluminizing mixture in order to accelerate the diffusion. However, as will be explained, this addition is not always desirable.

Although packing of the articles to be aluminized in a powder mixture of the above noted composition comprises a preferred form of this invention, other aluminizing procedures are contemplated. For example, the gas aluminizing technique can be used in accordance with this invention. In this case, the parts are placed in a retort apart from the aluminizing compound. The aluminizing compound preferably contains from 20 to 25% aluminum, and the parts will be directly exposed only to the aluminum halide containing gases within the retort. With the use of iron or chromium alloys in a well known manner, it is possible to replace the aluminum by means of an aluminum alloy. The gas aluminizing alternative process is, of course, accomplished with the use of a halogen salt which is added to the aluminizing materials in order that the necessary aluminum halide will be produced. For example, ammonium chloride in amounts of about 0.3% can be employed in combination with the aluminizing materials.

The improvements which are occasioned by reason of the surface preparation of the components are noteworthy. Thus, it has been discovered that the resistance to scaling and corrosion depends not only on the character of the aluminizing treatment but also on the surface condition subsequent to the treatment. It has been discovered that the lower the surface roughness, the more resistant the parts have been to attack by hot corrosive gases. As previously noted, it is preferable to maintain the surface roughness below 79 micro-inches. However, satisfactory results are maintained with a surface roughness of up to 98 micro-inches.

In order to achieve the desired surface roughness, it is first necessary to process the components whereby the initial surfac condition provides a roughness below the above noted values. The surface processing can comprise any of the well known machining, polishing, buffing or other techniques. After preparation of the surface, the components to be treated are packed in an aluminizing mixture of aluminum powder and inactive oxides. It is preferred that the aluminum powder have a particle size of less than 5 microns and it is preferred that the aluminum oxide or other inactive oxide employed have a particle size between 50 and 100 microns.

It is common practice to add to the aluminizing mixture a halogen salt, for example, in the manner above described. However, where the aluminum powder is maintained below the maximum size set forth, it is not necessary to add a halogen salt, since the surface condition in the final product can be maintained below the roughness values set forth and the aluminizing will effectively proceed without this addition. However, where it is desired to speed up the aluminizing reaction, ammonium chloride or a similar compound can be added in an amount not to exceed about 0.1%. The parts embedded in the aluminizing mixture are heated out of the presence of air for several hours at a temperature of about 1000° C. in accordance with standard procedure.

The following will serve as specific illustrations of the possible applications of the disclosed concepts.

Example I

The composition of the heat resisting alloy steel selected for this example is as follows:

	Percent
C	0.5
Si	1.25
Cr	14.0
Ni	16.0
W	3.5
Fe	Balance

Treating conditions for articles of the above composition included placement of the articles in a retort and embedding the articles in a powder mixture containing 5% aluminum, 0.3% ammonium chloride and aluminum oxide. The articles were maintained at 1100° C. during the aluminizing treatment to produce an aluminized layer 10 microns in thickness and including 5% aluminum. The articles produced in this manner were characterized by good corrosion and scaling resistance in the neighborhood of 1200° C. and were not susceptible to crack formation as a result of thermal shock.

Example II

Components of the following composition were selected for treatment:

	Percent
Ni	70.0
Cr	12.0
W	5.0
Al	5.0
Mo	3.5
Ti, Nb, Ta	2.5
Fe, C, Mn, Si	Balance

The components were previously processed to provide a surface roughness of less than 98 microns. The articles were then aluminized by placing them in a mixture of aluminum and aluminum oxide. The particle size of the aluminum was less than 5 microns and the articles were maintained at 1000° C. during the aluminizing. It was

found that the surface roughness of the articles was not increased to any appreciable extent and, therefore, the scaling and corrosion resistance of the articles was highly satisfactory.

Example III

An alloy of the following composition was selected for this example:

	Percent
Co	60.0
Cr	20.0
W	10.0
Nb	2.0
Ni	1.0
Fe, C, Mn, Si	Balance

Components prepared from the above alloy were aluminized by embedding them in a mixture containing aluminum powder having a grain size of less than 5 microns. The mixture contained about 5% aluminum powder along with aluminum oxide having a particle size between 50 and 100 microns. After completion of the aluminizing, the aluminized layer comprised approximately 5% aluminum and the original surface roughness of less than 79 micro-inches was not, in any way, harmed by the processing. The components produced in accordance with this example were particularly successful in withstanding exposure to temperatures in the neighborhood of 1200° C. The components did not reveal any scaling or intergranular corrosion and the tenacious aluminized layer was not affected by conditions of thermal shock.

As previously indicated, alloys containing chromium in the range of 5 to 35% and selected from those included in the list of alloys previously provided are particularly suitable for treatment in accordance with this invention. Other high temperature alloys are contemplated, however, and reference is made to alloys set forth in "High-Temperature Alloys," by Claude L. Clark, Pitman & Sons, Ltd., London, 1953, and ASTM Special Technical Publication No. 170-A.

It will be understood that various modifications can be made in the above described concepts which provide

the characteristics of this invention without departing from the spirit thereof, particularly as defined in the following claim.

We claim:

An article of manufacture adapted to withstand surface corrosion at temperatures as high as 1200° C. having a base of a chromium alloy consisting essentially of 5–35% by weight of chromium with the remainder of the alloy selected from the group consisting essentially of up to 80% by weight nickel, up to 80% by weight cobalt, up to 5% by weight molybdenum, up to 10% by weight tungsten, up to 3% by weight vanadium, up to 5% by weight titanium, up to 5% by weight tantalum, up to 5% by weight niobium, up to 8% by weight aluminum, up to 2% by weight silicon, up to 2% by weight manganese, up to 0.5% by weight boron, up to 0.5% by weight zirconium, and up to 50% by weight iron, said article having a vapor diffused aluminized portion formed by vapor diffusion at a temperature above 1000° C. in the surface of said base to a depth of about 10 microns and having a surface roughness less than 98 micro-inches.

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