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CORROSION RESISTANT TREATMENT OF METAL ARTICLES

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2 Sheets-Sheet 1

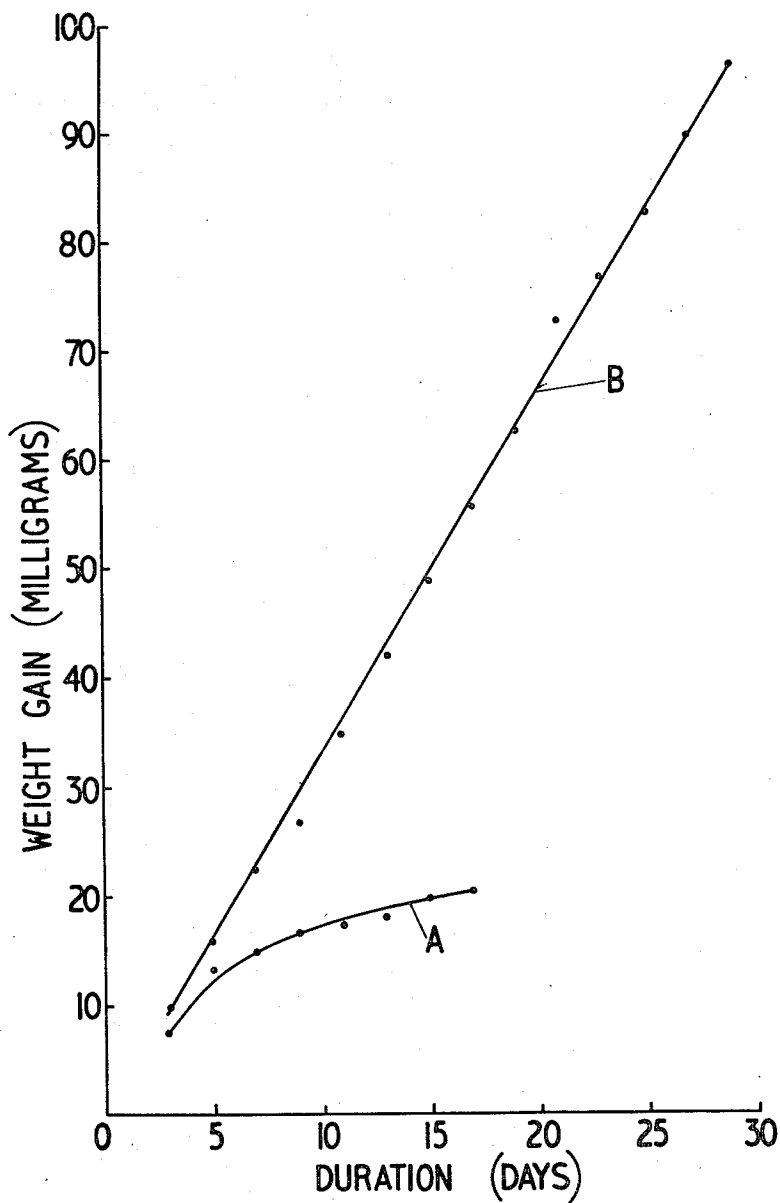


FIG. I.

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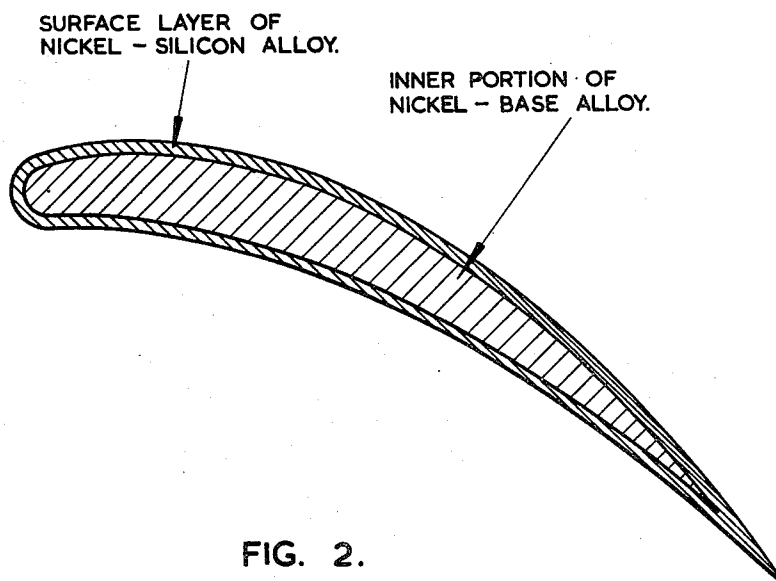


FIG. 2.

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CORROSION RESISTANT TREATMENT OF METAL ARTICLES

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Claims priority, application Great Britain Nov. 12, 1957 5 Claims. (Cl. 29—194)

This invention relates to methods of treating metal articles with a view to improving their corrosion resistance. The invention is, in particular, concerned with articles composed of alloys and metals for use at high temperatures and aims, on the one hand, to enable such articles to withstand better the corrosive conditions at temperatures to which they are presently subjected and, on the other hand, to permit articles of the same composition to be employed at even higher temperatures than is at present considered practical.

Such alloys and metals are used in gas turbines e.g. for gas turbine blades and other parts subjected to the corrosive effects of hot combustion gases.

In one particular connection, the corrosive effect depends to some extent upon the composition of the fuel used in the engine and this may therefore be a factor in limiting the life of, or the working temperature of the engine components. Thus, whilst it is desirable to employ in gas turbine engines the relatively cheap residual fuels, or crude oil, the possibility of so doing depends not a little upon the provision of materials which are capable of resisting the corrosive attack of the vanadium content of these fuels.

In vanadium corrosive atmospheres the invention aims to provide metal articles with an enhanced measure of vanadium corrosion resistance at temperatures up to about 700° C. and to prolong the time between overhauls of gas turbines running on a vanadium bearing fuel.

It is known that the presence of the element silicon in heat-resisting alloys does to some extent enhance the resistance of those alloys to corrosion at high temperatures. It is further recognised that the incorporation of silicon in the alloys is nevertheless often undesirable on account of the consequential reduction in mechanical strength.

It has been found, however, that provided that the silicon can be confined to the outer surface layer of the article then the protective property of the silicon may be availed of without reducing the mechanical strength of the underlying metal. However, it is important that this outer surface layer contains no additional element which by itself or in combination with silicon would form an oxide layer, at the temperatures envisaged, which would be non-protective.

The importance of this in relation to attack by fuels containing vanadium will be appreciated because alloys selected for use at high temperatures often include in their composition preferentially oxidisable elements other than silicon, for example chromium. Some of these elements are known to react with vanadium pentoxide, and the presence of such elements in the outer surface layer will destroy or diminish the protective nature of the oxide layer.

The resistance to corrosion, especially by fuel oil ash, of a metal article is enhanced, according to one aspect of the invention by forming on the outer surface of the article a discrete outer coating containing a nickel-silicon alloy to the exclusion of any other deleterious strong oxide-forming element.

By strong oxide-forming element is meant any element which by itself or in combination with the silicon is

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susceptible of forming an oxide layer which would not protect the underlying metal.

The invention further resides in applying to a metal article a discrete outer coating consisting of nickel and silicon in proportions corresponding to the nickel-silicon eutectic containing 12 percent silicon. The proportion of silicon may be varied within 1 or 2 percent.

The article to be coated may be given a preliminary degassing heat treatment and may be heat treated subsequent to the coating process to restore the physical properties of the metal.

Any suitable coating process may be employed to coat the article provided that, by appropriate process control, the outward diffusion from the underlying metal of any strongly oxide-forming element, which is deleterious to the coating, is minimized.

FIGURE 1 is a graph showing rate of corrosion, and FIGURE 2 is a cross-sectional view of a gas turbine blade.

In one method of coating a specimen article, described here by way of example, the article was composed of an alloy mainly of nickel, i.e. about 60 percent and including 18 to 21 percent chromium; 5 percent iron, 2 percent cobalt, 1.8 to 2.0 percent titanium and 0.1 percent carbon, and was shaped as a solid, substantially cylindrical body, 7/8 inch diameter and weighing 36 gms. One end face of the body was plane and the other end face slightly dished. Prior to coating the article was given an initial degassing process by heating it at 900° C. in vacuo for 24 hours and then cleaned with abrasive. The article was then given a coating about 0.003 inch in thickness of a mixture of powdered nickel and silicon in proportions corresponding to the nickel silicon eutectic containing 12 percent silicon. The powder was applied in suspension in xylene which was then dried off. The article so coated was then heated in an electric furnace in vacuo to 1150° C., maintained at that temperature for ten minutes and then allowed to cool. The resultant coating was in the form of a coherent sintered layer of nickel-silicon alloy.

It was found that the sintering process had had a deleterious effect upon the fatigue strength and creep strength of the article and to restore these properties, the article was given an isothermal heat treatment which consisted in cooling the coated article from the sintering temperature to 900° C., maintaining it at this temperature for 20 hours then cooling to room temperature after which it is aged at a temperature of 700° C. for 16 hours and allowed to cool.

A corrosion test was performed on an article coated as aforesaid by the application of small amounts of powdered vanadium pentoxide intermittently on the surface of the coating in an oxidising atmosphere at 700° C.

For this purpose the specimen article was supported on platinum wire at a point on its plain end face with its dished end face uppermost in an electrical furnace and maintained at a temperature of 700° C. Vanadium pentoxide in powder form was applied to its dished end face intermittently at a rate of 20 mgms. a day, the vanadium pentoxide, being molten at 700° C. spread over the whole surface of the specimen article. The article was weighed periodically to ascertain the gain in weight due to oxidation. The results are shown in the graph of FIGURE 1 in which the ordinate represents the weight gain of the specimen article in mgms. and the abscissa the duration of the test in days. The curve A represents the rate of oxidation of the specimen referred to.

For the purposes of comparison a similar specimen article of the same alloy without a protective coating was maintained at a temperature of 700° C. and vanadium pentoxide similarly added intermittently. The curve B represents the rate of oxidation of this specimen and it

will be seen that by means of the protective coating the rate of oxidation was substantially reduced.

The sintering time and temperature may be varied but only between limits which are consistent with yielding a coherent coating and preventing the outward diffusion of chromium or any other deleterious oxide-forming elements.

The isothermal heat treatment may be carried out at any temperature within the range 900°–1000° C. but for optimum corrosion resistance it has been found desirable to avoid heat treating at 1000° C., preferred temperatures within the range being 900° C., 950° C., 1025° C., although other temperatures may prove suitable. Generally, isothermal heat treatments at temperatures above 1025° C. tend to reduce the corrosion resistant properties of the coating.

On highly curved concave surfaces such as, for example, at the root fillets of turbine blades it was found that, during sintering, the bond between the particles of the coating at first was stronger than the bond between the coating and the article. This resulted in lack of contact between the sintered coating and the article. It was found that this undesirable feature could be avoided by submitting the article, or the curved surfaces thereof, to a preliminary treatment consisting of the application and sintering of a very thin coating of nickel silicon eutectic, not more than 0.0005 in. in thickness, under substantially the same conditions described above.

It may prove advantageous, when an alloy containing chromium is to be coated, to process the article initially by depleting the surface of chromium prior to the application of the nickel silicon coating. Alternatively, a coating of nickel could be applied to the article before the nickel silicon coating process was begun. Both these initial processes tend to inhibit the outward diffusion of the chromium during the sintering process. Another method of minimising the content of strong oxide-forming elements in the outermost surface layers which also will ensure complete coverage of the article is to repeat the coating and sintering procedure, and this may be done several times.

The elements nickel and silicon may previously be alloyed together and the alloy, converted to powder form, may be used to coat the article as an alternative to the simple mixture of nickel and silicon powders.

According to an alternative method of applying the coating, the powdered mixture or alloy of nickel and silicon is applied onto the article to be coated by flame spraying techniques. If necessary, this can be followed by high-temperature heat treatment of the flame-sprayed article in an inert atmosphere further to sinter the coating.

Yet another alternative method resides in coating the article with nickel and then impregnating the nickel with silicon by means of well known high temperature diffusion techniques. In each case the proportions of nickel

and silicon in the coating do not differ from that stated above.

FIGURE 2 is a tranverse cross-sectional view of a gas turbine blade having an inner portion consisting of nickel-base alloy such as that previously referred to and an overlying surface layer consisting of the nickel-12% silicon eutectic alloy.

What I claim is:

1. A metal article characterized by high resistance to corrosion by a vanadium-containing atmosphere that comprises an inner portion comprised of at least one metallic material, and an integral surface layer overlying said portion, said surface layer being an alloy consisting of nickel and silicon in proportions corresponding to the nickel-silicon eutectic containing 12% silicon.

2. A metal article characterized by high resistance to corrosion by a vanadium-containing atmosphere that comprises an inner portion consisting of an alloy containing at least one metal as the major constituent and also containing chromium, and an integral surface layer overlying said portion, said surface layer consisting of an alloy consisting of nickel and silicon in proportions corresponding to the nickel-12% silicon eutectic alloy, and substantially free of chromium.

3. A metal article according to claim 2 wherein said metal is nickel.

4. A method of improving the resistance of a metal article to corrosion by a vanadium-containing atmosphere by forming thereon a surface layer, the layer being formed by applying to the article a mixture consisting of nickel and silicon in proportions corresponding to the nickel-silicon eutectic containing 12% silicon, heating the article in vacuo at about 1150° for 10 minutes and allowing the article to cool.

5. A method according to claim 4 wherein the nickel and silicon are applied in powder form in suspension in a volatile medium, and comprising the step of drying off said medium.

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