PROCESS FOR DEPOSING A PROTECTIVE ALUMINUM COATING ON METAL ARTICLES

Fig. 1

Fig. 2

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2 chamber heated, to a high temperature, to the action of a halide (volatile at the temperature of said chamber) of the metal to be deposited, which volatile halide can be diluted with an inert or reducing gas and is formed by the reaction at a high temperature of a suitable substance on a donor substance which remains solid at the reaction temperature and which contains the metal to be deposited, preferably alloyed with at least one of the metals which constitute the refractory alloy to be protected, in such a manner that the metal to be deposited is transferred to the parts whilst wholly in a gaseous phase, without solid-to-solid contact between the donor and said parts. The donor can be employed again and again, the halogen element content being regenerated as the need arises.

As regards the efficiency of the protection, it is preferable to choose aluminium as the metal of addition by reason of the excellent protective coatings it provides on the surface of the refractory alloy as it combines with it. It is in this sense preferable to other metals, such as chromium for example, because it imparts to the protected articles a considerably longer life than does the latter metal. For example, for comparison purposes, it has been found that a cobalt-base refractory alloy known for having a quite marked sensitivity to oxidation and containing approximately 60% of cobalt, 20% of chromium, 10% of tungsten, 0.5% of carbon and various elements, and protected by a coating of chromium deposited in a halogenated atmosphere, manifests an overall gain of 50 to 60 grams per square metre at the termination of a cycle that comprises, in all, four successive periods of 24 hours at 1,100°C in an oxidising atmosphere, the periods being broken by brief retention at ambient temperature, this being aimed at obtaining thermal shock effects. The same alloy, protected according to the invention by a deposit of aluminium, manifests after the same test a gain in weight of under 10 grams per square metre. The simultaneous addition of aluminium and of chromium, or, indeed, of aluminium, chromium and silicon, or any other multiple addition of elements that are known for their ability to protect metals and alloys from oxidation and corrosion at high temperatures, does not yield results superior to those obtained by the addition of aluminium alone. Excellent behaviour has been obtained, in an oxidising environment, by the surface coating of alloy articles by aluminium alone, in conformity with the present invention.

The process of the present invention permits the obtaining, on the surface of the articles, protective coatings that are actually bound to the base metal as a result of the formation of an alloy between the base aluminium and the metal deposited, this occurring without the articles to be protected being subjected to any chemical attack and correspondingly to any deformation. The protective coatings obtained have smooth surfaces free of local excesses, a very important point because it has been verified that, apart from geometric and aerodynamic faults that these can bring about, these irregularities correspond to abrupt variations in the local concentration of the metal of addition. These differences in surface coating, when linked to rough patches, lead to unequal resistances to oxidation and corrosion. For these reasons the process of the invention is particularly advantageous because it allows a smooth and appreciably uniform deposit to be obtained whatever the shape of the article to be coated.

The following description, referring to the annexed drawings and given by way of non-limitative example, will explain how the invention may be carried into effect, the further features emerging both from the text and the drawings also forming part of said invention.

FIGURE 1 is a diagrammatical view in vertical cross-
section of one embodiment of the process of the invention.

FIGURE 2 is a diagrammatical view in vertical cross-section of another embodiment of the process of the invention.

In FIGURE 1, a chamber 1, the shape of which depends upon that of the furnace 2 which is employed and upon that of the articles to be coated, is provided with a lid 3, which does not require to be leakproof. The articles 4 to be protected are suspended from a stand 5 in such a manner as to be at a distance from the donor substance 6. Said donor is separated from the space containing the articles requiring coating by walls 7 that includes perforations. Thus any solid-to-solid contact between the articles 4 and the donor 6 is avoided. The distance between the articles 4 requiring coating and the donor alloy charge 6 may vary from one to several centimetres without the thickness and the quality of the deposit obtained being affected. The conveying of the protecting element from the donor alloy charge 6 to the articles 4 is effected solely through the intermediary of a gas, that is, a halide of the metal to be deposited, which halide is formed during the heating process.

The donor 6, which must remain in a solid state at the reaction temperature, is an alloy containing, as its first main constituent, one or more of the base elements of the alloy to be coated, for instance, cobalt, nickel, chromium, etc., and as its second constituent aluminium. It is obvious that no mention need be made of conventional and everyday impurities introduced by commercial supplies of said materials. The content of aluminium in the donor may vary, for example, from 6 to 50%, and is preferably between 30 and 40%.

The donor may be in any form, from a very fine powder to lumps.

One of the particular advantages of the present invention is that, due to the employment of a donor as described above, there is no need to add an inert compound, such for example as alumina in granular form, to the aluminium-base donor, in order to avoid the agglomeration of the latter. Such an addition would be highly disturbing because it would impede the free circulation of the gases and the active participation in the reaction of the whole mass of the donor placed in the chamber.

Once the charge has been constituted as indicated above, a halogen or halogenated compound is introduced, preferably fluorine or chlorine in a gaseous state, or a combination of halogen, for example fluorine and chlorine, together with aluminium to be coated. The amount of the halogen or halogenated compound introduced, in relation to the total mass of the donor, is not critical and may vary, for example, from 0.1 to 1% by weight.

The chamber 1, provided in this manner with its donor, its halogenated element and its articles that require coating, is placed in the furnace 2, the atmosphere of which may be constituted by a neutral gas such as argon, or by a reducing medium such as hydrogen or cracked ammonia.

The heating temperature is regulated in such a manner as to bring about a sufficient vapour pressure of the halide of aluminium to be deposited (a halide formed by a reaction when hot between the halogen and the donor within the chamber 1), as well as a quite deep simultaneous diffusion, into the articles 4, of aluminium deposited on their surface through the decomposition of such aluminium halide.

The duration of the heating period at the chosen temperature allows both the thickness of the deposit, and the content of aluminium in the surface coating alloy so formed to be regulated in a very precise manner.

As an indication, the temperature may vary between 950 and 1200° C. approximately, and the practical duration for the maintenance of this temperature may lie between 1 and 5 hours approximately.

The determination of the thickness of the deposit is effected to afford a compromise, in use, between a duration of protection in the presence of heat and a resistance to scaling at the time of thermal shock effects, both duration and resistance being as great as possible. In general, the thickness of the deposit will lie between 0.025 and 0.05, 0.100 millimetres, and preferably between 0.04 and 0.07 millimetres.

Numerous successive coating operations may be carried out while continuing to employ the same charge. Experience shows, indeed, that in every case the same thickness of deposit is obtained, everything in other respects remaining equal. It is sufficient merely to regenerate in part the halogenated element; in actual fact, this latter may escape by reason of the chamber lid leaking, and it is therefore necessary to maintain its concentration at an adequate level. Said concentration is moreover weak, as has been shown above, given that the halogen elements only serve to convey aluminium to be deposited and are continually being regenerated in the course of the reactions.

In the embodiment shown in FIGURE 2, the single chamber of FIGURE 1 is divided into two distinct chambers 1 and 8.

The chamber 8, intended to receive the donor 6, is placed in a furnace 9; said chamber is provided at two of its opposite ends with a gas inlet 10 having two pipes 11 and 12 and with a gas outlet 13. The gas outlet 13 allows the chamber 8 to communicate with the chamber 1 and is surrounded either with heat insulation or with a heating device 14.

The chamber 1, placed inside the furnace 2, encloses the stand 5 for the articles 4 that are to be coated and includes a gas outlet 15 as well as a loading door with an appropriate seal 16 that ensures an adequate freedom from leaks while allowing easy loading and unloading of the chamber.

The halogen (fluorine or chlorine, for example) is introduced in the form of a gas stream at the inlet 10 of the chamber 8 by means of the pipe 12. Said halogen may be mixed with a neutral or reducing gas (argon, hydrogen, etc.) called the "carrier gas," so as to effect a suitable dilution and at the same time ensure a forward propulsion of the gases. Said gases, more or less rich in gaseous halogen, pass over the donor 6 that is placed in the chamber 8, this being heated to a temperature sufficient for the production of a volatile halide to take place. The gas stream then passes into the second chamber 1 to be put in contact with the articles to be coated that are contained therein. This chamber 1 being raised to a temperature sufficient for the decomposition of the aluminium halide to be brought about upon contact with the articles to be coated and for the metal, once deposited, to diffuse into the articles, from the surface towards the heart.

The pipe 13 is arranged in such a manner that the temperature prevailing inside it is sufficient to avoid any premature reaction or decomposition in the middle of the gaseous mixture circulating therein; in general, this temperature is at least equal to that in the chamber 8.

The carrier gas and the excess aluminium halide finds an outlet by way of the pipe 15 and pass through suitable absorbers that allow said excess to be re-cycled if so required, with the aid of industrial processes that are well known and are not here described. By way of example, the temperature of the chambers may be maintained between 950 and 1200° C. approximately, the temperature of the first chamber 8 being lower than that of the second chamber 1.

Obviously numerous modifications may be applied to this embodiment without, however, going beyond the scope of the present invention, as defined by the appended claims. In particular, the arrival of the halogen gas may be effected at the outlet to the chamber 8 instead of at its inlet. Similarly, the position of the two chambers is only given by way of non-limitative example, both as regards their relative position and as regards the vertical or horizontal position of either chamber.

The articles made of refractory alloy that have been protected according to the process of the invention be-
have excellently for several hundred hours at temperatures of the order of 1100° C.

What is claimed is:

1. A process for protectively coating, with aluminum substantially alone, a metal article made of a refractory alloy, which comprises disposing the article which is to be protectively coated, in a chamber heated to a temperature comprised between about 950 and 1200° C.; providing this chamber with an aluminum halide which is volatile at the temperature of said chamber, said volatile aluminum halide being formed by the reaction, at a temperature comprised between about 950 and 1200° C., of a halogen with a donor substance being out of solid-to-solid contact with said article and consisting of an aluminum alloy which remains in the solid state at the reaction temperature; and allowing said volatile aluminum halide to decompose when contacting said article whereby a protective aluminium coating is deposited on said article without there being any chemical reaction of said metal article with said volatile halide.

2. A process as claimed in claim 1 wherein the donor substance is an alloy containing aluminum and at least one metal selected from the group consisting of cobalt, nickel, chromium and iron.

3. A process as claimed in claim 1 wherein the donor substance is an alloy containing aluminum and at least one metal selected from the group consisting of fluorine and chlorine.

4. A process as claimed in claim 1 wherein the content of aluminum in the donor substance ranges between 6% and 50% by weight.

5. A process as claimed in claim 1 wherein the content of the aluminum in the donor substance ranges between 30% and 40% by weight.

6. A process as claimed in claim 1 wherein the halogen is selected from the group consisting of fluorine and chlorine.

7. A process as claimed in claim 1 wherein the metal article is submitted to the action of the aluminum halide for a period of between 1 and 5 hours.

8. A process as claimed in claim 1 wherein the halogen is diluted with an inert gas.

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