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(54) **Coating of metallic substrates**

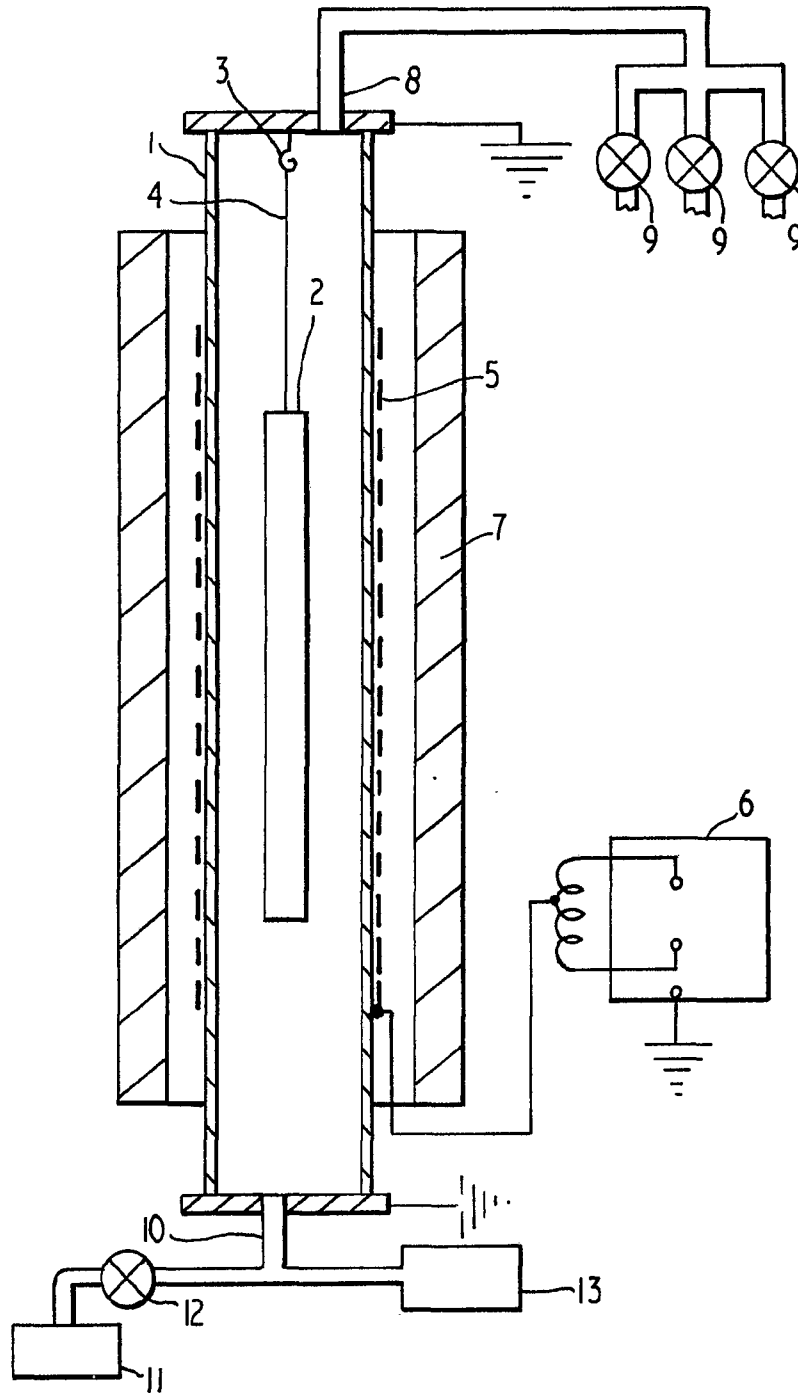
(57) Metallic substrates are protected against corrosion, carburisation and carbonaceous deposition by plasma activated vapour deposition of

ceramic material coatings thereon. Stainless steel fuel cans used in an Advanced Gas Cooled Reactor are protected e.g. by providing SiO<sub>2</sub> coatings from reaction of silane and CO<sub>2</sub>. Carbon steels may also be protected in this way.

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## SPECIFICATION

**Coating of metallic substrates**

This invention relates to the protection of metallic substrates against corrosion, carburisation and carbonaceous deposition by provision of ceramic material coatings thereon.

5 The invention provides a method of coating a steel or a Ni-base alloy substrate with a ceramic material to protect the substrate from corrosion, carburisation and/or carbonaceous deposition, which method comprises generating, adjacent and substrate, a glow discharge in an ionisable gas containing a component or components capable of chemical reaction in the plasma of the glow discharge to produce the ceramic material under conditions such that the ceramic material is formed on the substrate to constitute a coating. 10

Thus, the ceramic material is deposited by a vapour phase deposition process in which a plasma is used as a medium for a chemical reaction and for deposition. Such a deposition process is, in itself, known in the art where it may be referred to as plasma activated vapour deposition (or PAVD). See, for example, "Deposition of Ceramic Coatings by a Plasma Activated Process" by K. R. Linger, a paper delivered at the 9th Plansee Seminar in Austria on 23rd May 1977 and French Patent Specification No 2 392 508. It has, however, been found, on the basis of preliminary tests, that metallic substrates in general are given improved oxidation resistance properties at elevated temperatures to a surprising extent when coated with silica by the present method. Such coatings also may provide resistance to carburisation, carbonaceous deposition and other forms of corrosion such as aqueous corrosion. Other methods of providing silica coatings on metallic substrates are known, for example, as described in UK Patent Specification Nos 1 463 053, 1 483 144 and 1 530 337. 15 20

The preferred ceramic material in the invention is a ceramic oxide such as silica which is mentioned above. A silica coating may be obtained by using, as components in the gas phase, a silane where monosilane ( $\text{SiH}_4$ ) is particularly preferred and an oxidant such as carbon dioxide. Ionisable gases such as argon may conveniently be added to the reactants to assist the process. 25

The present invention may be carried out in an apparatus of the kind generally described in the aforementioned 9th Plansee Seminar paper. A specific example of such an apparatus will be described hereinafter.

An advantage of the invention when carried out for the purpose of conferring oxidation resistance is that it can be carried out at comparatively low temperatures (e.g. around  $100^\circ\text{C}$  to  $300^\circ\text{C}$ ). This enables a mild steel substrate, which would exhibit considerable reactivity at higher temperatures to be coated satisfactorily. This also enables overheating of fully engineered components to be avoided. In contrast the chemical deposition process described in abovementioned UK Patent Specification No 1 530 337 describes temperatures of  $400^\circ\text{C}$  and above. Furthermore, the coating rate using the invention is much greater than in the case of a thermally activated deposition process at temperatures below about  $1000^\circ\text{C}$ . 30 35

Examples of substrates which may be used in the invention are carbon steel and stainless steel substrates. Carbon steel is widely used as an engineering material but is prone to various forms of corrosive attack such as aqueous corrosion and oxidation in air at elevated temperatures (e.g.  $500^\circ\text{C}$ ). An example of a stainless steel substrate is a material used as a fuel can material in an Advanced Gas Cooled Nuclear Reactor, which is known in the art and is referred to herein as the AGR. Such a steel may be a Cr-bearing austenitic stainless steel, for example stabilised by Nb, a particular example of which is the so-called "20/25" steel which contains 20% Cr, 25% Ni, about 0.1% Nb and the balance Fe, wherein the proportions are by weight. In operation of the AGR, fuel cans are exposed to a hydrocarbon-containing coolant gas at elevated temperatures. Such exposure can give rise to oxidation of the steel constituting the fuel can. Some of the oxide thereby produced in non-adherent and could give rise to active dust in the reactor. In addition, carbonaceous deposits might be formed on the fuel can, which deleteriously affects the heat exchange balance between fuel can and coolant. Such a fuel can may be coated, for example with silica, directly by the method of the invention thereby to endow it with increased resistance to oxidation, oxide spallation and carbon deposition. It is possible that the effectiveness of the process may be due to the effect on coating structure, adhesion and possibly other properties of ion bombardment in a radial electric field whilst the ceramic material is being deposited in accordance with the invention. 40 45 50

However, it may not necessarily be advantageous to apply the coating at a low temperature when producing a coated fuel can for an AGR. Thus, the coated fuel can is likely to experience a temperature of about  $850^\circ\text{C}$  in use and it has been found that high temperature oxidation resistance may be achieved if the substrate is coated at a temperature corresponding to the maximum temperature likely to be experienced in use. 55

The invention will now be particularly described, by way of example only as follows, where reference will be made to the accompanying drawing, the sole figure of which shows (schematically) an apparatus for coating a metallic substrate. Comparative examples, i.e. examples that are not examples of the invention, are also included below. 60

Referring to the figure, a reaction vessel 1 of a right circular cylindrical shape and made, for example, of silica or glass is mounted vertically. A substrate 2 in the form of a stainless steel fuel

element can be suspended within the vessel 1 from a hook 3 by means of a suspension wire 4. The substrate 2 is earthed as shown by its connection to the suspension wire 4.

An external electrode 5 constituted by a wire mesh 5 is wound around the outside of the reaction vessel 1 and the mesh 5 is coupled to a radio frequency power supply 6 constituted by a radio frequency induction heater.

If during coating it is desired to increase the sample temperature beyond that which results from the effects of the electric field, such heating may be accomplished by placing the coil of the RF heater around the reaction vessel (and sample). In addition a susceptor may be placed within the RF coil and around the sample (either inside or outside the reactor vessel) to act as the sample heater. Alternatively a separate heater (oven 7) may be placed round the vessel, and the coil used remotely, as in the Figure.

The reaction vessel 1 is provided with a gas inlet 8 connected to gas supplies by way of valves 9. The reaction vessel 1 is also provided with an outlet port 10 which is connected to a vacuum pump 11 via a throttle valve 12 and which has a pressure gauge 13.

In operation, the substrate 2 and the external electrode 5 constitute two electrodes employed to generate a radio frequency glow discharge in the reaction vessel 1 containing a component or components capable of chemical reaction in the plasma of the discharge to produce a ceramic oxide. The external electrode 5 is connected to a tapping point of the radio frequency power supply 6 operating at a frequency of 1 MHz, though this value is not critical and probably any frequency in the range  $10^4$  to  $10^9$  Hz would work. The tapping point is found empirically and is typically such as to apply a few hundred volts to the external electrode 5 with respect to earth when the gas pressure is a few torr. The radial electric field so produced creates a glow discharge and the variables of voltage and gas pressure are adjusted to ensure that the plasma is most intense adjacent to the substrate 2, which is assisted by the inverse relationship between the field and radial distance from the axis. Chemical reaction to produce the ceramic oxide takes place in the glow discharge and the oxide is deposited on the substrate 2.

By fine adjustment of the radio frequency voltage and the gas pressure in the reaction vessel, the discharge may be confined to the region adjacent to the substrate 2 such that no glow extends to the walls of the reaction vessel 1. Since the chemical reactions causing the coating to form on the substrate 2 are associated with the glow, little or no deposit forms on the reaction vessel 1 itself and homogeneous nucleation in the gas phase is prevented. For this reason, it is generally preferred that the ratio of the radii of the reaction vessel 1 and the substrate 2 is large. However, if deposition on the reaction vessel 1 is not important the gap between the reaction vessel 1 and the substrate 2 may be small in order to effect a saving in the reactant components.

If desired, a plurality of substrates 2 may be suspended in a single large reaction vessel 1 so that all of the substrates 2 are coated in a single coating operation. There may, however, be problems in achieving uniformity of coating.

#### EXAMPLES

A cleaning and degassing operation was carried out by generating a glow discharge in the apparatus shown in the figure whilst passing a mixture of argon and hydrogen through the reaction vessel 1 via the gas inlet 8 and out through the outlet port 10. The discharge power was adjusted to heat the substrate 2. (Red heat is achieved at a power density of about  $1 \text{ W/cm}^2$  of substrate surface).

The flow of argon and hydrogen was turned off and a mixture of silane and carbon dioxide (containing typically in the range 0.5 to 10% by volume of silane) admitted to the reaction vessel 1 via the gas inlet 8. The voltage and power dissipation were adjusted again as required. The mixture became ionised and silica, generated by chemical reaction in the glow discharge, was deposited on the substrate. Deposition was continued until the desired coating thickness was achieved. Coating rate is dependent on the gas mixture and on power dissipation and is typically in the range of 1 to  $50 \mu\text{m/hour}$ .

If it is desired to deposit silica onto an oxidised substrate surface, the above procedure may be modified by omitting the cleaning and degassing stage and instead generating a glow discharge whilst passing carbon dioxide through the reaction vessel 1 in order to oxidise the surface of the substrate.

The above general procedure was applied to samples of carbon steel substrates where silica coatings of differing thicknesses were deposited using a mixture of silane and carbon dioxide containing 10% by volume of silane. Each of the coated samples was tested for oxidation resistance by heating in air at  $500^\circ\text{C}$  for a predetermined period of time, cooling and measuring the weight gain. Comparison was made with uncoated samples and the results are shown in Table 1 below as weight gain in  $\text{mg/cm}^2$ .

TABLE 1

Example	Coating Thickness ( $\mu\text{m}$ )	Heating Time (hours)				
		71	236	419	921	2093
A	0	3.08	4.67	5.11	7.03	9.2
1	0.75	0.041	0.08	0.118	0.192	0.368
2	4.9	0.025	0.034	0.053	0.061	0.093
3	7.9	0.010	0.02	0.031	0.038	0.056

It will be seen that resistance to oxidation improved with increased coating thickness by a factor of up to 200 after heating for 2093 hours.

The coated carbon steel samples were also found to have a reduced rate of attack by sea water by a factor of 8 over a 35 day period in comparison with uncoated carbon steel samples.

The above general procedure was also applied to samples of 20/25 Nb steel substrates. The samples were pre-oxidised by heating for 4 hours in  $\text{CO}_2$  at  $800^\circ\text{C}$ . Silica coatings were then deposited on the samples using a mixture of silane and carbon dioxide containing (i)  $\frac{1}{2}\%$  by volume of silane in respect of half of the samples (Example 4 below) and (ii) 1% by volume in respect of the other half of the samples (Example 5 below). The measured weight gain was 0.101 to 0.189  $\text{mg}/\text{cm}^2$ . Each of the coated samples was tested for oxidation resistance by heating in air at  $825^\circ\text{C}$  for a predetermined period of time, cooling and measuring the weight gain. Comparison was made with uncoated samples and the results are shown in Table 2 below as weight gain in  $\text{mg}/\text{cm}^2$ .

TABLE 2

Example	Coating Thickness ( $\mu\text{m}$ )	Heating Time (hours)			
		1000	2000	3000	5885
B	0	0.038 –	0.49 –	0.58 –	0.80 –
		0.51	0.63	0.88	1.20
4	~4	0.017 –	0.035 –	0.059 –	0.121 –
		0.059	0.092	0.131	0.212
5	~4	0.007 –	0.014 –	0.033 –	0.078 –
		0.024	0.043	0.074	0.147

It will be seen that there is an improvement in oxidation resistance of the coated samples by a factor of 10 in comparison with that of the uncoated samples.

Also, no spallation was measurable from the coated samples, whilst, after heating for 3000 hours, ~30 to 40% of the oxide on the uncoated samples had spalled.

Further, the coated samples were compared with uncoated samples in an environment known to cause carbonaceous deposition. It was found that the uncoated samples became black due to the deposition of many milligrams of carbonaceous material on their surfaces. Carbonaceous deposition was, however, prevented in the case of the coated samples.

#### EXAMPLE 6

The above general procedure was applied to samples of a steel known as PE16 which has the composition by weight of 16.5% Cr, 43% Ni, 1.2% Ti, 3.3% Mo, 1.0% Al and the balance Fe.  $\text{SiO}_2$  coated samples of the steel were exposed to a known carburising environment at  $750^\circ\text{C}$  and it was found that the coating totally prevented carburisation of the steel. In contrast, carburisation occurred in the case of uncoated samples of the steel.

Furthermore, the coated samples exhibited resistance to oxidation in air at  $825^\circ\text{C}$  in comparison with uncoated samples in a similar way to that shown in Examples B, 4 and 5 above.

## CLAIMS

1. A method of coating a steel or a Ni-base alloy substrate with a ceramic material to protect the substrate from corrosion, carburisation and/or carbonaceous deposition, which method comprises generating, adjacent the substrate, a glow discharge in an ionisable gas containing a component or components capable of chemical reaction in the plasma of the glow discharge to produce the ceramic material under conditions such that the ceramic material is formed on the substrate to constitute a coating. 5
2. A method according to claim 1 wherein the ceramic material is silica.
3. A method according to claim 2 wherein the ionisable gas contains, as the components, a silane and an oxidant therefor. 10
4. A method according to claim 3 wherein the silane is monosilane and the oxidant is carbon dioxide.
5. A method according to any of the preceding claims wherein the substrate is a stainless steel substrate. 15
6. A method according to claim 5 wherein the stainless steel is a Cr-bearing austenitic steel.
7. A method according to claim 6 wherein the substrate is in the form of a fuel can for a nuclear reactor.
8. A method according to any of claims 1 to 4 wherein the substrate is a carbon steel substrate.
9. A method according to any of the preceding claims wherein the substrate is oxidised before being coated. 20
10. A method of coating a substrate with a ceramic material substantially as described herein with reference to any of Examples 1 to 6.
11. A coated substrate made by a method according to any of the preceding claims