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(54) Low porosity metallic coatings.

(57) A metallic coating is formed on a refractory metal substrate, e.g. for providing corrosion resistance, by providing an initial porous metallic coating on the substrate by spraying and then heat treating, e.g. by HF heating, to sinter at least part of the initial coatings and give rise to diffusion into the substrate.

Working, e.g. by warm rolling, is carried out to densify the coating. The resulting coating is ductile and may, for example, be of an Al-bearing ferritic steel such as a steel having up to 8% by weight Al and/or up to 25% by weight Cr. The substrate may, for example, be a steel such as stainless steel.

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Low Porosity Metallic Coatings

The invention relates to a method of forming a protective metallic coating on a substrate (e.g. for providing corrosion resistance); an initial porous metallic coating is provided on the substrate by spraying and then a heat treatment is carried out to sinter at least part of the initial layer and give rise to diffusion of the initial coating into the substrate.

Corrosion is a problem in many areas of industry and it is believed that the effects of high temperature corrosion have recently become more severe. Examples of such forms of high temperature corrosion are vanadium pentoxide attack in boilers, chloride attack in burning furnaces, in fluidised beds, and sulphate attack and attacks by sulphur dioxide and hydrogen sulphide in chemical processing apparatus. Materials that are subject to corrosion may be protected by various coating techniques such as metal plating, metallizing and coating with metal powders and spraying of metals. However, metal plating and metallizing are complicated and expensive, and coating with metal powders and spraying with metals, whilst more straightforward to carry out, give coatings containing voids and pores and also of variable adhesion to the substrate.

UK Patent Specification No 1 581 172 describes a method of meeting the above problems by forming a surface layer on a stainless steel product by forming an initial layer of from 10µ to 2 mm in thickness on the surface of the stainless steel by applying powders of at least one of Fe, Cr, Ni, Ti, Mo, Nb, Co and alloys containing two or more of these metals on the surface, heating the initial layer at a temperature ranging from 1150 to 1480°C for 0.01 second to 10 minutes by means of high frequency heating at a frequency ranging from 0.1 KHz to 500 KHz so as to sinter at least part of the initial layer and to diffuse part of the metals of the initial layer into the stainless steel product to a depth of at least 1 μ, and to give a surface layer with a porosity of not more than 4%.

The invention is concerned with application of the method of UK Patent No 1 581 172 to production of metallic coatings, such as Al-bearing ferritic steel coatings, and with certain modifications such as provision of a working step thereby to give rise to a coating of increased smoothness and density.

The invention provides a method of forming a protective metallic coating on a refractory metal substrate which comprises the steps of

(i) providing an initial porous metallic coating on the substrate by spraying;

(ii) heat treating the initially coated substrate thereby to sinter at least part of the initial coating and to give rise to diffusion thereof into the substrate; and

(iii) working the coating to effect densification thereof.

Coatings so produced have been found to be dense, adherent, and ductile and also to provide good corrosion resistance as evidenced by tests described herein. Also they may have a high quality surface finish which is important from the corrosion resistance aspect.

The invention is applicable to the protection of a substrate in a variety of forms, for example a tube, metal sheet or strip and a shaped article. The substrate may, for example be an article such as a condenser, a fluidised bed component or a component for chemical process apparatus, or a complex shaped component such as a blade for a gas turbine engine, or may be a material for subsequent fabrication into such an article. The substrate may, for example, be made of a steel such as a stainless steel or a mild steel. Low quality substrates such as the latter may therefore be improved by means of the present invention.

The protective metallic coating may, for example, be a single element coating, e.g. Ti or Zr, or an alloy. Preferably it is a steel coating and is most preferably an aluminium-bearing ferritic steel coating, which steel may, for example, be a steel containing Fe, Cr and Al with or without additional constituents such as Y and/or Hf. A preferred Al-bearing ferritic steel is a steel containing Fe, Cr, Al and Y, for example as marketed under the UK Registered Trade Mark "FECRALLOY", because of its outstanding ability to withstand corrosion in aggressive environments such as those containing S, C, N and halogen. The Al-bearing ferritic steel used may contain additional constituents such as Si which may improve the corrosion resistance of the steel and also incidental constituents which may be present as a result of the materials used in manufacture thereof and of the manufacturing process itself.

Preferred Al-bearing ferritic steels in the invention are those having high Al concentrations, for example up to 8% or up to 10% by weight, and/or those having high Cr concentrations, for example up to 25% by weight. Al-bearing ferritic steels of such high Al and/or Cr concentrations are normally difficult to fabricate when in the form of coatings. The invention however does not require fabrication to be carried out and is therefore particularly advantageous in the provision of coatings of such steels on shaped articles. Particularly preferred Al-bearing ferritic steels are those containing from 10% to 25% Cr, from 2 to 10% Al, up to 1% Y, up to 0.5% Si and the balance Fe where all proportions quoted are by weight.

Step (i) may be carried out by methods known in the art for producing metallic coatings by spraying, for example by plasma jet spraying or by gas spraying. Preferably, the spraying is carried out in an inert environment such as an atmosphere of argon in order to minimise oxidation and give a substantially oxide-free initial coating. At this stage, however, there may be some loss of certain intended constituents of the coating. For example some Al and Y, if present, may be lost during the spraying.

Step (ii) may be carried out, for example, at a temperature in the range from 950°C to 1300°C such as 1100°C. It may, for example, be carried out by means of high frequency heating which is particularly appropriate when the substrate is in elongated form such as a tube since the latter can readily be heated by causing a high frequency heating coil to traverse the length of such a substrate. Other forms of heat treatment that may possibly be suitable are conventional furnace heating and laser heating. The latter may be suitable for heat treating coatings on the insides of tubes which are normally difficult to heat by means of high frequency heating.

Step (iii) may be caried out by methods known in the art and its general effect is to densify the coating. It is preferably carried out as a warm working step such as warm rolling, for example by working the product of step (ii) before it has completely cooled down, e.g. at a temperature in the range of 600°C to 800°C. In the case where the substrate is elongated such as a tube, it may be possible to carry out steps (ii) and (iii) sequentially along the length of the substrate, e.g. by arranging for a means for heat treating the coated substrate (such as an H.F. coil) and a means for working the coated substrate (such as rollers) to traverse the coated substrate together at a spaced interval. In a similar way, it may be possible to carry out steps (i), (ii) and (iii) sequentially, e.g. by arranging a spraying means, such heat treating means and such means for working to traverse the substrate together at spaced intervals from one another. "Traverse" is not necessarily to be taken to mean that the substrate is always stationary although usually this will be the case. Thus, "traverse" means that there is relative movement between the substrate and the means for effecting any of steps (i), (ii) and (iii) as appropriate.

Normally, step (iii) is carried out after step (ii). However, it may be possible to carry out step (ii) before step (iii) with a view to improving the surface finish of the coating.

Further densification of the coating may be effected by cold working operations such as drawing through a die, swaging or reeling.

The thickness of the coating in the invention may be up to 1½ mm, for example 1 mm, though it may be possible to produce thicker coatings. Also, it may be possible to carry out the invention more than once in order to produce a thicker coating.

It might be beneficial for certain applications to provide an intermediate layer between substrate and coating to inhibit diffusion. Such an intermediate layer might be useful when embrittlement is likely to be a problem in use of the coated substrate. Furthermore, the coated substrate may be subject to further treatment in order to enhance the performance of the coating. For example, a coating that contains less Al than intended due to losses thereof in step (i) as discussed above may be alonized in order to increase the Al content. "Alonizing" is a process for diffusing Al into the surface of Fe base or Ni base alloys and is described in "Alonized Heat Exchanger Tubes Give Good High Temperature Service" by McGill and Weinbaum at Corrosion/76, March, 1976, Houston, Texas.

Various ways of carrying out the invention will be described in detail below by way of example only.

Example 1

(i) An Al-bearing ferritic steel in the form of wire and of composition Fe - 20.5 Cr - 4.75 Al - 0.44 Y - 0.28 Si where the figures are proportions by weight was flame sprayed onto a substrate in the form of a 10" long 321-type stainless steel tube of 1½" outside diamter and 1" internal diameter thereby to give an initial coating on the tube.

(ii) The initially coated tube was heat treated at 1320°C by traversing it at 5 mm/sec through a high frequency coil of a 25 KHz shaft hardener machine rated at 28 KW. The tube was rotated at 120 r.p.m. during the heating step in order to prevent overheating. If necessary, the tube may be water-cooled in order to prevent melting.

(iii) The product of step (ii) was warmed rolled at a temperature in the range 600°C to 900°C to give a final coated tube which was observed to have a smooth, adherent coating.

The final tube was tested by taking a ¼" thick ring from the tube, slitting the ring and opening up the slit until the ring was almost flattened. It was observed that the coating remained adherent. By way of comparison, a similar test was carried out on a tube coated according to step (i) only above (i.e. without carrying out steps (i) and (iii). When the slit was opened to a gap of about 2", the coating was observed to spring away from the surface of the substrate.

Example 2

(i) The procedure of step (i) of Example 1 was repeated.

(ii) The initially coated tube and a loose fitting mandrel of "FECRALLOY" steel for the tube were heated in a muffle furnace at 1100°C for ¼ hour and 1 hour respectively.

(iii) The mandrel was placed in the tube and the combination transferred to a lathe placed in a 3 jaw chuck, clamped tight with the tail stock centering the tube. The chuck was rotated at 350 r.p.m. and pressure applied to the tube by means of a roller device engaging at 0.020"/revolution.

The final tube was tested as described in Example 1 and the coating was found to be adherent. Micro-examination of the final tube showed a marked reduction in the porosity of the coating.

Claims

1. A method of forming a protective metallic coating on a refractory metal substrate which comprises the steps of

(i) providing an initial porous metallic coating on the substrate by spraying; and

(ii) heat treating the initially coated substrate to sinter at least part of the initial coating and to give rise to diffusion thereof into the substrate,

characterised in that

the coating of the product of step (ii) is worked to effect densification thereof.

2. A method as claimed in claim 1 wherein the protective metallic coating is an aluminium-bearing ferritic steel coating.

3. A method as claimed in claim 1 or claim 2 wherein step (iii) is carried out by warm working the product of step (ii).

4. A method as claimed in claim 3 wherein the warm working is carried out by warm rolling the product of step (ii) at a temperature in the range of 600°C to 800°C.

5. A method as claimed in any of the preceding claims wherein the substrate is elongated and wherein steps (ii) and (iii) are carried out sequentially along the length thereof.

6. A method as claimed in claim 5 wherein steps (i), (ii) and (iii) are carried out sequentially along the length thereof.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,Y	GB - A - 1 581 172 (NIPPON STEEL CORPORATION) * Claims * --	1	C 23 C 9/02 C 23 C 7/00 C 23 C 17/00 B 05 D 1/08
X	DE - A - 2 403 312 (S.A. COCKER-ILL-OUGREE-PROVIDENCE ET ESPER-ANCE-LONGOZ EN ABREGE COCKERILL) * Claim 1 * --	1	
Y	CH - A - 448 671 (E.I. DU PONT DE NEMOURS & COMPANY) * Claims * --	2	
Y	CH - A - 506 635 (VEREINIGTE DEUTSCHE METALLWERKE AKTIENGESELL-SCHAFT) * Examples; claims * --	1,3-6	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
X	US - A - 4 061 801 (M. HAMADA et al.) * Examples; claims * --	1,3	C 23 C B 05 D
Y	PATENTS ABSTRACTS OF JAPAN, unexamined applications, C Section, vol. 3, no. 75, June 27, 1979 THE PATENT OFFICE JAPANESE GOVERNMENT, page 66 C 50 * Kokai-no. 54-50 438 (TOKYO SHIBAURA DENKI K.K.) * --	2	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	05-09-1983	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C Field, vol. 4, no. 190, December 26, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT, page 53 C 37 * Kokai-no. 55-128 573 (SUMITOMO KINZOKU KOGYO K.K.) --	1,3,5	
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C Field, vol. 5, no. 164, October 21, 1981 THE PATENT OFFICE JAPANESE GOVERNMENT, page 101 C 76 * Kokai-no. 56-93 869 (SHIN NIPPON SEITETSU K.K.) ----	1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.³)