

Description

This invention relates to the thermal spraying of stainless steel, especially as applied as an intermediate stage in the provision of a non-stick coating layer over a substrate metal.

It is well known to spray on to a roughened substrate surface a fluoropolymer dispersion, to remove the dispersant or solvent, and to cure or sinter so as to give a coating layer.

In order to improve the adhesion of this layer to the substrate it is also well known first to flame-spray metal droplets or particles on the substrate so as to give a rough surface for the fluorocarbon polymer adhesion. An example of such flame sprayed metal is stainless steel, which is a general name for alloys of iron, chromium, (typically about 18%) nickel (typically about 8%) and minor additives such as titanium, manganese, silicon, etc. However, it is known in the art that problems of coating breakdown can arise and it is recognised generally that many of these have their roots in corrosion phenomena as between the substrate and the flame-sprayed metal.

For example, it is accepted that aluminium is not a very suitable substrate metal for such techniques, and this is believed to be because of the risk of "white rust" corrosion, that is to say formation of aluminium oxides within the coating layers.

The present invention has originated from a consideration of this problem and involves utilisation of a form of stainless steel with an unusually high chromium level and optionally with increased nickel level.

On an aluminium substrate this runs completely contrary to previous expectations, and the use of additional chromium is counter-indicated not only by cost but also by the expectation of increased possibility of white rust (corrosion due to aluminium salts), due to increased chromium content. However, and as discussed in detail below, we believe we have identified a different corrosion problem as being more significant although hitherto not appreciated, and we can alleviate that problem to obtain improved coatings, any risk of "white rust" formation being more than offset by curing this other problem having its origin in "red rust" (corrosion due to ferrous salts) formation.

FR-A-1404049 discloses a method of applying a stainless steel coating on to a substrate by plasma spraying. Series 200, 300 and 400 steels are disclosed. In this case, the steel coating represents the finished protective layer and entirely covers the substrate.

EP-A-92309 discloses a method of applying a non-stick coating to a substrate in which the substrate is first subjected to grit blasting and a layer of stainless steel or molybdenum is then flame

sprayed, to cover at least 65% of the roughened surface. A PTFE coating is applied to the flame sprayed surface.

It is an object of the present invention to provide a method of applying a fluoropolymer coating to a substrate which results in a more resistant and hard wearing coating.

According to the present invention, there is provided a method of coating a substrate with a layer of fluoropolymer which comprises submitting the surface of the substrate to thermal spraying with a stainless steel alloy to provide a roughened surface, the alloy being arranged to cover from 50 to 85% by area of the underlying surface, and subsequently applying the fluoropolymer to the roughened surface, characterised in that the stainless steel alloy has a chromium content of 25 to 35% by weight.

The chromium content of the stainless steel is significantly greater than the normal 18% of standard stainless steel.

Preferably, also there is some small adjustment in the nickel content of the stainless steel, which can be up to 15%, that is to say rather greater than the normal 8% figure for standard stainless steel.

A preferred composition of stainless steel for carrying out the method of the invention is therefore 25 to 35% by weight of chromium, 8 to 15% by weight of nickel, 0.1% maximum by weight of carbon, 2% maximum by weight of manganese, and 0.4% maximum by weight of silicon, with the remainder being iron and incidental impurities.

The method as defined above is typically carried out to provide a rough surface with protruding particles. The roughness of the particles themselves is preferably from 25 to 50 μm transverse dimension, most preferably by way of example.

Typically, the substrate surface itself has previously been roughened before being thermally sprayed. Such previous roughening can typically have the dimensions of from 15 to 20 μm peak-to-valley distance.

In the method of the invention as defined above a wide range of substrate metals can be used, but it is a more particular advantage of the invention that even the more difficult substrate metals such as aluminium may be utilised.

The fluorocarbon polymer may be applied from liquid media (dispersant or solvent vehicle) and subsequently dried (e.g. at 120°C to 150°C) and cured or sintered (e.g. at 200 - 450°C, for up to 30 minutes) which together achieve a non-stick and durable, corrosion resistant, layer.

The invention of course further extends to a substrate an article having a surface comprising such a fluorocarbon layer secured to an intermediate corrosion-resistant layer as described above. The article in question can be a tool (secateurs,

shears, fork).

The above invention, using an excess of chromium in the thermally-sprayed alloy, is not predictable from prior art, especially in the context of an aluminium substrate where the use of excess chromium might be expected to give even more aluminium oxides. However, although we do not wish to be governed by any theory as to the operation of the method, it appears likely that the phenomenon of red rust, previously unexpected in stainless steel is in fact Present, and although not always immediately noticeable, persists over a long Period. It would appear to have its origin in the drastic thermal spraying conditions, apparently leading to at least superficial loss of chromium in at least some of the metal particles probably dependent upon their individual history as they pass differently through different temperature zones.

The following observations appear to support the above hypothesis.

1. Glass panels metal sprayed with traditional stainless steel grades of wire produced red corrosion products in neutral salt fogs (ASTM B4117), static 5% sodium chloride solutions and static 10% acetic acid solutions within a 25 hour exposure duration.
2. Aluminium plaques (of both cast LM6 and wrought 1200 grades) metal sprayed with traditional stainless steel grades of wire produced both red and white corrosion products in boiling 10% acetic acid solution, in some cases after only 20 minutes exposure.
3. Electron microprobe analysis of the metal deposited on to panels showed a cored structure, consisting of a very thin surface layer containing approximately 14% chromium and in some cases the surprising situation of a bulk central region with virtually no chromium present. The other alloy elements were evenly distributed.

The non-staining properties of stainless steel are due to the formation of a tenacious and resistant oxide film based on chromium. It is generally regarded that chromium levels below 14-15% are insufficient to impart protection and the structure of the deposited layer is therefore such that the iron oxide film formed is extremely thin. Any abrasion is likely to break the film to expose the central core. Insufficient chromium is present to heal the break in the film and corrosion proceeds unabated.

4. Aluminium vessels which had been metal sprayed using traditional stainless steel wire were used to boil a 10% acetic acid solution for 3 hours. In all cases a red discolouration was found, allied sometimes with areas of white cor-

rosion products. In an effort to identify the red product a pan was left standing for 30 minutes in a 10% oxalic acid solution. After this time the acid was discoloured and the pan restored to its original metallic appearance. Polarographic analysis of the acid solution indicated the presence of Fe^{2+} and Fe^{3+} ions. Another similarly treated pan was filled with deionized water and was still discoloured even after a 2 hour boil.

5. Panels of typical cookware compositions such as cast or wrought aluminium, stainless steel or cast iron when coated with the specified wire in the prescribed manner have not shown any tendency to form either red or white corrosion products in typical cooking environments such as boiling salted water, hot detergents, salty steam and boiling acetic acid solutions after a minimum three hour exposure.

Claims

1. A method of coating a substrate with a layer of fluoropolymer which comprises submitting the surface of the substrate to thermal spraying with a stainless steel alloy to provide a roughened surface, the alloy being arranged to cover from 50 to 85% by area of the underlying surface, and subsequently applying the fluoropolymer to the roughened surface, characterised in that the stainless steel alloy has a chromium content of 25 to 35% by weight.
2. A method as claimed in Claim 1, characterised in that the stainless steel contains from 8 to 15% by weight of nickel.
3. A method as claimed in Claim 1, characterised in that the stainless steel comprises 25 to 35% by weight of chromium, 8 to 15% by weight of nickel, 0.1% maximum weight of carbon, 2% maximum by weight of manganese and 0.4% by weight of silicon, the remainder being iron and incidental impurities.
4. A method as claimed in any preceding claim, characterised in that the particles of the sprayed alloy range from 25 to 50 μm in the transverse dimension.
5. A method as claimed in any preceding claim, characterised in that the underlying surface is itself roughened, prior to spraying, the peak-to-valley distance of the underlying roughened surface preferably being from 15 to 20 μm .
6. A method as claimed in any preceding claim, characterised in that the underlying surface is



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The non-staining properties of stainless steel are due to the formation of a tenacious and resistant oxide film based on chromium. It is generally regarded that chromium levels below 14-15% are insufficient to impart protection and the structure of the deposited layer is therefore such that the iron oxide film formed is extremely thin. Any abrasion is likely to break the film to expose the central core. Insufficient chromium is present to heal the break in the film and corrosion proceeds unabated.

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5. Panels of typical cookware compositions such as cast or wrought aluminium, stainless steel or cast iron when coated with the specified wire in the prescribed manner have not shown any tendency to form either red or white corrosion products in typical cooking environments such as boiling salted water, hot detergents, salty steam and boiling acetic acid solutions after a minimum three hour exposure.

Claims

1. A method of coating a substrate with a layer of fluoropolymer which comprises submitting the surface of the substrate to thermal spraying with a stainless steel alloy to provide a roughened surface, the alloy being arranged to cover from 50 to 85% by area of the underlying surface, and subsequently applying the fluoropolymer to the roughened surface, characterised in that the stainless steel alloy has a chromium content of 25 to 35% by weight.
2. A method as claimed in Claim 1, characterised in that the stainless steel contains from 8 to 15% by weight of nickel.
3. A method as claimed in Claim 1, characterised in that the stainless steel comprises 25 to 35% by weight of chromium, 8 to 15% by weight of nickel, 0.1% maximum weight of carbon, 2% maximum by weight of manganese and 0.4% by weight of silicon, the remainder being iron and incidental impurities.
4. A method as claimed in any preceding claim, characterised in that the particles of the sprayed alloy range from 25 to 50 μm in the transverse dimension.
5. A method as claimed in any preceding claim, characterised in that the underlying surface is itself roughened, prior to spraying, the peak-to-valley distance of the underlying roughened surface preferably being from 15 to 20 μm .
6. A method as claimed in any preceding claim, characterised in that the underlying surface is



an aluminium surface.

7. A method as claimed in any of Claims 1 to 6, characterised in that the fluoro polymer is applied to the substrate in a liquid medium, and is dried and cured or sintered.
8. A method as claimed in Claim 7, characterised in that the drying preferably being carried out at 120°-150°C.
9. A method as claimed in Claim 7 or Claim 8, characterised in that the curing or sintering preferably being carried out at 200°-450° for up to 30 minutes.
10. A coated substrate obtainable by the method as claimed in any preceding claim.

Patentansprüche

1. Verfahren zum Beschichten eines Substrates mit einer Fluorpolymerschicht, bei welchem die Oberfläche des Substrates mit einer rostfreien Stahllegierung thermisch besprüht wird, um eine aufgerauhte Oberfläche zu erhalten, wobei die Legierung so aufgebracht wird, daß sie 50 bis 85 Flächenprozent der darunterliegenden Oberfläche bedeckt, und anschließend das Fluorpolymer auf die aufgerauhte Oberfläche aufgebracht wird, dadurch gekennzeichnet, daß die rostfreie Stahllegierung einen Chromgehalt von 25 bis 35 Gew.-% aufweist.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der rostfreie Stahl 8 bis 15 Gew.-% Nickel enthält.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der rostfreie Stahl 25 bis 35 Gew.-% Chrom, 8 bis 15 Gew.-% Nickel, maximal 0,1 Gew.-% Kohlenstoff, maximal 2 Gew.-% Mangan und 0,4 Gew.-% Silicium enthält und der Rest aus Eisen oder zugehörigen Unreinheiten besteht.
4. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die Teilchen der Sprühlegierung im Quermaß eine Größe im Bereich von 25 bis 50 µm aufweisen.
5. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die darunterliegende Oberfläche selbst vor dem Spritzen aufgerauht wird, wobei die Rauhtiefe der darunterliegenden aufgerauhten Oberfläche vorzugsweise 15 bis 20 µm beträgt.

6. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die darunterliegende Oberfläche eine Aluminiumoberfläche ist.
7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Fluorpolymer auf das Substrat in einem flüssigen Medium aufgebracht wird und getrocknet, gehärtet oder gesintert wird.
8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Trocknung vorzugsweise bei 120°-150°C durchgeführt wird.
9. Verfahren nach Anspruch 7 oder Anspruch 8, dadurch gekennzeichnet, daß das Härten oder Sintern vorzugsweise bis zu 30 Minuten bei 200°-450°C durchgeführt wird.
10. Beschichtetes Substrat, das durch das Verfahren nach einem der vorangehenden Ansprüche herstellbar ist.

Revendications

1. Procédé de revêtement d'un substrat avec une couche de fluoropolymère qui comprend la vaporisation thermique de la surface du substrat avec un alliage en acier inoxydable pour fournir une surface rugueuse, l'alliage étant placé pour couvrir de 50 à 85% de la surface sous-jacente, et ensuite application du fluoropolymère sur la surface rugueuse, caractérisé en ce que l'alliage d'acier inoxydable a une teneur en chrome de 25 à 35% en poids.
2. Procédé suivant la revendication 1, caractérisé en ce que l'acier inoxydable contient de 8 à 15% en poids de nickel.
3. Procédé suivant la revendication 1, caractérisé en ce que l'acier inoxydable comprend 25 à 35% en poids de chrome, 8 à 15% en poids de nickel, 0,1% au maximum en poids de carbone, 2% au maximum en poids de manganèse et 0,4% en poids de silicium, le reste étant du fer et des impuretés accidentelles.
4. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que les particules d'alliage vaporisé se situent de 25 à 50 µm en dimension transversale.
5. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la surface sous-jacente est elle-même rugueuse, avant la vaporisation, la distance pic-vallée de



la surface rugueuse sous-jacente étant, de préférence, de 15 à 20 μm .

6. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la surface sous-jacente est une surface d'aluminium. 5
7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que le fluoropolymère est appliqué au substrat dans un milieu liquide, et est séché et cuit ou aggloméré. 10
8. Procédé suivant la revendication 7, caractérisé en ce que le séchage est, de préférence, réalisé à 120-150 °C. 15
9. Procédé suivant la revendication 7 ou la revendication 8, caractérisé en ce que la cuisson ou l'agglomération est, de préférence, réalisée à 200-450 °C pendant jusqu'à 30 minutes. 20
10. Substrat enduit susceptible d'être obtenu par le procédé suivant l'une quelconque des revendications précédentes. 25

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