United States Patent [19]

Streel

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[54] **METHOD OF COATING STEEL PRODUCTS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 825,515, May 19, 1969, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **148/134**

[51] **Int. Cl.** **C21d 9/00,** C23c 13/02

[58] **Field of Search** 29/196, 196.2, 196.3, 196.6; 148/13, 14, 134, 31.5, 127

[56] **References Cited**

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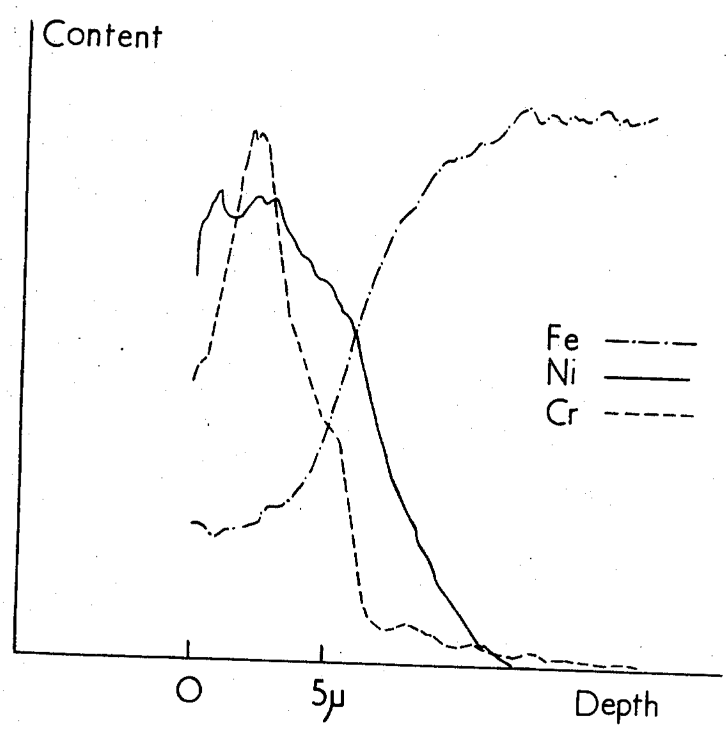
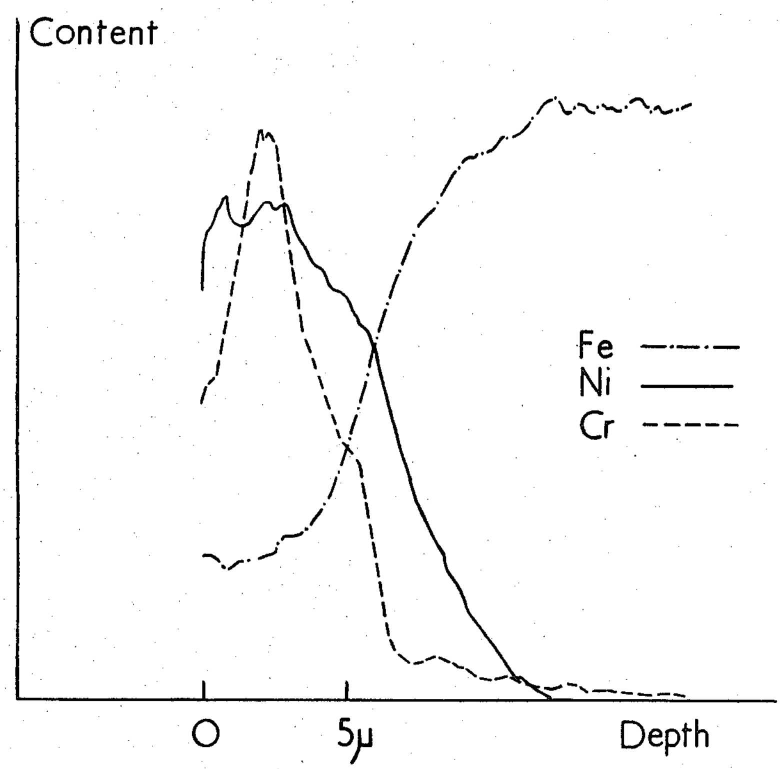
[57] **ABSTRACT**

An as-worked mild steel product is preheated to a temperature insufficient to cause recrystallization. A metallic coating is applied to the preheated surface by metallization under vacuum, and the coated product is recrystallization annealed at a temperature between 650°C and 1,000°C.

11 Claims, 1 Drawing Figure




Content
Fe
Ni
Cr
O
5μ
Depth

METHOD OF COATING STEEL PRODUCTS

This application is a continuation-in-part of copending application Ser. No. 825 515 "Method of coating with a metallic coating obtained by metallization under vacuum, steel products such as strip, bar and wire" of D. T. Streel, filed May 19, 1969, now abandoned. The benefit of the filing date of the parent application is hereby claimed.

The invention relates to a method of coating, with a metallic coating obtained by metallization under vacuum, steel products such as strip, bar, and wire.

It is known to subject a hot-rolled steel product to a process of cold working to obtain a product of the desired size, but as this causes strain-hardening it is necessary to subject the product to recrystallization annealing, in a neutral or reducing atmosphere at a temperature of approximately 700°C maintained for a duration of several hours. The product annealed in this manner is then provided with a metallic coating, since it is known that to protect steel products against atmospheric, chemical, alimentary or other corrosion, they should be covered with a coating constituted of a metal selected for the particular resistance which it offers to a given corrosion agent.

Accordingly, it is also known to use nickel, chromium, nickel/chromium, zinc, copper, or aluminium to form the coating. The application of a coating consisting of one of these metals or one of their alloys may take place by various known methods and in particular by the method of metallization under vacuum in a continuous process.

In the present description, by "metallization under vacuum" there should be understood any operation for applying a metal on a metallic product in the course of which operation evaporation of the metal to be deposited takes place. If these methods of application of a coating are used, bearing in mind certain advantages which they have, the result is that, as the forces of cohesion of the coating to the steel depend on the state of the surface. Accordingly, surface faults frequently result and are at present eliminated to a certain extent by subjecting the coated product to an additional treatment which may be mechanical or thermal, in addition to the aforementioned recrystallization annealing.

However, this procedure has a major disadvantage, in view of the fact that this additional treatment is a supplementary operation which increases the cost of the coating to a considerable extent, even so as to make the manufacture of coated product uneconomical.

The method in accordance with the invention is based on the discovery that it is possible to omit the additional treatment which has been provided up to the present, and to realize adherence of the coating applied to a product by metallization under vacuum, by carrying out a single thermal treatment, i.e., by combining in one single phase the annealing of the product and the thermal treatment supplying the uniform adherence of the coating.

The invention provides a method of coating a cold worked mild steel product, the product having its as-worked metallurgical structure, comprising the steps of preheating the product to a temperature insufficient to cause substantial recrystallization, applying a metallic coating to at least a part of the surface of the product by metallization under vacuum, and recrystallization annealing the coated product at a temperature between

650°C and 750°C and below the fusion point of the metallic coating.

The cleaning of the surface to be coated may take place for instance chemically, by heating, or by electrolysis.

As concerns the preheating of the surface to be coated, it is advantageous to fix the limits of the temperature range to be reached by dependence on the nature of the metal applied directly to the steel by evaporation under vacuum.

The method may be used for applying a coating for instance of chromium, nickel, cobalt, molybdenum, cadmium, aluminium, copper or an alloy of these metals.

In the case where the metal applied directly to the steel by metallization under vacuum to form the coating is chromium, nickel, cobalt, molybdenum or one of their respective alloys, the preheating temperature of the surface to be coated is preferably between 350°C and 500°C.

On the other hand, in the case where the metal applied directly to the steel by metallization under vacuum is aluminium, copper, cadmium, or some other metal which diffuses rapidly in steel under the effect of heat, or an alloy based on one of these metals, the preheating temperature of the product to be coated is preferably lower than 450°C.

It is possible to deposit several successive layers of different metals. These successive depositions may be found to be particularly advantageous when it is desired to carry out the depositing of a coating for protection against corrosion having the cumulative advantages of coatings with good adherence, good cohesion and slight porosity — as is the case for coatings of aluminium — and coatings having resistance to corrosion, satisfactory hardness and a good appearance — as is the case with coatings of nickel, chromium or chromium/nickel alloys.

In these cases, it may be advantageous to deposit, by the above method, a first layer of aluminium or of an alloy of aluminium such as "Duralumin" (Trade Mark) after preheating the product to a temperature which is suitable for the depositing of this metal, then a second layer, for instance of a chromium/nickel alloy, the coated product then being subjected to a single annealing phase at a temperature determined by taking into account the nature of the chromium/nickel alloy selected.

Where the annealing is carried out on a coiled product in a bell furnace, its duration may be from 30 minutes to 50 hours; where the annealing is carried out continuously on an uncoiled product, the duration of annealing is generally less than 30 minutes. In the present description, there is to be understood by "duration of annealing" solely the actual duration of the annealing at the temperature selected, i.e., the period during which the annealing temperature should be maintained without taking into account the time necessary for reaching this temperature or the cooling time.

In accordance with a variation of the invention, the coated product is heated rapidly to a temperature such that no coarsening of the grain of the product occurs which would be prejudicial to subsequent use of the coated product, and the heating is stopped as soon as the temperature selected has been reached. It is advantageous to carry out this annealing by sweeping the surface of the product by means of one or several electron guns.

In accordance with another variation, the annealing is carried out in an atmosphere, which may be an atmosphere of controlled composition, the pressure of which is lower than 10^{-2} torr.

The invention will be further described with reference to a specific example thereof and with reference to the accompanying drawing the sole FIGURE of which shows a graph of concentration of Fe, Cr, and Ni in the surface of a coated steel sheet.

A method in accordance with the invention may be put into effect in the following manner, given by way of example only.

A strip of ordinary mild non-killed steel, its composition being C ≤ 0.12 percent, Mn 0.2 percent to 0.5 percent, P 0.050 percent, S 0.040 percent, and its thickness being approximately 2 mm, is subjected to cold working in order to obtain a sheet the thickness of which is 0.9 mm.

This sheet is then subjected to a cleaning/scouring process in the known manner, by means of an alkali bath, on one face, in an ordinary atmosphere. It then passes into an enclosure maintained at a vacuum, for instance of approximately 10^{-5} to 10^{-4} torr, where it is preheated to a temperature of approximately 450°C. In the enclosure the coating metal, consisting of an alloy of 80 percent nickel and 20 percent chromium, is evaporated and then deposited on the cleaned and heated surface until the thickness of the coating is approximately 5 microns.

The sheet coated in this manner issues continuously from this enclosure, is coiled, and is then subjected to a single annealing phase in a bell furnace at a temperature of approximately 700°C. This temperature is maintained for a period of approximately 5 hours. This single annealing phase, which brings about simultaneously the recrystallization of the sheet and the adherence of the coating, is carried out under hydrogen which has been made perfectly dry by any known means.

Samples of sheets obtained by the above method have been subjected to mechanical tests, i.e., to bending tests and to stamping tests in accordance with the Ericksen test; through these tests, it was seen that the coating is adherent, that no splitting, cracking, or separation of the coating occurs, even when the bending is carried out at 180°C, bringing the two faces in contact with each other.

Moreover, these results are confirmed by micrographic section examinations, which have shown that the coating metal has penetrated to a depth of approximately 5 microns in the steel of the sheet. On the other hand, porosity was very much reduced and had become practically non-existent which was confirmed by two types of tests known in the coating industry, i.e., the ferroxyl test and the sulfo-cyanide test.

Tests were also carried out on a large number of samples and showed that the results obtained were reproducible.

Moreover, samples were examined by electronic microprobe, in cross-section; the results are tabulated in the table given below, in which the values given indicate the approximate composition as a function of the depth of penetration.

	0 to 2.5μ	2.5 to 5μ	5 to 7.5μ	7.5 to 10μ	10 to 12.5μ
Fe	23%	27.4%	59%	88%	100%
Cr	17.5%	17%	4%	1%	traces
Ni	59.5%	55.6%	37%	11%	0

From this table it can be seen that the chromium has penetrated to a depth of approximately 10 microns, but beyond this depth it is found in slight content only. If one refers to the surface composition, one can see that the content at this depth of 10 microns is approximately 17 times weaker, whereas the nickel, at this same depth, is found with a content of approximately 5.5 times weaker than at the surface. On the other hand, it is clear that iron is found in the coating layer with a content of approximately 25 percent, which means that the coating layer consists of a stainless steel containing nickel, chromium and iron. It has moreover appeared, surprisingly, that the coating layer has a composition corresponding to that of stainless steel known under the denomination ASTM B83–46.

The graph in the accompanying drawing was recorded by means of a microprobe and shows the variations of the contents of iron, chromium and nickel in the diffusion layer (approximately 0–10 μ). The curves illustrated were obtained by plotting the contents of Fe, Ni and Cr as ordinate and the depth (microns) as abscissa.

As concerns Ni and Cr, there is a general decrease in concentration from the external face of the coating layer to the base steel where these contents quite rapidly tend to zero. As concerns iron, there is a general continuous increase in concentration. The zone of diffusion of these three elements is clearly marked and in the interior of this zone the variations in concentration follow a quite precise law on which one can rely to obtain a well determined local composition.

This shows that the method makes it possible to obtain systematically, easily and in an economical manner a sheet the body of which is ordinary mild steel whereas the coating layer which covers it is a stainless steel, which adheres in a uniform manner in view of the reciprocal penetrations of the nickel and chromium of the coating layer into the ordinary steel and of the iron of this ordinary steel into the coating layer. From this result, which could not have been foreseen at this treatment temperature, there arises an important advantage from the practical point of view, since one obtains a sheet which is able to replace, in numerous instances, the use of sheet which is totally of stainless steel which is far more expensive and more difficult to work, in particular as far as concerns welding.

An important feature of the method, which has a considerable economic advantage, resides in that only a single annealing phase is needed, at temperatures which are relatively low and the duration of which is not excessive, this being due to the physical contact between the sheet and the coating layer deposited by metallization under vacuum.

I claim:

1. A method of coating a cold worked mild steel product, the product having its as-worked metallurgical structure, comprising the steps of preheating the product to a temperature insufficient to cause substantial recrystallization, applying a metallic coating to at least a part of the surface of the product by metallization under vacuum, and recrystallization annealing the coated product at a temperature between 650°C and 750°C and below the fusion point of the metallic coating.

2. A method as claimed in claim 1, wherein the metallic coating comprises at least one member of the group consisting of Cr, Ni, Co, Mo, Al, Cu, and alloys thereof.

3. A method as claimed in claim 1, wherein the metallic coating adjacent the steel comprises at least one member of the group consisting of Cr, Ni, Co, and Mo.

4. A method as claimed in claim 3, wherein said preheating temperature is between 350°C and 500°C.

5. A method as claimed in claim 1, wherein the metallic coating adjacent the steel comprises at least one member of the group consisting of Al and Cu.

6. A method as claimed in claim 5, wherein said preheating temperature is below 450°C.

7. A method as claimed in claim 1, comprising coiling the coated product and performing the annealing in a bell furnace for a period of between 30 minutes and 50 hours.

8. A method as claimed in claim 1, in which the annealing is performed during continuous passage of the coated product, the coated product being annealed for a period of less than 30 minutes.

9. A method as claimed in claim 1, in which the annealing is performed by sweeping the coated product with at least one beam of electrons during continuous passage of the coated product, the coated product being annealed for a period of less than 30 minutes.

10. A method as claimed in claim 1, wherein the metallic coating comprises an alloy of cadmium having a melting point above 650°C.

11. A method as claimed in claim 1, wherein the metallic coating adjacent the steel comprises an alloy of cadmium having a melting point above 650°C.

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