

# United States Patent

Faber

[15] 3,642,517

[45] Feb. 15, 1972

[54] **PROCESS FOR INCREASING THE STABILITY OF PROTECTIVE CHROMIUM LAYERS ON METAL**

- [72] Inventor: **Guy Faber**, Ober-Rohrdorf, Switzerland  
[73] Assignee: **Aktiengesellschaft Brown, Boveri & Cie**,  
Baden, Switzerland  
[22] Filed: **June 5, 1968**  
[21] Appl. No.: **734,570**

[30] **Foreign Application Priority Data**

Sept. 6, 1967 Switzerland .....12392/67

[52] U.S. Cl. ....117/71 M, 29/196, 29/196.1,  
29/196.6, 117/62, 117/66, 117/119, 117/130 R

[51] Int. Cl. ....B44d 1/14

[58] Field of Search .....117/66, 71 M, 119, 130, 131,  
117/62; 29/196, 196.1, 196.6

[56] **References Cited**

**UNITED STATES PATENTS**

2,744,032 5/1956 Highfield .....117/131 X

3,294,498 12/1966 Carter .....117/131 UX  
3,312,546 4/1967 Mayer et al. ....29/196.6 X  
2,993,264 7/1961 Grenoble .....117/71 M

*Primary Examiner*—Ralph S. Kendall  
*Assistant Examiner*—C. K. Weiffenbach  
*Attorney*—Pierce, Scheffler & Parker

[57] **ABSTRACT**

A process for increasing the stability of a protective chromium layer on metal used in a nitrogen-containing atmosphere at high temperatures, the chromium layer being coated with a layer of a metal having less affinity than chromium such as unalloyed iron, nickel or cobalt, and in which the chromium is soluble, the whole then being diffusion annealed in a neutral atmosphere at a temperature above 1,000° C. until the thickness of the chromium-alloyed portion of the metal coating is at least 0.01 mm.

**6 Claims, No Drawings**

## PROCESS FOR INCREASING THE STABILITY OF PROTECTIVE CHROMIUM LAYERS ON METAL

This invention relates to a process for increasing the stability of protective chromium layers on metals used in a nitrogen-containing atmosphere at high temperatures.

Known protective layers on heat-resistant steels and alloys can be used at temperatures above 600° C. The purpose of these protective layers is to delay the corrosion of the substrate by e.g., sulphur or oil ash.

Protective layers may be divided into three classes. The first class comprises corrosion-resistant alloys or metal, e.g., pure chromium, which are applied in layers to the substrate and firmly attached to the substrate by diffusion annealing. The second class includes protective layers formed by enriching the surface of the protected substrate by corrosion-resistant metals such as chromium and/or aluminum. Finally, alloys can be manufactured for use as protective layers or plating. To this end, thin layers of each metal forming the alloy (one of these is generally chromium) are applied to the substrate and the whole is annealed until the diffusion process gives a homogeneous alloy firmly attached to the metal to be protected.

Protective layers of pure chromium have very great resistance to corrosion—i.e., they are very slowly corroded by oxygen and sulphur. The disadvantage of pure chromium, however, is that it easily absorbs and combines with nitrogen at high temperatures. The resulting compound of chromium and nitrogen is very brittle, with the result that the chromium layer may crack open if the temperature changes and exposes the substrate to corrosion.

Chromium-enriched metal surfaces are much less liable to absorb nitrogen but have less resistance to corrosion than pure chromium. This reduced resistance to corrosive media such as oxygen and sulphur, particularly after a long period of use, is due to the fact that the chromium on the surface is oxidized, i.e., is removed from the metal to be protected. For a time, more chromium can be diffused to the surface from the interior of the metal, but as most of the chromium has been concentrated at the surface by the enrichment process and the content falls rapidly inside the substrate, the supply is soon exhausted and the chromium content in the surface layer is reduced to the point where it gives no further protection against corrosion and the substrate begins to scale.

Chromium alloys behave similarly when used as protective layers. The chromium passes to the surface by the same mechanism, but generally the supply of chromium is somewhat larger, with the result that it takes longer before the alloy at the surface has lost so much chromium that it is no longer corrosion resistant and begins to scale. When scaling has proceeded far enough for layers richer in chromium to come to the surface, the process is repeated.

The principal object of this invention is to prevent, or at least greatly delay, the absorption of nitrogen by protective chromium layers at high temperatures. To this end, the chromium layer is coated with a layer of metal having less affinity than chromium for nitrogen and in which chromium is soluble, after which the whole is diffusion annealed in a neutral atmosphere at a temperature above 1,000° C. until the diffusion path of chromium in the surface layer is at least 0.01 mm.

The chromium layer, which is extremely resistant to oxygen and sulphur, is coated with a thin layer which does not in itself give any protection against corrosion. The surface layer is advantageously of unalloyed iron, but other metals can be used, e.g., nickel or cobalt. To be suitable, the metal in the surface layer must have less affinity than chromium for nitrogen, otherwise it will be attacked at least as quickly. The chromium must also be soluble in the other metal, so that it can migrate into the surface layer during diffusion annealing. The surface layer can be applied galvanically, by flame spraying, dipping or any other method. The layer thickness should be from 0.01 to 0.05 mm.

The metal or workpiece to be protected is then diffusion annealed in a neutral atmosphere, e.g., hydrogen or argon. The temperature and duration of annealing should be chosen so that the diffusion path of the chromium into the surface layer is not too short. It should be at least 0.01 mm. The values chosen depend on the material in the surface layer, and it should be noted that the diffusion process is faster at higher annealing temperatures. To be sufficiently effective, the diffusion annealing should be carried out at a temperature over 1,000° C. It should not last too long or occur at an unduly high temperature, however, since the alloy formed should not be almost homogeneous but should leave a chromium layer and a surface layer with rapidly decreasing chromium content—i.e., a layer with a high internal and low surface content of chromium. Thirty minutes is the minimum period for annealing.

It is sufficient to keep within the above limits, without any further restrictions on the thickness of the surface layer and the temperature and duration of diffusion annealing. This is a considerable advantage in the process according to the invention. It is important for the chromium content to decrease rapidly outwards. If the chromium has not diffused as far as the top of the surface layer, the external chromium-free layer and the low-chromium-content layers underneath scale and flake off during operation in corrosion atmospheres and at high temperatures, until a layer is uncovered which contains enough chromium to be corrosion resistant. To prevent the top layer from becoming too thin through this automatic process, diffusion annealing must be continued until the diffusion path of chromium into the surface layer is at least 0.01 mm.

In the method described, the chromium layer is prevented from absorbing nitrogen by the surface layer. The surface layer, formed possibly after scaling, is not subject to the ordinary corrosion mechanism (oxidation of chromium at the surface, migration of chromium to the surface, loss of chromium from the surface layer, and scaling) since the chromium layer underneath contains adequate reserves of the metal. The stability of a protective chromium layer is considerably improved by the surface layer, which is cheap and relatively easy to manufacture. The surface layer can be used at temperatures above 750° C. or for a very long period without the protective layer becoming brittle or cracking as a result of absorbing nitrogen.

In general the diffusion temperature can range between 1,000° and 1,200° C., and is preferably about 1,100° C. The diffusion time can range between 30 minutes and 4 hours and is preferably about 1 hour.

### EXAMPLE 1

A workpiece which is provided with a corrosion-resistant protective layer of chromium 0.1 mm. thick. In order to clean it and to obtain sufficient adhesion with the metal layer that is subsequently applied, it is first of all etched electrolytically in 10 percent sodium hydrate (current strength 2a./dm.<sup>2</sup> during 30 min.). The workpiece is then rapidly rinsed in water and immediately afterwards dipped in a bath of 300 g. FeCl<sub>2</sub>/liter water where it receives electrolytically a layer of iron 0.02 mm. thick (current strength 2a./dm.<sup>2</sup> during 30 min.). After this, the workpiece is heated in a vacuum furnace to 1,080° C. and kept at this temperature for 35 min. whereby chromium diffuses into the iron layer.

### EXAMPLE 2

A workpiece of the same kind as in Example 1 is cleaned, etched and washed in the same way. The workpiece is then dipped in a nickel bath (Watt's type) where it is covered electrolytically with a layer of nickel, 0.015 to 0.02 mm. thick (current strength 2a./dm.<sup>2</sup> during 30 min.). Thereupon the workpiece is heated in a vacuum furnace up to 1,120° C. and kept at this temperature for 60 minutes. Due to the lower diffusion speed of chromium into nickel, a longer diffusion time is required than in Example 1.

I claim:

3

1. A process for increasing the stability of a protective chromium layer on a metal substrate when subjected to a nitrogen-containing atmosphere which comprises applying a surface coating to the chromium layer of a metal having less affinity for nitrogen than chromium and in which the chromium is soluble, said coating having a thickness substantially thinner than the chromium layer and from about 0.01 to 0.05 mm., diffusion annealing the chromium layer with the metal coating thereon in a neutral atmosphere at a temperature above 1,000° C. until a portion only of the chromium layer has diffused into the metal of the surface coating to form an alloy surface coating on the chromium layer remaining, the diffusion path of chromium in the surface coating being at least 0.01 mm.

4

- 2. A process as claimed in claim 1 wherein the metal of the surface coating applied to the chromium layer is iron.
- 3. A process as claimed in claim 1 wherein the metal of the surface coating applied to the chromium layer is nickel.
- 4. A process as claimed in claim 1 wherein the metal of the surface coating applied to the chromium layer is cobalt.
- 5. A process as claimed in claim 1 wherein the diffusion annealing step is carried out for at least 30 minutes.
- 6. A process as claimed in claim 1 wherein the alloy surface coating on the chromium layer remaining obtained by the diffusion annealing step has decreasing amounts of chromium toward the external surface of the coating.

\* \* \* \* \*

15

20

25

30

35

40

45

50

55

60

65

70

75