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HARD DIFFUSION FORMED REACTION COATINGS

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No Drawing. Continuation-in-part of application Ser. No. 768,187, Oct. 16, 1968, now Patent No. 3,620,816. This application Nov. 12, 1971, Ser. No. 198,413

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ABSTRACT OF THE DISCLOSURE

A novel process for producing hard coatings by diffusing one or more reactive elements in molten lead and reacting with one or more hardening elements of the group carbon, nitrogen, boron, and silicon present in ferrous products. The process offers flexibility in compositional control and coating parameters.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending application Ser. No. 768,187 entitled "Method of Diffusion Coating Metal Substrates Using Molten Lead as Transport Medium," filed Oct. 16, 1968, now U.S. Pat. 3,620,816.

BACKGROUND OF THE INVENTION

This invention relates to a novel process for producing hard surface compound layers on formed ferrous products. Lead is used as the medium to transfer a reactive element such as chromium to combine with a hardening element such as carbon present in the ferrous product. Formation of chromium carbide on steel by pack chromizing is a well known art. Such hard compounds may also be applied as coatings by a variety of methods such as pyrolytic plating and spraying but these processes are not related to the present invention.

In our pending U.S. patent application, "Method of Diffusion Coating Metal Substrates Using Molten Lead as Transport Medium," Ser. No. 768,187, now U.S. Pat. 3,620,816, we have shown that a lead medium very successfully produces corrosion resistant chromized and other surface alloyed impregnation zones on ferrous materials. Such patent application is directed to corrosion resistant products with particular emphasis on avoiding carbon reactions which deteriorate corrosion resistance. We have now found that a lead medium offers other utility and may be used to form hard compounds when carbon and other hardening agents are present in the ferrous product.

U.S. Pat. 3,184,331 to Carter discloses a process for diffusion coating of ferrous materials in molten calcium and other "active metal" baths. This is directed to corrosion resistance and avoidance of carbon contamination. Calcium is a strong "getter" for carbon and nitrogen. For example, Table II of Carter shows that the carbon content in his chromized coating on type 1070 steel (0.70% C) may be reduced to only 12% of the level in the substrate. A lead media behaves quite differently from such an "active" bath and as shown herein is an excellent medium for producing high carbon, hard coatings. Lead has an exceedingly low solubility for iron at the temperature of interest; simple iron containers may be used and the lead does not corrode the ferrous parts to be coated. The lead may be alloyed with other inert diluents if the desirable properties of lead are retained.

The object of this invention is to provide a novel process for diffusing at least one reactive metal through a lead bath and forming a hard compound coating on

ferrous articles containing one or more elements of the group carbon, nitrogen, boron, and silicon.

DESCRIPTION OF THE INVENTION

Our process offers many advantages: (1) absolute uniformity of the hard coating over irregular surfaces, (2) thickness control of the diffusion formed coatings by regulation of temperature and time, (3) uniform coating in small orifices, and (4) ease of producing alloyed or mixed compounds since two or more reactive elements may be readily codiffused through the lead.

The process consists of contacting the ferrous parts with molten lead which contains the diffusing reactive element. Contact with air must be avoided or minimized. Various contacting methods may be employed including the use of a slurry paint. In the preferred method, the ferrous parts, lead, and diffusing reactive elements are sealed in a ferrous container and agitated to insure solution of the diffusing elements and to provide relative motion between the ferrous parts for uniform coating. A range of temperatures and times may be used. We have typically used 1950° F. for 6 hours. For experimental coating of small parts, we have sealed the constituents in an evacuated tube made of mild steel or 400 series stainless steel and shaken the tube every 15 minutes while at temperature. A perforated spacer separates the tube into two compartments so that at the end of the run the tube may be inverted and the lead drained from the parts. In addition, the spacer keeps the parts and the chromium source under the lead during the run; iron and chromium float in molten lead. Only a small amount of residual lead remains which can be removed as desired. The lead is reuseable and easily purified.

In a simple example of our invention, C1018 and C1080 steel were reacted with 3 grams of chromium in 200 grams of lead at 1950° F. for 6 hours. Since chromium is only slightly soluble in lead at 1950° F., all of the chromium does not dissolve. As chromium reacts to form chromium carbide, additional chromium dissolves from the supply. Any source of chromium such as unalloyed metal or ferrochromium may be used. A surface reaction layer was observed metallographically with both steels. Microhardness readings were taken on polished cross-sections using a Leitz Miniload tester and unless otherwise indicated a load of 15 grams was employed. The reacted C1018 exhibited a hardness of 1380 and 455 DPH at a depth from the surface of 7 and 12 microns, respectively (25.4 microns=1 mil). With the availability of a greater carbon level in C1080, the hard carbide coating is over 1 mil deep. At a depth of 25 microns the hardness was 1500 DPH.

Cast iron was reacted with chromium in lead at 1950° F. for 4 hours and resulted in a 1.3 mil coating. The hardness was 1840 DPH (50 g. load) at a depth of 25 microns. Beneath the coating at a depth of 75 microns the hardness was 295 DPH (50 g. load).

To illustrate the uniformity of coating, a hole 1/16 inch is diameter by 5/16 inch long was drilled through a specimen prepared from "Drill Rod" (high carbon steel). After reacting with chromium in lead at 1950° F. for 6 hours, a uniform one mil coating was observed in the hole and over the outside surfaces. The hardness at a depth of 13 microns halfway through the length of the hole was 1500 DPH and the hardness on the outside at the same depth was 1440 DPH. Thus, the hardness was the same within experimental error. A similarly-treated sample with a blind hole 1/16 inch in diameter by 5/16 inch deep was found to be uniformly coated including the bottom of the blind hole.

Samples of C1018 steel have also been reacted with chromium in a lead bath after first providing commercial

carburizing and nitriding treatments such as cyaniding and Tufftriding. The ferrous materials can contain carbon, nitrogen, boron, or silicon as potential hardening elements. The uniform composition of such elements in the ferrous material can be limited since these elements will diffuse outward to the surface to react with the infusing reactive element from the lead. These hardening elements may be present from a prior surface diffusion treatment.

Molybdenum and columbium have been co-diffused with chromium in lead. It will be apparent to those skilled in the art that many reactive elements can be diffused in lead singly or in combination to form reaction compounds with one or more elements of the group carbon, nitrogen, boron, or silicon. Such reactive elements include but are not limited to molybdenum, tungsten, vanadium, columbium, tantalum, titanium, zirconium, hafnium, yttrium, and aluminum.

For greatest utility the reaction compounds should have a minimum hardness of 900 DPH. The hardness can be measured only when the coatings grow to sufficient thickness so that a microhardness indentation can be made on a polished cross-section. However, the compounds have considerable utility when present as thin coatings such that the hardness can not be varified.

Our examples have been directed to ferrous materials but the process could be employed with other substrates. The hard surfaced materials produced by our process will find utility principally in wear resistant applications but it should be noted that certain of these hard compounds also possess other desirable properties such as corrosion resistance.

It will be understood that various modifications and variations may be effected without departing from the spirit or scope of the novel concepts of our invention.

We claim as our invention:

1. The process of forming a hard compound coating consisting of a metal and nonmetal reaction product on a ferrous base substrate which substrate contains an element selected from the group consisting of carbon, nitrogen and boron and mixtures thereof which comprises the steps of contacting said substrate with a molten alloy bath consisting principally of lead and containing at least one diffusing element reactive with the group consisting of carbon, nitrogen, boron and mixtures thereof and reacting the surface zone of said substrate with said diffusing element to form a hard compound coating, which coating is characterized by a surface microhardness of at least 900 diamond pyramid numerals when the compound coating is grown sufficiently thick that it can be measured on a cross-section with a diamond pyramid indentor using a 15 gram load.

2. The process as defined in claim **1** wherein at least one reactive diffusing element is present from the group chromium, molybdenum, tungsten, vanadium, columbium, tantalum, titanium, zirconium, hafnium, yttrium, and aluminum.

3. The process as defined in claim **1** wherein chromium is the reactive diffusing element.

4. The process as defined in claim **1** wherein at least one reactive diffusing element is present from the group molybdenum, tungsten, vanadium, columbium, tantalum, titanium, zirconium, hafnium, yttrium, and aluminum.

5. The process as defined in claim **1** wherein carbon, nitrogen, or mixtures thereof are present in the ferrous article.

6. The process as defined in claim **1** wherein carbon is present in the ferrous article.

7. The process as defined in claim **1** wherein carbon, nitrogen, or mixtures thereof are present in the ferrous article and at least one reactive diffusing element is present from the group chromium, molybdenum, tungsten, vanadium, columbium, tantalum, titanium, zirconium, hafnium, yttrium, and aluminum.

8. The process as defined in claim **1** wherein carbon is present in the ferrous article and at least one reactive diffusing element is present from the group chromium, molybdenum, tungsten, vanadium, columbium, tantalum, titanium, zirconium, hafnium, yttrium, and aluminum.

9. The process as defined in claim **1** wherein carbon is present in the ferrous article and chromium is the reactive diffusing element.

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