United States Patent

[11] 3,620,816

[72] Inventors **John J. Rausch**
Route 2 Box 177, Antioch, Ill. 60002;
Ray J. Van Thyne, 10148 S. Coah Ave.,
Oak Lawn, Ill. 60453

[21] Appl. No. **768,187**
[22] Filed **Oct. 16, 1968**
[45] Patented **Nov. 16, 1971**

[54] **METHOD OF DIFFUSION COATING METAL SUBSTRATES USING MOLTEN LEAD AS TRANSPORT MEDIUM**
8 Claims, No Drawings

[52] **U.S. Cl.** **117/114,** 117/119, 117/131
[51] **Int. Cl.** **C23c 1/00,** C23c 1/06
[50] **Field of Search** ..... 117/114, 114 A, 114 B, 114 C, 131, 119

[56] **References Cited**

UNITED STATES PATENTS

2,399,848	5/1946	Becker et al.	117/22
3,184,330	5/1965	Carter	117/114
3,184,331	5/1965	Carter	117/114
3,186,865	6/1965	Page	117/131 X
3,261,712	7/1966	Carter	117/114
3,467,545	9/1969	Carter	117/114
3,481,769	12/1969	Carter	117/114 C

Primary Examiner—Alfred L. Leavitt
Assistant Examiner—J. R. Batten, Jr.
Attorney—Albert Siegel

ABSTRACT: A method of diffusing a metallic coating into a metallic substrate using molten lead, in some embodiments, as the transport medium for the metal being deposited. Has particular utility for depositing chromium on a ferrous base substrate to form a relatively high chromium content surface layer thereon. Also quite useful in providing aluminum containing surface zones. Further directed to diffusion alloying with the stabilization of ferritic phase or other means of reducing undesirable surface layer carbide formation.

METHOD OF DIFFUSION COATING METAL SUBSTRATES USING MOLTEN LEAD AS TRANSPORT MEDIUM

BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, numerous attempts have been made to surface alloy ferrous base substrates with metals such as chromium or other metal carbide formers or other metals to improve the surface properties of the substrate at comparatively low cost. Some work has been done in chromium diffusion coatings (see for example U.S. Pat. Nos. 3,343,928 and 3,377,196). The major problems that are encountered in attempting to form a chromium diffusion coating on steel at elevated temperatures stem from the carbon content of the steel and the mobility of such carbon. If the carbon content is relatively high, a surface layer of chromium carbide is formed which not only is considerably less desirable for most purposes than chromium per se but also such carbide layer effectively serves to block further chromium diffusion into the steel. The result has been that in steels containing moderate amounts of carbon, successful diffusion chromizing has been most difficult to achieve and the overcoming of such difficulty represents one of the objects of out invention.

Additionally, as is set out in some detail below, we find that in many steels we can readily chromize—i.e., diffuse chromium into the surface thereof to form an excellent stainless steel-like surface by applying the coating by means of a lead bath transport media or the like.

Furthermore, in order to understand certain aspects of out invention, before proceeding further while it will be obvious to many of those skilled in this art, we would note that most of the steels in common usage exist in the form of one crystalline phase, namely ferritic, at room temperature and in a second crystalline phase, namely austenitic, at elevated temperatures. This is to say as the temperature of the steel is increased beyond a certain level, there is a transformation of the ferritic phase into the austenitic phase. Among other phenomena it is known that the carbon of the steel is considerably more soluble and available to form carbides with carbide forming elements such as chromium in the austenitic phase than in the ferritic. Furthermore, in order to diffusion coat the steel within any reasonable time, because of the reaction kinetics, one must operate normally at a temperature where the steel is in the austenitic form. As a result of the temperature requirements to properly surface diffuse a carbide forming element, the workers in the past dealt principally with relatively low carbon steels in order to eliminate the problem of carbide blocking of the diffusing metal and thus the range of steels which could be diffusion chromized for example, has been quite narrowly limited.

We have discovered that by stabilizing the ferrite allotrope, we can readily surface diffuse carbide forming metals such as chromium to form very desirable surface coatings on the ferrous base material and this represents one of the objects of our invention.

Accordingly, a principal object of our invention is to provide a process of forming chromium enriched surface zones on ferrous base substrates by surface diffusing chromium thereon in a molten lead transport medium.

Another object of our invention is to provide a novel method of forming an aluminum enriched surface zone on various metal substrates particularly ferrous base by the surface diffusion of aluminum in molten lead.

Still another object of our invention is to provide a novel method of surface alloying steel with elements that are normally carbide forming and that would otherwise undesirably react with the carbon in the steel.

These and other objects, features and advantages of our invention will become apparent to those skilled in this particular art from the following detailed disclosure thereof.

SUMMARY OF THE INVENTION

This invention is directed to a novel metal diffusion process whereby chromium or other metals, particularly aluminum, are readily alloyed with the surface of a ferrous metal substrate. In some embodiments hereof, preferred, the alloying metal is diffused into the substrate by transfer through a bath or carrier vehicle of molten lead. In other embodiments hereof, such lead carrier need not be employed. Furthermore, we have discovered that the interfering effect of carbon in ferrous substrates can be substantially overcome as herein taught. All of this will be set forth in detail as this description proceeds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One of the simplest embodiments of our process involves the use of a ferrous base substrate, particularly steel, and a bath of molten lead containing adequate chromium to saturate the lead therewith and to provide a source of continuous chromium resaturation for that which is consumed during the surface alloy process. The chromium is added to the lead in any convenient soluble form such as elemental powder or granules or as an alloy such as ferrochromium or in any compound reducible to chromium. In one means of practicing our process, we use a relatively fine form of metal or alloy which is contained in a screened cage or the like to avoid contact between the solid chromium source and the ferrous parts which are being surface alloyed with chromium by transfer through the molten lead. We also found that the use of bulk porous chromium or ferrochromium is also effective in chromizing ferrous parts.

In carrying out this most simple embodiment of our invention, the lead bath is heated to operating temperature while protected by an inert atmosphere. Generally, we have operated at temperatures in the range from 1700° to 2500° F. for times varying between 1 to 18 hours. The excellent results that we have obtained at these ranges of operating conditions indicate that both higher and lower temperatures can be usefully employed to surface diffuse chromium onto a ferrous base substrate. Obviously, the lower temperature extreme is the melting point of the lead and at the upper extreme, one must avoid melting the substrate being coated. As with practically all diffusion processes, it will be appreciated that the rate of surface alloy growth is directly proportional to temperature of operation for the length of time employed.

When the ferrous parts, which are being surface alloyed, have been in the bath for the required time at the required temperature to produce the desired alloy layer thickness, such parts may be directly removed from the bath permitting excess liquid to drain therefrom. We have found that unless care is exercised in this removal and draining step a very adherent residue deposit is found on the surface of the substrate parts. Such deposit, which is quite porous, produces an unattractive, dull appearance and cause, in some cases, premature rust formation when the parts are exposed to a typical salt spray environment test. The removal of such porous deposit reveals the bright alloy surface and results in a very marked improvement in salt spray corrosion resistance. The deposit can be readily observed by metallographic examination of section parts and typically has a thickness of around 0.2 mils but may vary, depending on the geometry of the part, draining conditions and other factors.

Although this porous layer can be removed by chemical and mechanical means, we find it desirable to minimize or avoid its initial formation. While we are not absolutely certain as to why this deposit is formed, apparently it originates largely from the rejection of solute, e.g. chromium, during cooling of the lead base liquid while draining and we have found several methods which either minimize the formation of such coating or which reduce the adherency of the deposit. For example, we have found that draining of the parts in a chamber immediately above the lead bath which is at a temperature substantially the same or higher than that of the bath, results in a

marked decrease in the amount of residue on the drained parts, and this is a desirable step to use in the practice of our process.

We have also found that the cooling of the bath to precipitate excess solute, prior to draining, results in less residue and the residue that does form is less adherent which simplifies the final cleaning operation of the piece being surface alloyed.

Accordingly, this method of reducing undesirable coating formation on the piece being chromized should be considered as a desirable optional step in the practice of certain embodiments of our invention.

It will be noted that certain unique advantages stem from diffusion alloying utilizing molten lead. Lead has a relatively low vapor pressure at the high temperatures used in our process and has adequate solubility for chromium than iron is obviously important.

Additionally, the molten lead is quite chemically inert to many of the metallic diffusing elements which are used in the practice of our invention.

In order to make use of the benefits of chromium alloying with a ferrous base substrate, it is highly recommended that the chromium content at the surface be at least 14 percent by weight.

A further aspect of our process over and above the use of a molten lead bath in conjunction with a simple alloying material such as chromium or aluminum involves the addition of other materials to the bath which we find yield quite beneficial results. For example, we can add to the bath other metals or additives which produce a more corrosion resistant surface layer or which improve wettability and/or interact with carbon to control its deleterious effects. In the example set forth below we will cite the use of a number of such additives.

Among the additives which are most desirable for use herewith are those which stabilize the low temperature allotropic form of iron having a body-centered-cubic crystal structure which is commonly referred to as ferrite. In pure iron, the following quantities of the named elements stabilize the ferrite allotrope to 1900° F.

Element	Quantity Required to Stabilize Ferrite to 1900° F. (weight percent)
AR	1.5
As	4
Be	0.5
Cr	12.5
Ge	5
Mo	4
P	0.6
Sb	4.5
Si	2.1
Sn	2.0
Ti	0.8
V	1.6
W	6.0

It is to be understood that greater quantities of these elements can be tolerated and will result in further raising the thermal stability of ferrite.

These elements singly or in various combinations may be incorporated in the lead bath along with chromium to enhance the surface alloying process in the manner previously described. Similarly, they can be used separately to precondition the surface prior to chromium impregnation.

When carbon is present in the ferrous alloy—as is the case in all commercial steels—it will react with the infusing chromium. If sufficient carbon is present it causes the formation of chromium carbides which in turn decrease the corrosion resistance and rate of formation of the surface alloyed zone. If carbide forming elements, particularly those having greater thermodynamic stability than chromium carbides, are employed in the bath they will preferentially react with the carbon, thereby increasing the effectiveness of the chromium.

We have also used the noncarbide forming ferrite stabilizing elements to modify the interaction of chromium and carbon. If these elements are diffused into the surface they cause carbon to diffuse inwardly by stabilizing ferrite (which has much lower solubility for carbon) at the surface thereby causing carbon to migrate into the receding austenite zone in which it has greater solubility. We have effectively employed silicon, tin, and aluminum for this purpose.

Such a process is much more broadly applicable than merely chromizing in a lead bath. For other purposes it is desirable to enrich the surface of a medium to high carbon steel in titanium, for example, and the same problem of rapid formation of titanium carbide is observed which can be alleviated by use of a codiffusing ferrite stabilizer. We have shown that this novel procedure is most useful when the ferrite stabilizer is much more rapid diffusing than the other surface alloying element. Furthermore, this codiffusion procedure can be employed with other surface coating techniques.

Our invention may be further understood by references to the following examples thereof:

EXAMPLE 1

We prepared a materials charge consisting of 218 grams of lead and 6 grams of chromium powder. Such charge and the test piece to be diffusion chromized were sealed in a steel tube and then uniformly heated in a furnace maintained at 1800° F. for a period of 16 hours. For purposes of this example, we used four test pieces namely:

1. A titanium stabilized low-carbon steel containing approximately 0.06 percent carbon;
2. AISI 1020 Steel;
3. AISI 1035 Steel; and
4. AISI 1080 Steel

A charge and a test piece were placed within an evacuated steel tube which was composed of two chambers separated by a perforated washer such that the liquid could be drained from one chamber to the other at the completion of the run.

Following the treatment at 1800° F. for 16 hours, the four specimens were sectioned and examined metallographically. The chromium-rich alloy surface layer was distinguished by etching the specimens with a solution of 5 percent nitric acid in methyl alcohol. As is recognized by those skilled in the art, such an etching procedure readily attacks the steel substrate but does not attack the ferritic surface layer if the chromium content thereof exceeds 12 percent. Thus, the chromium-rich layer can be readily examined and its thickness measured under a microscope. By using such procedures, we find that the surface alloy layer thickness decreases with increasing carbon content of the substrate material in the following manner:

Substrate Material	Surface Alloy Layer Thickness (mils)
Ti-stabilized Steel	2.3
AISI 1020	1.3
AISI 1035	0.6
AISI 1080	0.3

The alloy layer was uniform on all of the specimens except on AISI 1080, which had slightly irregular thickness.

EXAMPLE 2

A charge of 224 grams of lead and 0.25 of aluminum along with specimens of the same type as in example 1 was run at 1600° F. for 18 hours. Again the same type of steel tube was employed. The specimens were sectioned and examined metallographically. The depth to which aluminum alloy formation had occurred was determined by microhardness traverses. A uniform decrease in hardness was measured from the surface inward to a point at which the hardness of the substrate material was reached. The alloy layer thicknesses measured in this manner were as follows:

Substrate Material	Surface Alloy Layer Thickness (mils)

Ti-stabilized Steel	2.0
AISI 1020	2.0
AISI 1035	1.3
AISI 1080	1.2

EXAMPLE 3

Specimens treated as in example 2 were subsequently sealed in a tube with 231 grams of lead and 7 grams of chromium and treated at 1800° F. for 16 hours. Surface alloy layer thicknesses were determined by using a combination of the etching and microhardness methods used in the previous examples. The following data were obtained:

Substrate Material	Chromium-rich Surface Alloy Layer Thickness	Total Alloy Layer Thickness (mils)
Ti-stabilized Steel	1.8	3.8
AISI 1020	2.0	4.1
AISI 1035	0.8	3.1
AISI 1080	0.8	3.0

EXAMPLE 4

A run was made in which steel specimens were surface alloyed with chromium and aluminum simultaneously. Specimens of AISI 1018 and 1035 were run in a mixture of 100 grams lead, 2 grams chromium, and 0.025 grams aluminum at 1900° F. for 2 hours. The following layer thicknesses were obtained:

	Thickness (mils)	
Steel	Chromized layer	Total Alloy Layer Thickness
1012	1.2	2.5
1035	0.7	1.5

In the region between these layers there was a zone of fine carbide precipitation formed on the 1035 steel specimen.

EXAMPLE 5

A run was made in which steel specimens were surface alloyed with titanium and aluminum simultaneously. A specimen of AISI 4130 steel was treated in a mixture of 200 grams lead, 1 gram titanium and 5 grams aluminum at 1900° F. for 2 hours. The thickness of the codiffused layer obtained was 5.5 mils. The run was repeated on another specimen of 4130 with no aluminum in the bath and no diffusion coating was observed.

EXAMPLE 6

Specimens of AISI 1018 and 1035 steel were immersed to the bottom of a bath composed of 100 grams of lead and 20 grams of aluminum sealed in an evacuated steel tube. After being run at 1900° F. for 1 hour the tube was inverted and the parts drained. The specimen of 1018 steel, which was a one-fourth inch diameter rod, had a uniform iron-aluminum alloy surface layer extending to a depth of 7.5 mils. There was no evidence of carbon or carbide precipitation in this zone. Below the surface layer, and extending into the core, there was a marked increase in the amount of pearlite compared to what normally would be present in this steel after normal heat treatment. Thus, the formation of the aluminum alloy layer caused the carbon from that zone to be driven into the core of the steel. The 1035 steel, which was a disc having a cross section of 0.168×0.168 inches, developed an aluminum alloy layer 6.5 mils thick. Again, the core showed pronounced enrichment in carbon.

EXAMPLE 7

A specimen of 1018 steel was immersed in a charge of 100 grams lead, 2 grams chromium, and 0.1 grams silicon. After being treated for 2 hours at 1900° F. there was a chromized layer having a thickness of 1.2 mils formed on the surface. Beneath this layer there was a uniform carbon-free ferrite zone having a thickness of 2.5 mils.

EXAMPLE 8

A run was made consisting of a charge of 100 grams of lead and 2 grams of low carbon ferrochromium powder (−150 mesh). A ¼–20 nut of resulfurized steel (AISI 1112), was run in the lead bath solution for 2 hours at 1900° F. A chromized layer having a thickness of 1.15 mils was produced. When the experiment was repeated using high purity chromium powder instead of the ferrochromium, substantially the same results were obtained.

EXAMPLE 9

A run was made at 1900° F. for 16 hours in a steel tube (AISI 1018) having a charge of 100 grams of lead, 0.094 grams titanium sponge and one standard ¼×20 nut made of an ordinary free machining resulfurized steel; such steels normally have a carbon contents in the range of from 0.1 to 0.12 percent. After the run the nut was drained of lead and slowly cooled. It was examined and found to be fully decarburized below metallographically detectable levels; that is, there was no evidence of pearlite which means that the free carbon content was below 0.025 percent. The tube wall, in contact with the Pb-Ti solution, was uniformly and fully decarburized to a depth of 55 mils. A diffusion zone extending to a depth of 5 mils was observed on both the tube wall and nut.

EXAMPLE 10

The above tests were repeated using the strong carbide forming elements Ta and Cb. Substantially the same results were obtained with respect to the decarburization effects observed.

EXAMPLE 11

A test was carried out to show the effectiveness of the strong carbide forming elements in enhancing the chromizing reaction. A run was made consisting of 100 grams lead, 3 grams chromium, and 1 gram of columbium. The latter two were in powder form having a mesh size of −48 to +100. A ¼–20 nut of resulfurized steel (AISI 1112) was immersed in the lead solution and run for 2 hours at 1900° F. The resulting chromized layer had a thickness of 1.95 mils. The core of the nut was very coarse grained and showed no evidence of pearlite.

EXAMPLE 12

Example 11 was repeated under identical conditions with the exception that the columbium powder was excluded from the charge. The chromized layer produced under these conditions had a thickness of only 1.15 mils. The nut showed a uniformly decarburized zone extending to 15 mils below the chromized layer. The core showed an appreciable quantity of pearlite.

EXAMPLE 13

A charge was prepared consisting of 220 grams of lead, 2.4 grams of nickel, and 4.4 grams of chromium. Four specimens of AISI 1110 steel were included and the vacuum sealed charge was run at 1900° F. for 15 hours, after which the liquid was drained from the specimens. Metallographic examination showed that a uniform surface alloy layer having a thickness of 0.8 mils was formed. At a distance of 0.12 mils from the outer surface the composition of the layer was 10.4 percent Ni, 58.6 percent Cr, balance Fe. After 100 hours salt spray exposure a

specimen, having a surface area of 3 cm.² showed only one very minor rust spot.

EXAMPLE 14

Four ¼–20 nuts of AISI 1112 steel were immersed in an iron container charged with 200 grams of lead and 5 grams of chromium powder (—42 mesh). These were heated at 1900° F. for 4 hours after which the parts were drained at a temperature substantially the same as that of the bath. The remaining adherent lead was removed and after salt spray testing for 24 hours the parts showed numerous rust spots. Metallographic examination showed a relationship between the location of the rust spots and areas in which a thin (0.2 mils) porous layer existed above the chromized layer; the result of solute rejection from the cooling, adherent lead. When this layer was removed, either mechanically or by pickling, the chromized nuts withstood 100 hours of salt spray exposure without rusting.

We have found that our process results in very uniform coatings having, for example, high chromium content which is uniformly graded and can be controlled and reproduced over precise limits. The "throwing power" of the process is excellent as evidenced by our ability to uniformly coat complex geometries, recesses and blind holes. We have successfully chromized a mild steel part having a blind hole diameter of one-eighth inch and depth of one-fourth inch. Even more extreme geometries should offer no difficulty in this respect.

While the foregoing description of the various embodiments of our invention is directed principally to the use of a molten lead bath as the alloying material transfer medium, it certainly will be understood by those skilled in this art that the molten lead need not be in the form of a molten pool per se but it is also possible to carry out our process, for example by "-painting" the substrate with a lead-alloying addition complex and then heating the thus coated material to surface alloy. It also would be understood that in the practice of various embodiments of our invention, particularly those directed to the use of the various ferrite-stabilizing additives enumerated above, that is some cases the use of a lead bath carrier is unnecessary. Furthermore, our process certainly has applicability in the alloying of the surface of nonferrous metals and alloys. It also should be noted that the bath need not be completely lead—it may contain considerable amounts of other constituents in addition to the material acting as the alloying agent.

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

We claim as our invention:

1. The process of diffusion coating a ferrous base substrate which includes the steps of contacting said substrate with a molten alloy bath consisting essentially of lead and at least one diffusing element from each of a first group of metals and a second group of ferrite stabilizing elements wherein the first group of metals consists of chromium, aluminum and mixtures thereof, and wherein the second group of ferrite stabilizing elements consists of antimony, arsenic, beryllium, columbium, germanium, molybdenum phosphorus silicon, tin titanium, vanadium, tantalum and tungsten with the total amount of said first group metals and said second group elements being sufficient to stabilize the ferrite phase of said substrate, and diffusing said diffusing elements into said substrate.

2. The process as defined in claim 1 wherein the metal of said first group is chromium.

3. The process as defined in claim 1 wherein the metal of said first group is aluminum.

4. The process of diffusion coating a ferrous base substrate which includes the steps of contacting said substrate with a molten alloy bath consisting essentially of lead and at least one diffusing metal soluble in lead selected from the group consisting of chromium, aluminum, and titanium and diffusing said diffusing metal into said substrate.

5. The process as defined in claim 4 wherein said diffusing metal is chromium.

6. The process as defined in claim 4 wherein said diffusing metal is aluminum.

7. The process as defined in claim 4 wherein said diffusing metal is titanium.

8. The process of diffusion coating a ferrous base substrate with chromium and nickel which includes the steps of contacting said substrate with a molten alloy bath consisting essentially of lead and the soluble diffusing metals chromium and nickel, and diffusing said metals into said substrate.

* * * * *