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PROCESS FOR ALUMINIZING FERROUS METALS

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My invention relates to a method of providing a protective aluminum surface on ferrous metals, and more particularly to an improved method of providing a protective diffusion coating of aluminum on ferrous metals from an alkali metal bath.

The co-pending application of the common assignee, Serial No. 377,507 filed June 24, 1964 in the name of Roger D. Moeller for "Aluminum-Containing Diffusion Coating for Metals," which is a continuation-in-part of Serial No. 85,457 filed January 30, 1961, now abandoned, discloses a method of providing protective diffusion layer coatings on base metals from molten alkali metal baths containing the coating material in dissolved form. The coating substance passes to the base metal by diffusion and then passes into the base metal, forming a graduated alloy composition rather than a simple coating on the surface of the base metal. This results in protective coatings of high oxidation and corrosion resistance with good mechanical properties. The application specifically discloses, among other things, the protection of ferrous metal bases with a diffusion coating of aluminum. While ferrous metals have heretofore been coated with aluminum by such methods as hot dipping, the higher quality diffusion layers had not been obtained. Aluminum diffusion coatings have been applied by so-called pack cementation methods, wherein a part is packed with aluminum, ammonium chloride and alumina (inert filler). Upon heating, aluminum chloride vapor is formed which deposits on the part. However, uniform coatings, particularly of edges, recesses and bores of complex shapes, are not obtained. Further, thin coatings (e.g., 1 mil or less) cannot be obtained and liquid aluminum frequently contacts the part and forms a thick, non-uniform, undiffused layer. Thin coatings are particularly necessary for applications on screws, bolts, fasteners, and the like where the dimensions of the final article must be strictly controlled. Aluminum provides a hard case on the surface of ferrous metals, particularly carbon or low alloy steels, which improves their behavier in oxidative and corrosive environments, as well as improves certain mechanical properties such as resistance to galling.

While the process described in the co-pending patent application leads to high quality aluminum diffusion coatings, I have found that further significant improvement can be obtained by the invention described below.

An object of the present invention is an improved process for providing a protective aluminum coating on ferrous metals from an alkali metal bath.

Another object is such an improved process which provides, during a shorter residence time in the bath, a diffusion coating of aluminum which has improved oxidation resistance.

Another object is to provide a catalyst for the bath which increases the plating rate and improves the quality of the coating.

Still another object is to control the concentration of the aluminum in the bath and other bath conditions in a manner to obtain uniform, high quality aluminum coatings on complex shapes.

Yet another object is to provide thin, uniform diffusion coatings of aluminum on ferrous metal bases.

The foregoing and other objects and advantages of my invention will become apparent from the following detailed description.

In accordance with my present invention, a diffusion coating of aluminum may be applied on ferrous metals by providing a molten bath of an alkali metal, adding thereto aluminum and chromium, placing the ferrous base metal in said bath, and maintaining said ferrous metal in said bath until an aluminum diffusion coating of desired thickness is obtained.

I have found that the addition of chromium to the alkali metal bath, which is preferably sodium in view of its relative cheapness and satisfactory performance, serves to accelerate the plating rate of aluminum and greatly aids in the formation of an attractive, bright coating of excellent oxidation and corrosion resistance. For example, a 4-mil diffusion coating on carbon steel can be applied in 5 hours from a sodium bath maintained at 1600° F., which time is considerably shorter than before. Further, complex shapes can be coated with thin, even coatings.

The mechanism of the chromium behavior is not understood; it apparently does not form part of the final aluminum diffusion coating, based upon metallographic examination. The effect of the chromium is particularly surprising when it is noted that diffusion coatings of chromium cannot be applied on a ferrous metal base from a sodium bath. The concentration of the chromium in the bath may satisfactorily vary over a broad range. For example, the concentration may be about $\frac{1}{100}$–$\frac{1}{5}$ weight percent Cr to Na, while a concentration of about $\frac{1}{20}$–$\frac{1}{10}$ weight percent Cr to Na is generally used. The chromium may be conveniently added to the bath in granular or powder metal form.

The concentration of the aluminum in the bath is very important in producing coatings of high quality, and I find that a lower concentration than previously employed considerably improves results. Thus, an aluminum concentration in the bath of about $\frac{1}{20}$–$\frac{1}{5}$ gram of aluminum per square inch of exposed metal surface area is highly satisfactory while about $\frac{1}{10}$ gram per square inch surface area is about optimum. Since the bath container or capsule metal is also coated with aluminum (to a like degree when such metal and the base metal are the same), the aluminum concentration must take this into account, and the term "exposed metal surface area" includes the surface area of both the base metal to be coated and the container metal. The precise concentration will depend upon the intended service for the coated part. For example, a thin coating (e.g., 0.1–0.5 mil) is useful for anti-galling applications, while a thicker coating (e.g., 1–5 mils) is desirable for sustained oxidation resistance. Previously, in the co-pending application, concentrations of about 1 gram aluminum per square inch surface area were employed and this could result in the formation of undesirably thick coatings without any improvements in qualities. The part to be coated should also be kept out of direct contact with solid aluminum metal, for example, by suspending the part to be coated on a screen in the bath. The contact with solid or molten aluminum is believed to partly account for the difficulties with the pack-cementation methods.

The time-temperature relationship for my improved aluminum coating process is about 1250° F.–1650° F. for a period of about ¼–16 hours. A longer time is required for a coating of a given thickness at a lower temperature and the thickness of the coating will also determine residence time in the bath. The coating thickness at a given temperature is a function of approximately the square root of the residence time. A 4-mil coating on carbon steel, for example, is obtained in about 5 hours at 1600° F. A coating of 0.2 mil is obtained in approximately 15 minutes at 1600° F., and requires about 1–2 hours at 1250° F. I find the best results are obtained by the use of higher temperatures in the indicated range, for

example above 1500° F. and preferably about 1600° F., for relatively moderate times, for example about 5 hours. However, ferrous metals which suffer diminishment of mechanical properties at such higher temperatures may be coated at lower temperatures.

I also find that, while the choice of the container material is not critical and stainless steels may be used as in the co-pending patent application, nonetheless, improved results are obtained with the use of carbon steel containers for coating of carbon steel samples. Apparently, the alloy constituents in the stainless steels may affect the coating of carbon steels.

The following examples are offered to illustrate my invention in greater detail.

EXAMPLES

A 3½-in. length of 1½-in. outside diameter by 0.065-in. thick 1015 carbon steel tubing was welded to a ⅛-in. thick end cap of the same material. Tabs of carbon steel test material to be coated were 1/16-in. thick by approximately ½-in. wide by approximately ¾-in. long with a 1/16-in. diameter hole centered near one end. Commercially pure sodium, 1100 aluminum sheet, and reagent grade chromium were used.

Four weighed and measured tabs were suspended on a wire frame of the same material as the tabs. This frame was fitted in the capsule so as to place the lower ends of the tabs approximately ¼ in. from the bottom of the capsule. The capsule, which now had the bottom cap welded on, the tabs in place, and contained measured quantities of aluminum and chromium, was placed in an inert gas (argon) glove chamber.

The quantities of additives were calculated on the basis of weight percent relative to sodium (for chromium) and on the basis of per square inch of metal surface (tabs, wire and capsule) exposed to the bath (for aluminum).

The sodium was cleaned mechanically to remove surface oxide in the inert atmosphere and a weighed amount placed in the capsule. A small furnace in the chamber heated the capsule to facilitate filling with sodium. The upper end cap was then welded to the capsule while in the inert atmosphere chamber.

The capsule was then withdrawn from the inert atmosphere chamber and placed in a capsule holder which was placed in a furnace, preheated to a selected temperature. The furnace was designed to roll the capsule at 15 revolutions per minute while the capsule was rocked through ±30° from the horizontal about the transverse axis of the tube at 5 cycles per minute. Generally, four capsules were run at a time. The capsule was processed in this manner for the selected time. After processing, the capsule was removed from the furnace in the capsule holder and allowed to air-cool.

The capsule was then opened in air by sawing off the upper end cap. The capsule and its contents were again placed in the inert atmosphere chamber, where the alkali metal (plus additive) bath was melted out. The tabs and wire frame were withdrawn from the capsule, and also from the inert atmosphere chamber. The parts, which were now covered with frozen alkali metal, were placed in butyl alcohol for cleaning.

After a distilled ater wash and drying, the tabs were visually inspected, remeasured, and reweighed. One of the tabs was sectioned and mounted for metallographic examination and measurement of coating thickness. One of the tabs was immersed in hot nitric acid and its resistance noted qualitatively. One of the tabs was suspended from a stainless steel wire and placed in a box furnace at 1500° F. Weight changes due to oxidation were determined weekly.

The following table summarizes the experimental method and the results of the oxidation testing for various samples using the above method, and also the results of oxidation testing of an uncoated steel sample. The marked difference in protection is noted.

Table

Additives to 50 gr. Na Bath		Treatment		Thickness Increase to 0.060" Tab	Weight Increase to 2½ gr. Tab	Tab Coating Thickness (Metallog.)	Wt. Gain of Tab Exposed to Air at 1,500 ° F. for 500 Hr. (interpolated)
Al**	Cr	Temp., ° F.	Time, Hr.				
Gr.	*Gr.*			*Inches*	*Gr.*	*Inches*	*mg./cm.²*
*1/5	5	1,500	5	.0180	.285	.0120	
*1/5	5	1,600	5	.0192	.280	.0046	
*1/10	5	1,500	5	.0036	.062	.0021	0.36
*1/10	5	1,600	5	.0033	.051	.0032	0.27
*1/20	5	1,600	5	.0010	.024	.0023	1.60
As-received Low Carbon Steel (in 40 Hrs.)							58.00

*Tab and capsule material was 1015 low carbon steel.
**Al concentrations in terms of grams per sq. in. exposed surface area.

The above examples are only illustrative rather than restrictive of my invention. Various modifications may be made by those skilled in the art without departing from the spirit of my invention. Therefore, the present invention should be understood to be limited only as is indicated in the appended claims.

I claim:

1. An improved method of providing a diffusion coating of aluminum on a ferrous metal base which comprises providing a molten sodium bath in an inert atmosphere, adding effective amounts of aluminum and chromium to said bath, placing said ferrous metal base material in said bath, and maintaining said base metal in said bath until a diffusion coating of the desired thickness is obtained.

2. The method of claim 1, wherein approximately 1/20–1/5 gram of aluminum per square inch of exposed metal surface area is added to said bath.

3. The method of claim 1, wherein chromium is added to said bath in an amount approximately 1/100–1/5 weight percent Cr to alkali metal.

4. A method of providing an improved diffusion coating of aluminum on a ferrous metal base which comprises providing a molten sodium bath in an inert atmosphere, dissolving in said bath approximately 1/20–1/5 gram of aluminum per square inch of exposed metal surface area, adding chromium to said bath in an amount approximately 1/100–1/5 weight percent Cr to Na, positioning said ferrous metal base in said bath, and maintaining said base metal in said bath at a temperature of approximately 1250–1650° F. for approximately ¼–16 hours.

5. The method of claim 4 wherein said ferrous metal is a carbon steel.

6. The method of claim 4 wherein said temperature is maintained between about 1500° F. and 1650° F.

7. A method of providing an improved diffusion coating of aluminum on a carbon steel base which comprises providing a molten sodium bath in an inert gas atmosphere, dissolving approximately 1/10 gram aluminum per square inch surface area of exposed metal surface area, adding chromium to said bath in an amount approxi-

mately 1/20–1/10 weight percent Cr to Na, placing said carbon steel in said bath, and maintaining said bath at a temperature of about 1600° F. for about 5 hours.

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