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SILICON-CONTAINING DIFFUSION COATING FOR FERROUS METALS

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ABSTRACT OF THE DISCLOSURE

A process for forming a silicon-containing diffusion coating on a ferrous or refractory base metal by placing the base metal in a molten sodium bath containing silicon dissolved therein, and further containing an active surface of zirconium in the bath. In certain preferred embodiments, both silicon and aluminum are dissolved in the molten sodium bath and codiffused into the base metal.

This invention relates to a method of providing a silicon-containing diffusion coating on a ferrous base metal or alloy, and more particularly to a method for providing a codeposited aluminum-silicon diffusion coating on a ferrous metal.

Industrial and commercial uses of metals at high temperatures and in corrosive environments have continually increased, and operations requiring metals with improved special properties are steadily rising. For a great many uses, it is essential that metal parts resist oxidation and other chemical surface reactions at high temperatures and abnormal conditions. Further, it is frequently desirable to have metal alloys of variable composition, for example, a very hard corrosion-resistant surface and base having good working characteristics—properties which are frequently not found with an alloy of uniform composition. Metals having corrosion-resistant surfaces at high temperatures are required, for example, for the following items: furnace parts, turbine blades, petroleum refinery equipment, jet engine sheet metal work, superheated tubes, and chemical plant equipment. The list of applications for ferrous metals with corrosion-resistant surfaces is virtually limitless. Thus, a process which can efficiently improve the high temperature corrosion properties of metals, particularly ferrous metals, is of considerable interest.

In U.S. Patent 3,085,028, a method and means is suggested for depositing silicon on a ferrous metal. The suggested process is restricted in its applications to relatively limited specific coatings.

In the copending application of Roger D. Moeller, "Aluminum-Containing Diffusion Coating for Metals" S.N. 377,507, filed June 24, 1964, now U.S. Patent 3,220,876, and assigned to the assignee of this application, there is disclosed a method for providing a codeposited aluminum-silicon diffusion coating on a ferrous metal. While the process described in the copending patent application leads to high quality codeposited aluminum-silicon diffusion coatings on a ferrous metal, for certain specific requirements I have found that further significant improvements can be obtained with respect to these codeposited coatings.

Accordingly, it is an object of the present invention to provide a method of forming an improved silicon-containing diffusion coating on a ferrous base metal.

Another object is to provide a method of applying a protective aluminum-silicon diffusion layer on a ferrous base metal.

A further object is to provide a silicon or aluminum-silicon diffusion coating on a ferrous metal in order to increase its hardness and resistance to high temperature surface corrosion.

In accordance with the present invention, a ferrous base metal is provided with a silicon-containing diffusion coating by placing the base metal in a molten sodium bath containing at least silicon dissolved therein, and further containing an active surface of zirconium metal in the bath, and then maintaining the ferrous metal in the bath for a sufficient time for the dissolved silicon to diffuse into the ferrous metal to form a diffusion coating containing silicon on the base metal.

In certain preferred aspects of practicing the invention, both silicon and aluminum are dissolved in the molten sodium bath, while maintaining an inert atmosphere, and while maintaining a sheet of zirconium immersed in the sodium bath, and then the ferrous base metal is maintained in the bath while both the aluminum and silicon are diffused into the ferrous metal to form a codeposited diffusion coating therewith.

It is an essential feature of this invention that a surface of zirconium be present in the molten sodium bath during the time that the silicon or silicon-aluminum diffusion coating is being formed on the ferrous base metal. The active zirconium surface is preferably and conveniently in the form of a sheet, foil, film, or plate, in desired straight or curvilinear configuration. By use of the term "sheet" herein, these various structural shapes and embodiments are contemplated. The zirconium may be used in an "as-received" condition, but preferably is conventionally degreased, cleaned, washed and dried before immersion in the molten sodium bath.

By use of the process of this invention, the diffusion coatings that are obtained tend to be more adherent, more uniform, more rapidly formed, and more ductible and flexible than similar diffusion coatings obtained in the absence of the improved process of this invention. Furthermore, the use of zirconium appears unique for obtaining these improved results in that the addition of other getter-type materials to the bath, such as titanium or calcium, under similar reaction conditions, has resulted in no improvement or even substantially complete inhibition of formation of a satisfactory coating.

Diffusion of the coating material into the ferrous base metal occurs, forming a graded layer, with resulting formation of a solid solution, alloy, or intermetallic compound. Diffusion layers with graded boundary layers varying from 0.1 mil up to 60 mils may be obtained, although diffusion coatings typically varying from 0.5 mil to 10 mils are preferred. The diffusion of the coating material into the ferrous base accounts for the change in metallurgical properties of the resulting article, for instance, improved mechanical and chemical properties. The resulting diffusion layer has a number of distinct advantages over a simple plating layer: an atomic bond is formed and the surface is graded in composition. There is no sharp interface, which is beneficial in preventing spalling or breaking of the coating. At the same time, a protective adherent case or layer of superior hardness and chemical inertness is formed on the base metal.

While the mechanism of diffusion transport of the dissolved silicon or aluminum-silicon into the ferrous base metal, and the formation and nature of the alloy diffusion layer (e.g., intermetallic compound or solid solution), is not fully understood, and particularly the role played by the zirconium, it appears that the molten sodium is required for the success of the process. The molten sodium provides an excellent environment for maintaining the ferrous base metal clean of oxide and organic films, not only initially but throughout the coating operation. Further, the sodium provides the vehicle for diffusion material transport and maintains a constant supply of silicon or aluminum-silicon at the base metal surface.

The present process may be used for applying an improved diffusion coating of silicon or aluminum-silicon

on various base metals. However, it is particularly with respect to ferrous base metals such as mild steel, enameling iron, stainless steels, and the like that this process is of particular significance and effectiveness in yielding improved diffusion coatings having greater uniformity, adherence, and flexibility. This process is of particular utility in providing a silicon or aluminum-silicon diffusion coating on ferrous metals where uniform dimensional tolerances must be maintained, such as the providing of precision machined parts with a thin, uniform diffusion coating.

The effectiveness of the presence of the zirconium sheet in the molten sodium bath in providing the improved results herein is readily apparent, although the mechanism thereof is not fully understood. The zirconium does not appear to dissolve in the molten sodium to any significant extent, and no zirconium is ordinarily detected in the case (diffusion coating layer) that is formed on the ferrous base metal. Where zirconium is added to the bath in the form of fine granules or powder, these fine granules tend to interfere with the smoothness of the coating obtained. Consequently, the zirconium should be present in the form of a structured active surface, such as a sponge-like mass, and preferably as a foil, film, plate, or sheet. It is believed that the zirconium may function somewhat as a "getter" whereby certain oxygenated, nitrogenous or carbonaceous compounds which may interfere with the formation of a uniform diffusion coating, possibly by being leached out of the ferrous metal at the high temperatures employed, are absorbed on the zirconium surface and prevented thereby from interfering in the formation of a zirconium and readily deposited diffusion coating.

Sodium, which included alloys thereof such as sodium-potassium (NaK), is the molten carrier used in the practice of this invention. An inert environment, i.e., a non-oxidizing one, such as may be obtained with a vacuum or by maintaining an inert gaseous atmosphere provided by noble gases such as helium, is maintained over the molten sodium. The diffusion rate into the ferrous metal and the solubility in the sodium of the silicon or aluminum-silicon codeposited therewith are functions of temperature, and it is accordingly desirable to maintain the temperature of the molten sodium bath as high as possible. The maximum temperature is limited by the boiling point of the sodium or alloy thereof at a given pressure. A satisfactory temperature range for a sodium bath is about 1000–1500° F.

The desired concentration of the silicon and of the aluminum-silicon diffusion coating materials in the sodium bath is essentially self-controlled by their solubility in the bath. This may vary from a range of about 10 to 1000 parts per million, and may reach several percent, being markedly dependent upon the temperature of the bath and the solubility of the solute. Generally, with respect to aluminum, it is preferred to maintain a small reservoir or pool of molten aluminum in the molten sodium bath so as to insure saturation conditions of the aluminum in the bath.

The aluminum and codeposited materials used to form the diffusion coating can be dissolved in the molten sodium bath in any convenient manner. Preferably, the aluminum is introduced as a pure metal in either powdered or molten form. The silicon may be introduced also as the pure element in either granules or powdered form.

The factor which controls the time required for forming a diffusion coating of desired thickness is the rate of diffusion of the coating metal into the base metal. The diffusion rate is dependent upon such factors as the temperature of the bath, the concentration of coating material in the bath, the metallic structure of the base metal, and circulation of the bath constituents. In general, higher bath temperatures result in shorter coating time and therefore are preferred for most applications.

Since the boiling point of sodium is about 1600° F., at which temperature sodium evaporates at a rapid rate, a temperature of 1500° F. is generally preferred as a maximum working temperature. While a diffusion coating of 0.1 mil may be obtained in as short a time as a minute, coatings of 0.5 mil to 10 mils are preferred for protecting the ferrous base metal. A period of time varying from 1 minute to 5 hours is suitable. Thicker coatings will be used where the coating is subject to a degradative attack in addition to functioning as a protective coating for the ferrous metal. Where silicon is deposited alone or codeposited with aluminum, amounts of silicon varying from 2 to 20 weight percent, based on the weight of the sodium, are added to the molten sodium bath. Since approximately 1.5 weight percent aluminum dissolves in molten sodium under optimum conditions, the molten bath will additionally contain from 0.5 weight percent aluminum to 4 percent aluminum, based on the weight of sodium, where an aluminum-silicon codeposited diffusion coating is desired.

It has been found that a codeposited diffusion coating of aluminum-silicon on a mild steel (AISI 1008 steel) represents a preferred feature of this invention, the coating being codeposited from a bath containing preferably from 2 to 5 weight percent aluminum, from 2 to 20 weight percent silicon, based on the weight of the sodium bath, and additionally containing from 2 to 20 grams of zirconium, preferably in the form of a sheet varying from 5 to 30 mils in thickness.

By having zirconium present in the molten sodium bath during the deposition of a diffusion coating of silicon or aluminum-silicon on a ferrous base metal, it has been found that the diffusion coating that is obtained has greater uniformity, adherence, and flexibility compared with coatings heretofore obtained in the absence of the zirconium in the bath. A slightly thicker case is also formed under comparable conditions. In general, by increasing the bath temperature or increasing the time that the base metal is maintained in the molten bath, thicker coatings will be obtained. It will, of course, be understood that the rate of deposition of the diffusion coating is not a linear function, but depends upon the relationship and interaction of many factors not fully understood. In actual practice, the rate of diffusion appears to vary logarithmically with time.

In addition to having the zirconium present in the bath, agitation of the molten sodium bath is a further factor that is important with respect to the time required to form a satisfactory diffusion coating layer of a given quality and thickness on the base metal. The forming of a codeposited aluminum-silicon diffusion coating on a ferrous base metal presents a particularly difficult problem because of the apparent formation of a diffusion barrier at the liquid-liquid interface between the aluminum and the sodium, presumably caused by an oxide film of aluminum. It is believed that the formation of this thin impermeable alumina film at the interface partitions the liquid aluminum from the liquid sodium, thereby preventing proper solution of the former in the latter and thus preventing the subsequent mass transfer and reaction with the surface of the base metal. However, by continuously disrupting the liquid-liquid interface, metallic sodium is brought into contact with metallic aluminum permitting solution, transfer and reaction.

One technique for effecting this continuous disruption of the interface is by mechanical agitation of the reaction chamber and its contents, for example by use of rotating and see-saw type capsules. Alternatively, the capsule or container and its contents may be vibrated, or the contents only or the liquid only vibrated, to cause a wave or ripple action at the liquid-liquid interface. Suitably, mechanical movement of a rake or chain through the liquid may be used to cause interface disruption. Also feasible is introduction of an inert gas stream below the liquid-liquid interface to agitate the interface. To obtain the desired interface disruption, the target to be diffusion coated

may be maintained in motion in addition to agitation of the molten sodium bath.

A bath process, a semi-continuous process, or a continuous diffusion coating technique may be used in the practice of this invention. Generally a batch process is preferred because of the greater degree of control feasible with respect to the dominant variables of the process. Conveniently, for a batch process a container to hold the bath and the specimens to be diffusion coated is fabricated of stainless steel tubing of desired diameter cut to desired lengths. An end cap is welded to one end to form a vessel into which the bath materials are placed, and another end cap is welded on the opposite end. Specific capsule configurations may also be used to support some of the constituents, to provide a reservoir, or to house unusually shaped specimens. The specimen to be coated may be placed into the bath loose, suspended on wire, or encased in a screen envelope.

Various types of furnaces may be used to house the capsule, the simplest being a static furnace which is temperature controlled to maintain an isothermal environment for the capsule. In other applications, a tube furnace is used inclined at 30° from the horizontal within which the capsule is rotated about its longitudinal axis at about 15 r.p.m. Additionally, a rocking motion may be added to the rotation motion. For this type of application, a tube furnace is used in which the capsule is rotated at 15 r.p.m. while the furnace and capsule are both rocked through ±30° from the horizontal about a mid-point pivot.

An open vessel bath may be used for the batch, semi-continuous, or continuous process. The temperature is maintained by a furnace around the vessel containing the bath. A recirculating argon environment is maintained over the bath solution to prevent any oxidation occurring. Baffles are installed above the open bath to keep the vapor within the reaction vessel and to reduce the heat transfer to the argon atmosphere in a "dry box" which is used to house the open vessel. Various automatic equipment may be used in conjunction with the bath and furnaces for measuring and controlling the operations thereof.

The following examples are offered to illustrate the scope and practice of this invention in greater detail, and are not intended to be construed as limitations thereof.

Example 1.—Comparison of calcium, titanium, and zirconium addition

Capsule tests were conducted in which mild steel targets were rotated for 15 minutes at temperatures of 1200° F. and 1050° F. The molten sodium bath contained either silicon alone dissolved therein, or aluminum also dissolved therewith, and additionally 7.5% by weight, based on the sodium weight, of calcium, titanium, and zirconium as bath additives. The results obtained are shown in Table I.

TABLE I

	Bath (g.)			Bath Additive	Case (mils)	Preece Test
	Na	Si	Al			
1,200° F.	40	3	3	3 g. Ca	None	Fails.
	40	3	-----	3 g. Ca	None	Do.
	40	3	3	3 g. Zr	3.2	Good.
	40	3	-----	3 g. Zr	3.2	Do.
	40	3	3	3 g. Ti	3.0	Do.
1,050° F.	40	6	3	3 g. Ca	None	Fails.
	40	6	-----	3 g. Ca	None	Do.
	40	3	3	3 g. Zr	1.0	Good.
	40	3	-----	3 g. Zr	2.0	Do.
	40	3	3	3 g. Ti	1.0	Spotty.

As may be noted from the foregoing results, where calcium was used, it completely inhibited formation of a diffusion coating. While titanium permitted the formation of a diffusion coating, this coating lacked the smoothness and continuity of the coating obtained with zirconium present in the bath. A modified Preece test was used in which a mild steel specimen was treated with an acidified copper sulfate solution. This test (shown in Making, Shaping, and Treating of Steel, 7th edition, page 711, U.S. Steel Corp., 1957) serves to determine the continuity and integrity of a protective coating on a ferrous base metal.

Wet chemical analysis of the case obtained at 1200° F. in the presence of zirconium, where aluminum and silicon were codeposited, showed 4% aluminum, 13% silicon, and zirconium not detectable. For the run at 1200° F. in the presence of zirconium, where only silicon was dissolved in the bath, the case contained 27% by weight of silicon and a trace of zirconium.

Example 2.—Diffusion coating of refractory base metals

A tantalum-tungsten alloy (90Ta, 10 W) and a columbium alloy (Du Pont B–66, 5 Mo, 5 V, balance Nb) were run in a sodium bath at 1450° F. for 5 hours in a capsule containing 40 grams sodium, 3 grams silicon, and 3 grams zirconium. The case depth obtained for each alloy was 0.1 mil in thickness.

In another run under similar conditions using the same targets, but where the bath composition contained 40 grams sodium, 5 grams aluminum, 3 grams silicon and 5 grams zirconium, the case obtained on the tantalum-tungsten target was 0.3 mil, whereas that on the columbium alloy was 1.4 mils.

Example 3.—Effect on diffusion coating thickness of presence of zirconium

The series of runs was made in which capsules containing mild steel targets (AISI 1015) were rotated at 15 r.p.m. for 10 minutes at 1150° F. and at 1250° F. in a molten sodium bath containing aluminum and silicon dissolved therein, serving as controls, with other capsules additionally containing zirconium. The results obtained are shown in Table II.

TABLE II

	Bath Composition (g.)				Wt. Gain (mg./cm.²)	Thickness Increase (2 sides) (mils)	Case Depth (mils)	Chemical Analysis Wt. Percent	
	Na	Al	Si	Zr				Si	Al
Temp. 1,150° F.	40	3	6	-----	4.51	1.1	0.4	22.68	2.27
	40	3	6	5	7.82	1.7	1.4	22.22	.06
Temp. 1,250° F.	40	3	6	-----	9.60	2.6	0.4	18.16	2.24
	40	3	6	5	19.80	3.0	1–3.1	22.70	.30

As may be noted from the results shown in Table II, for both temperatures shown, heavier diffusion coatings were obtained when zirconium was additionally present in the bath. As may be noted from the column headed Chemical Analysis, the presence of zirconium in the bath partially inhibits the deposition of aluminum. This may offer an advantage for those applications where a silicon-rich case is desired containing a lesser amount of aluminum.

The corrosion resistance was determined of the foregoing coated mild steel specimen on which an aluminum-silicon diffusion coating had been obtained by treatment in a molten sodium bath containing 40 grams sodium, 3 grams aluminum, 6 grams silicon, and 3 grams zirconium for 10 minutes at 1150° F. The specimen was exposed in a highly corrosive atmosphere simulating that encountered in the exhaust stream of an automotive muffler. A complete cycle involved suspending the specimens for 20 hours above a bath consisting of a dilute solution of hydrobromic and sulfuric acids maintained at 180° F., followed by removal of the specimens and drying them for 4 hours at 250° F.

After 23 cycles of this severe treatment, the weight change after exposure was +.51 mg./cm.^{2}. By contrast, after about 5 cycles a sample of uncoated mild steel is very badly attacked.

Example 4.—Effect of variation of temperature and of silicon content in open bath

Runs were conducted in an open bath under an inert environment in which a strip of 10-mil thick zirconium was present in the molten sodium bath as a bath modifier under the following conditions.

Temperature (°F.)	Exposure Time (Min.)	Wt. percent Al	Wt. percent Si
1,100	10, 30	4	5, 10, 15
1,150	10, 30	4	5, 10, 15
1,225	10, 30	4	5, 10, 15
1,275	10, 30	4	5, 10, 15

For all of the foregoing runs, a satisfactory case was obtained.

It will of course be understood that many variations are possible in the practice of this invention, depending upon the coating thickness desired, the base metal used, and the particular silicon or aluminum-silicon diffusion coating desired, as well as the particular configuration of the zirconium surface present in the bath, and these variants are therefore considered to lie within the practice of this invention. Accordingly, the scope of this invention should be determined in accordance with the objects thereof and the appended claims.

I claim:

1. The method of providing a diffusion coating containing silicon on a base metal selected from the class consisting of ferrous metals and refractory metals which comprises placing the base metal in a molten sodium bath maintained under an inert environment and containing silicon dissolved therein and maintaining said base metal in said bath in the presence of a zirconium surface until a diffusion coating containing silicon is obtained on said base metal.

2. The method of providing a silicon diffusion coating on a ferrous metal which comprises providing a bath of molten sodium under an inert environment, dissolving silicon therein, and placing said ferrous metal in said molten bath in the presence of a zirconium surface, and maintaining said ferrous metal in said bath until a diffusion coating of silicon is obtained on said ferrous metal.

3. The method of claim 2 wherein said bath is maintained at a temperature between 1000 and about 1500° F. at ambient atmospheric pressure.

4. The method of claim 3 wherein the zirconium is in the form of a sheet varying between 1 and 30 mils in thickness.

5. The method of providing a diffusion coating on a base metal selected from the class of refractory metals and ferrous metals which comprises dissolving aluminum and silicon in a molten sodium bath maintained under an inert environment, placing said base metal in said bath in the presence of a zirconium sheet, and maintaining said base metal in said bath until a diffusion coating containing aluminum and silicon is obtained on said base metal.

6. The method of claim 5 wherein said bath is maintained at a temperature between 1000 and about 1500° F. at ambient atmospheric pressure.

7. The method of claim 5 wherein said sheet of zirconium is between 1 and 30 mils thick.

8. The method of providing a diffusion coating on a ferrous metal which comprises dissolving aluminum and silicon in a molten sodium bath maintained under an inert environment, placing said ferrous metal in said bath in the presence of a zirconium sheet, said bath being maintained at a temperature between 1000 and about 1500° F., and maintaining said ferrous metal in said bath until a diffusion coating containing aluminum and silicon is obtained on said ferrous metal.

9. A method of providing a codeposited diffusion coating of aluminum and silicon on a ferrous base metal which comprises providing a molten sodium bath containing from 2 to 5% aluminum, from 2 to 20% silicon, and from 2 to 20% zirconium, by weight of the sodium, the zirconium being in the form of a sheet, said bath being maintained under an inert environment, placing said ferrous metal in said bath, and maintaining said ferrous metal in said bath maintained at a temperature between 1000 and about 1500° F. for a period of time varying from 1 minute to 5 hours, until a diffusion coating of desired thickness containing aluminum and silicon is obtained on said ferrous metal.

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