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PROCESS FOR DIFFUSION COATING METALS

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This application is a continuation-in-part of application Serial No. 330,540, filed December 16, 1963, now U.S. Patent 3,184,331, which is a continuation-in-part of application Serial No. 139,369, filed September 20, 1961, now abandoned, which in turn is a continuation-in-part of application Serial No. 44,015, filed July 20, 1960, now abandoned, which is a continuation-in-part of application Serial No. 835,171, filed August 21, 1959, which is now abandoned.

This invention relates to a process for providing metal articles with a diffusion coating of one or more dissimilar metals alloyed with a base metal. More particularly this invention relates to the use of a novel molten metal diffusion coating bath which contains a controlled amount of a Group II(A) metal nitride.

In the aforementioned applications, there is described a diffusion coating process in which a metal article is coated by contacting the article with a molten bath containing a transfer agent and one or more diffusing elements. In general, the process involves immersing the article to be coated in a molten metal bath for a predetermined time, removing the diffusion coated article from the bath, and thereafter cooling and cleaning the coated article. This process provides chromium coated ferrous articles which have outstanding resistance to corrosion. However, the coated articles sometimes after being cleaned are found to have surface stains which, in addition to being unsightly, may form incipient corrosion points on the metal surface.

It is, therefore, the principal object of this invention to provide an improvement in the alloy diffusion coating process whereby staining of diffusion coated articles can be controlled. Other objects will be apparent from the detailed description which follows.

The objects of this invention are accomplished by contacting a metal article with a molten bath containing a transfer agent selected from the group consisting of calcium, barium, and strontium, at least one diffusing element, and a controlled amount of a nitride of the respective transfer agent. After treatment in the bath for a predetermined time, the article is removed from the bath, cooled, and thereafter cleaned and polished if desired. The coating step is carried out at a temperature between about 800° C. and the melting point of the article to be coated. By including at least about 3% by weight of the nitride in the bath, staining upon removal of the article from the coating bath is effectively inhibited. It is theorized that the nitride acts as a wetting agent for the transfer medium. As the article is removed from the bath, the nitride and the transfer agent form a protective coating over the article thereby protecting it from elements in the atmosphere which cause staining. It has been found that as little as 0.2% by weight of oxygen in an inert gaseous atmosphere, e.g., argon, will cause some staining on ferrous articles. A protective coating is also essential to prevent reaction with and resulting staining due to carbonaceous materials. The coated article with its protective coating is preferably immediately immersed in a quenching medium where it is rapidly cooled to a temperature of about 100° C. to 120° C. Care should be taken so as not to break the protective film while the coated article is at a temperature at which it will react with oxygen or a carbonaceous material.

In practicing this invention, the coating bath can be prepared in a number of different ways. The transfer agent, one or more of the diffusing elements and a nitride can be admixed and heated together to the desired processing temperature. Alternatively, the diffusing elements may be added to the molten transfer agent and the nitride introduced by passing nitrogen gas over or directly into the melt. If the latter procedure is followed, care should be taken to introduce the nitrogen into the bath at a point remote from the walls of the retaining vessel since the reaction of the nitrogen and the transfer agent is exothermic and could produce sufficient heat to cause the vessel to rupture. Other methods for preparing the coating bath will be apparent to those skilled in the art.

As previously mentioned, one or more of the diffusing elements may be included in the bath. These elements will be selected on the basis of the type of metal substrate being coated and the type of coating desired. The process of the present invention is most useful in providing chromium diffusion coatings on ferrous metal substrates where it has been found that the nitride in the bath in addition to providing a protective coating also gives improved utilization of chromium in the coating bath. As a result, less frequent additions of chromium are required to maintain a desired level of chromium in the surface coating. Other known diffusing elements, such as nickel, manganese, cobalt, zinc, titanium, molybdenum, niobium, vanadium and aluminum, may be used in the nitride containing bath. The amount of the particular element is not critical. However, higher concentrations of some elements will be required in view of their relative solubility in the transfer agent. Depending on the composition of the coating desired, a fraction of 1% to as much as 50% by weight of the bath may be made up of the diffusing elements. It has been found that when aluminum is used, the bath must be carefully monitored since the aluminum tends to combine with the nitrogen present.

A wide variety of metal substrates may be coated using coating baths of this invention. Refractory metals such as the alloys based on nickel, cobalt, niobium, molybdenum, tungsten, tantalum, and to a lesser extent, vanadium, may be used. Significant benefits are attained in coating metal articles which have a tendency to develop stains at elevated temperatures much as do ferrous articles previously mentioned.

In practicing this invention it is essential that the transfer agent represent a significant liquid phase in the coating bath. The transfer agent must wet the surface of the article. Usually this liquid phase will constitute over 50% by weight of the bath. While the content of transfer agent may vary between wide limits, a practical lower limit for most coating operations will be above about 10% by weight of the bath. Preferably, from about 60% to about 97% by weight is used. In addition to the transfer agent, nitride and diffusing elements, various diluents such as lead, copper, and tin may be added to the bath. However, certain diluents may tend to salt out the nitride since they change the solubility limits for the nitride in the bath.

With respect to the nitride, at least about 3% by weight of the bath should be nitride. The maximum amount of nitride from a practical viewpoint is determined by the solubility of the particular nitride in the bath, i.e., the saturation point at the temperature being used. When the saturation point is reached, the nitride tends to cake out. For example, at 1150° C., calcium can dissolve no more than about 30% by weight of Ca_3N_2. The bath is perfectly fluid at 25% Ca_3N_2, but at levels above 30% the nitride tends to cake out and the viscosity of the bath increases to a level which makes coating impractical. The saturation point for barium and strontium nitrides appears to be much higher, i.e., over 50%, with

as much as 65% Ba_3N_2 giving fluid baths at 1150° C. The preferred concentration will be determined by a number of factors but generally will be in the range from about 5% to 30%. For example, the rate of cooling will influence the amount of nitride required. At the elevated temperatures used, the pure transfer agent, i.e., calcium, barium or strontium, tends to sublime or evaporate from the surface of the article as it is removed from the coating bath. Increasing the nitride concentration provides a heavier protective coating as well as a coating which remains on the surface at the elevated temperature.

The particular operating temperature of the bath which is most effective for providing coatings of the various diffusing elements can be readily selected. Generally, temperatures less than about 800° C. are not practical because of the slow rate of diffusion at such temperatures. The temperature must, of course, be held below the level at which the article to be coated would melt. In a preferred embodiment of this invention in which calcium is used as the transfer agent, a temperature from about 1000° C. to 1200° C. is used. The maximum practical temperature may be considered to be the normal boiling point of the transfer agent used.

The residence time of the article in the coating bath influences the thickness of the coating obtained. For example, in the case of calcium and calcium nitride operating at 1100° C. in which the bath contains from 1–10% by weight of chromium powder, a 0.5 mil coating may be obtained in about four minutes. Heavier coatings can be obtained by increasing the time and/or coating temperature. Thus, at 1200° C., a 0.5 mil coating is obtained in one minute, and at 1100° C., a 2.0 mil coating is obtained in about 70 minutes.

With respect to the use of the baths according to this invention in providing chromium coatings, it has been found that the presence of the nitride often increases the effective use of chromium. Coatings with equivalent surface concentrations of chromium often can be obtained with less chromium in the bath when the nitride is present as contrasted with results when the nitride is not used. It is theorized that the presence of the nitride improves the dispersibility of the fine chromium powder, e.g., —300 mesh, which is commonly used. Clumping of the powder in the bath has been observed in the absence of nitride. Clumping reduces the effective area of the powder and results in a decrease in the rate of transfer of chromium to the surface of the article being coated.

As mentioned previously, the article being coated is preferably transferred from the molten bath to a quenching medium. This medium may be a known quenching liquid such as water or oil, a gaseous medium such as helium, or a fluidized solid. Preferably, a molten sodium bath is used for quenching chromium coated ferrous articles. By using increased concentrations of nitride of the transfer agent in the coating bath, the time of transfer to the quenching medium can generally be extended without producing objectionable staining since heavier protective coatings are provided as the nitride concentration is increased. The preferred transfer time can be readily determined by those skilled in the art and will, of course, be influenced by the physical properties desired in the coated article.

As a general rule, no special treatment of the metal article is required before immersion in the coating bath. It is, of course, desirable that the surface of the article be clean and free from scale, burrs or sharp surface irregularities. The metal may be treated by conventional degreasing techniques, buffed or otherwise treated to present clean smooth surfaces.

This invention will be further illustrated by the following examples in which parts and percentages are by weight unless otherwise indicated. The thicknesses of the coatings formed on the articles can be determined

by metallographic examination or by measuring the thickness of the stripped film after the substrate is dissolved away by hot 30% nitric acid. The compositions of the surface coatings can be determined by X-ray fluorescence. The CASS test (copper acetic acid salt spray test) referred to in the examples was carried out in accordance with the procedures described in a brochure published November 14, 1960, by the Chemical and Metallurgical Dept., Quality Control Office of the Ford Motor Co., identified as Quality Laboratory and Chemical Engineering and Physical Test Method, B Q5–1.

Example I

A molten bath was prepared in a heated iron crucible. The bath contained 2004 grams of calcium, 127 grams of calcium nitride, 75 grams of chromium, 38 grams of nickel, and 19 grams of aluminum. The chromium was introduced into the bath in the form of finely-divided powder of —325 mesh. The top of the crucible was enclosed by a chimney into which argon was introduced. Panels, 2" x 5" x .02", prepared from aluminum killed, basic oxygen furnace steel sheet (nominal .05% carbon content) were immersed in the stirred molten bath at the temperatures and times indicated in the following table.

TABLE 1

Sample	Time (Min.)	Temp. (° C.)	Coating Thickness (Mils)	Composition (percent)		
				Chromium	Nickel	Aluminum
1	10	1,150	1.34	33.4	3.5	[1] n.d.
2	15	1,125	1.36	34.4	2.7	[1] n.d.

[1] Not determined.

The samples were removed from the molten bath after periods of time indicated in the foregoing table, transferred through air and quenched in an oil bath within five seconds after removal from the bath. It was observed that both samples were coated with a thin, uniform, unbroken film of material from the bath as they were removed from the molten bath. After quenching, Sample No. 1 exhibited no staining and Sample No. 2 had one very small stain on one surface.

Example II

A molten metal bath was prepared in an iron crucible equipped with a chimney. The crucible was heated to a temperature of about 1150° C. and 100 grams of calcium was then added. Nitrogen and argon were each introduced into the system at the rate of 0.5 liter/minute through a ¼-inch stainless steel tube. After the calcium had melted the tube leading in the nitrogen was placed below the surface of the molten calcium and 900 grams of calcium was added. The molten calcium was stirred for 75 minutes after which an additional 650 grams of calcium was added to the bath. The nitrogen/argon uow was continued for three hours after which the nitrogen flow was turned off, the chimney filled with pure argon and an analysis of the bath was made. It was found that the bath contained about 80.3% calcium and 17.4% calcium nitride. Four steel panels, 2" x 5" x .02", prepared from aluminum killed, basic oxygen furnace steel plate (nominal carbon content of about .05%) were immersed in the stirred bath for periods of ½, 1, 1.5 and 2 minutes, respectively. Upon removal of the samples from the molten bath they were transferred through air in about two seconds to an oil bath and quenched. The samples were cleaned by washing them in water containing dilute (10% by weight) nitric acid. They were then passivated by treating them for 12 minutes at 155° F. in a 20 weight percent nitric acid solution containing 2 weight percent of

$Na_2Cr_2O_7$. After being rinsed with water the samples were CASS tested for 64 hours. All samples were found to be completely unstained after the initial clean-up. After CASS testing there was no superficial rusting observed.

In a comparative test, steel panels of the type just described were treated in a molten coating bath containing about 2% calcium nitride. The procedure described above was followed. After initial cleaning, the samples were found to have moderately stained areas. After CASS testing, all showed considerable superficial rusting.

The procedure just described was repeated except the time of transfer of the panels from the molten coating bath was increased to 15 seconds. After initial cleaning, the samples were found to be heavily stained.

Example III

A molten coating bath was prepared in an iron crucible equipped with a chimney. The bath contained 2300 grams of calcium, 230 grams of chromium (—325 mesh), and 60 grams of nickel. The composition of the bath was varied by passing nitrogen into the melt to provide the percentages of calcium nitride listed in Table 2 which follows. Mild steel samples of the type described in Example II were immersed in the bath which was stirred and maintained at a temperature of 1150° C. The samples were held in the bath for two minute periods. In two experiments the argon was purged from the chimney with nitrogen. After removal from the bath, the samples were held in air and permitted to cool for three minutes. The samples which were all uniformly coated with a thin film of bath material were weighed, then cleaned and examined for staining. The results of the examination are recorded in Table 2 which follows:

TABLE 2

Experiment	Percent Ca_3N_2	Chimney Gas	Staining
1	8	Argon	No.
2	8	Nitrogen	No.
3	18	Argon	No.
4	20	do	No.
5	20	Nitrogen	No.

The samples were again weighed. It was found that the amount of coating material carried out of the bath on the panel surfaces was doubled by increasing the calcium nitride content from 8% to 20%.

Example IV

A series of stirred molten baths were prepared in an iron crucible. The baths contained 4% of chromium, 1.5% of nickel, and 5, 15, and 30% of calcium nitride, respectively. Samples, 3" x 4" x .02", of aluminum killed, basic oxygen furnace steel (nominal .05% carbon content) were treated at temperatures between 1175° C. and 1100° C. for times sufficient to give about 1.2 to 1.3 mil coatings. The samples were transferred from the argon atmosphere surrounding the bath through air to a quenching medium. The samples were generally covered by a thin, uniform film of material from the bath. Oil, argon and fluidized sand were used to quench the separate samples. The coated panels, after being cleaned with water and a dilute (10% by weight) nitric acid solution, were examined for staining. Very little, if any, staining was observed on most panels. Some staining did result where the film of bath material was broken by touching the sample surface as it was withdrawn from the bath thereby permitting air to contact the surface of the panel.

The procedure described above was repeated using a bath containing 3% calcium nitride. The sample was carefully removed from the bath and transferred to the quenching medium in two seconds. No staining was observed.

The procedure described in this example can be repeated substituting strontium and strontium nitride for the calcium and calcium nitride with comparable results.

Example V

A coating crucible was formed by closing one end of a steel pipe 2½ inches in diameter and 11 inches long. 384 grams of barium was melted in the pipe at a temperature of 1145 to 1150° C. after which 16 grams of —325 mesh chromium metal was added. The bath was maintained at the aforementioned temperature under a protective argon atmosphere. Low carbon steel disks 1 inch in diameter and 20 mils thick were treated in the bath. It was found that with as much as 65% barium nitride in the bath using a coating time of nine minutes a surface chromium content of 40% was obtained which was substantially free from stains.

Example VI

This experiment illustrates the reduction in loss of calcium from a molten bath achieved by increasing the concentration of calcium nitride in the bath. A series of experiments were carried out using a stirred molten coating bath initially containing 2500 pounds of calcium and a controlled percentage of chromium. The bath was maintained under a protective argon atmosphere. Calcium was added as needed to maintain the bath at its initial level. The chromium concentration was maintained between about 4 and 5% by weight by incremental addition of chromium powder to the bath. Full bumpers and wings cut from the ends of the bumpers were treated in the bath at a temperature of 1150° C. to provide surface coatings having a thickness of about 1.5 mils and a surface concentration of 35–45% by weight of chromium. The results of the coating runs are summarized in Table 3, which follows:

TABLE 3

Run	Area Coated (sq. ft.)	Calcium Added to Maintain Initial Level (lbs.)	Area Coated (sq. ft./lb. Calcium Added)	Ca_3N_2 Content of Bath (Weight Percent)
1	[b] 2,320	380	6	1
2	[b] 5,500	470	17	1
3	[a] 260	10	26	1.1
4	[b] 1,940	50	39	2.8
5	[a] 720	50	144	4.4

[a] 15-inch long wings cut from 1964 Ford Falcon bumpers, treated vertically in the bath in pairs with the cut edges down.
[b] 1964 Ford Falcon bumpers treated in pairs and hung vertically in bath.

It will be noted from the data in Table 3 that as the concentration of calcium nitride was increased the number of square feet of area coated per pound of calcium added also increased. It is theorized that the reduction in loss of calcium due to vaporization was primarily responsible for the increased calcium utilization.

Example VII

This example illustrates the improved utilization of chromium achieved by using a coating bath having a controlled calcium nitride content. Experiments were carried out using a stirred molten coating bath initially containing 2500 pounds of calcium and a controlled percentage of chromium. The bath was maintained under a protective argon atmosphere. The chromium concentration was maintained between about 4 and 5% by weight by incremental addition of chromium powder to the bath. Wings cut from the ends of the bumpers as described in Example VI were treated in the bath at a temperature of 1150° C. to provide surface coatings having a thickness of about 1.5 mils and a surface concentration of

35–45% by weight of chromium. The results of the coating runs are summarized in Table 4, which follows:

TABLE 4

Run	Area Coated (sq. ft.)	Incremental [1] Cr Added (lbs.)	Area Coated (sq. ft./lb. Cr Added)	Ca_3N_2 Content of Bath (Weight Percent)
1	260	10.6	24.5	1.1
2	200	7.5	26.8	6.9
3	325	10.0	32.5	10.5

[1] The run was started with 100 lbs. of chromium in the bath. Incremental additions indicated were required to continue deposition of high quality coatings having the chromium concentrations mentioned above.

As shown in Table 4, the surface area coated per pound of chromium added to the bath markedly increased as the concentration of calcium nitride was increased.

Example VIII

Samples, approximately 1" x 2" x 0.06", of niobium, vanadium and tantalum were treated in a stirred bath containing 450 grams of calcium, 50 grams of chromium powder, 20 grams of nickel, 20 grams of cobalt, 20 grams of manganese and 40 grams of calcium nitride in a molybdenum crucible for 4 hours at 1300° C. under a protective argon atmosphere. Upon removal of the samples from the bath, each sample was covered with a uniform coating of bath material. The samples were cooled, cleaned and found to be free from stains. The vanadium sample had a thick coating which contained appreciable concentrations of chromium, manganese, cobalt and nickel and smaller concentrations of vanadium and niobium at the surface. The tantalum was coated with an alloy containing chromium, manganese, cobalt, nickel and niobium. The niobium sample was coated with appreciable concentrations of chromium, manganese, cobalt, nickel and a trace of tantalum. In addition to illustrating the protective nature of the coating baths of this invention in coating refractory metal substrates, this example also illustrates the efficiency of these baths as transfer agents in forming diffusion coatings of a plurality of metals on a substrate.

As indicated in the examples, coated products with excellent corrosion resistance which are free from stains are provided by the process of this invention. Elimination of the stains not only improves the appearance of the coated articles but often improves their corrosion resistance. These products have a number of obvious uses in the metals field. They may be used in fabricating hardware, automobile parts, appliances and various accessory uses for machinery.

The most important advantage accruing from the use of a nitride in the treating bath is in providing a protective coating on the coated article thereby preventing staining. An additional advantage resides in the increased utilization of the diffusing elements in the coating baths. It has also been found that by using concentrations of the metal nitrides within the scope of this invention a reduction in dust formation, i.e., presence of particles of the transfer agent in the atmosphere surrounding the coating bath, is achieved.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In an alloy diffusion coating process wherein a metal article is contacted with a molten bath containing at least about 10% by weight of a metal transfer agent selected from the group consisting of calcium, barium and strontium and at least one metal diffusing element, the improvement which comprises including in said molten bath a controlled amount of a nitride of said metal transfer agent, said amount being in the range from about 3% by weight to saturation of said bath.

2. The process of claim **1** wherein said transfer agent is calcium and said nitride is calcium nitride.

3. The process of claim **2** wherein said diffusing element is chromium.

4. A process for diffusion coating a ferrous metal article comprising contacting said article with a molten bath containing at least 10% by weight of a metal transfer agent selected from the group consisting of calcium, barium and strontium, at least one diffusing element selected from the group consisting of chromium, nickel, manganese, and cobalt, and from about 5% to about 30% by weight of a nitride of said transfer agent, said bath being maintained at a temperature between about 800° C. and the melting point of said article, removing said article from said bath with a protective coating of said transfer agent and nitride adhering thereto, and immediately thereafter quenching said article.

5. The process of claim **4** wherein said transfer agent is calcium, said diffusing element is chromium and said nitride is calcium nitride.

6. The process of claim **5** wherein said calcium nitride is present in an amount from about 5% to 10% by weight of said bath.

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