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ADDITION OF NITROGEN GAS TO ATMOSPHERE IN ALLOY DIFFUSION COATING

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ABSTRACT OF THE DISCLOSURE

Inclusion of nitrogen in the essentially inert atmosphere surrounding the molten diffusion coating bath containing a metal transfer agent and at least one metal diffusing element causes stain and evaporation inhibiting nitrogen compounds (nitrides) to form on the coatings of the articles as they leave the bath.

BACKGROUND OF INVENTION

In U.S. Pats. 3,184,292 and 3,184,331 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 particularly 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.

U.S. Pat. 3,261,712 describes controlling the staining of the diffusion coated articles by including in the molten bath a controlled amount of a nitride of the metal transfer agent. In some types of manufacturing operation and with some types of coating baths and substrates the inclusion of a nitride of the metal transfer agent in the bath does not fully remedy the problems cited. For example, the allowable operating temperature range for a bath is reduced by nitrogen additions which raise the melting point of the bath; whereas calcium alone is molten at 900° C., calcium-calcium nitride (30%) contains undissolved solids at temperatures below about 1100° C. Another type of limitation occurs if one or more diffusing elements tend to react with nitrogen. For example, aluminum forms a nitride apparently more stable than calcium nitride. Consequently, if nitrogen is added to a calcium bath which contains aluminum as an intended diffusing agent, the aluminum preferentially reacts with the nitrogen to form insoluble aluminum nitride, thus greatly depressing the effectiveness of aluminum transfer from the bath to the substrate while in addition causing operational problems due to the aluminum nitride settling to the bottom of the crucible containing the coating bath. Finally, while nitrogen addition to the coating bath aids greatly in controlling staining of diffusion coated articles, under some circumstances still additional protection against staining is required.

SUMMARY OF INVENTION

According to the present invention there is provided an alloy diffusion coating process wherein a metal article is contacted 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 and at least one metal diffusing element, the improvement comprising removing the coated article from the bath into a

gaseous atmosphere having a nitrogen content of at least about 25% by weight and up to 75% of an essentially inert gas. Preferably, the metal article is treated in a calcium bath containing chromium as the diffusing element and is coated at a temperature of at least 800° C., preferably between about 800° C. and the melting point of the article to be coated. After treatment in the bath, the coated article is removed from the bath into a gaseous atmosphere, preferably argon having an oxygen content of less than 1% by weight and which contains at least about 25% nitrogen by weight, preferably from 30% to 100%. The article is then quenched and thereafter cleaned and polished if desired.

DETAILED DESCRIPTION OF INVENTION

By including nitrogen in the atmosphere, staining upon removal of the coated article from the bath is effectively inhibited. It is theorized that the dragout on the sample, which 100% covers and protects the surface immediately upon its removal from the coating bath, is immobilized and fixed in place by its reaction with nitrogen in the atmosphere. The lowered vapor pressure of the calcium-calcium nitride layer thus formed renders it stable in contrast to the original dragout, which being higher in metallic calcium content tends to disappear via an evaporation mechanism. It has been found that as little as 0.2% by weight of oxygen in an essentially inert gaseous atmosphere will cause some staining on ferrous articles. The formed protective coating is also essential to prevent reaction with and resulting staining due to carbonaceous material and reduces flaming, spitting and dusting due to the reaction of air with hot calcium metal carried out of the system. 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 ways with the transfer agents and diffusing agents, such as chromium, nickel, manganese and cobalt, mentioned in the aforesaid patents and used to coat metal articles disclosed therein. Also, the particular operating temperature of the bath and the resident time of the article in the bath are for times and temperatures now known in the art as shown by the aforesaid patents.

It is frequently desirable to maintain at different compositions the atmosphere in contact with the molten bath and the atmosphere in which the coated article is cooled. The temperature of the cooling atmosphere is not critical; it will be heated by cooling the coated article and generally will be between ambient and several hundred degrees centigrade. Commonly, the coated article will be held in the gaseous atmosphere for about 0.25 to 5 minutes, preferably from about 1 to 3 minutes. Generally, the desire is to cool the surface of the coated article to below a prescribed temperature while not prolonging its stay in the gaseous atmosphere. Generally, a cool gaseous atmosphere is desired, i.e., a temperature lower than the furnace temperature, and the hold time depends on the rate of surface cooling for the specific coated article.

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 strip 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 proce-

dures described in a brochure published Nov. 14, 1960, by the Chemical and Metallurgical Department, Quality Control Office of the Ford Motor Company, identified as Quality Laboratory in Chemical Engineering and Physical Test Method, BQ5–1. The following equipment and general procedure was followed in all of the following examples. A crucible 12" high and 4" in diameter was placed vertically in a furnace with a chimney having a 4" x 1" cross section placed on the crucible. This chimney was then surrounded by a second furnace. The chimney extended 8" above the second furnace and the extension was held at a temperature below 100° C. The rest of the chimney and the crucible were heated as desired by the two independent furnaces. In the crucible was melted a coating bath and this was stirred with an air driven stirring motor operating a three-bladed stirring propeller with 1" blades. The atmosphere above the furnace and in the chimney could be separately controlled. A sample was coated in the crucible, withdrawn into the chimney which contained gas of controlled composition at a controlled temperature, held in the chimney for a predetermined length of time, then removed, transferred through air and then quenched in oil. The oil and frozen bath on the samples were mostly removed in hot water, then clean-up was completed by a one-minute dip in 10% nitric acid. The samples were then inspected and sometimes were passivated in 20–25% nitric acid plus 2% $Na_2Cr_2O_7$ at 145–175° F. for 4–10 minutes, rinsed, rubbed briefly with an aqueous slurry of MgO rinsed again, air dried and corrosion tested.

EXAMPLE 1

Aluminum-killed, basic oxygen furnace steel initially containing 0.05% carbon and 90 mils in thickness was placed in a molten coating bath containing 72% calcium, 22% calcium nitride and 6% chromium. The bath was maintained at 1150° C. The coated steel samples were withdrawn into an 875° C. chimney, then transferred through air in 2 seconds to an oil quench. Three different chimney atmospheres were tried. The chimney atmospheres and the results of the test on the samples are shown in Table 1 which follows:

TABLE I

Chimney Atmosphere		Time of sample in chimney (min.)	Appearance of sample after clean-up operation	Rust stains in 16 CASS hours per 10 sq. in. sample
Percent A	Percent N_2			
100	0	0	Very slight white stain	18
100	0	0.25	No stain	2
100	0	0.50	do	0
100	0	1	Mottled dark stain	0
100	0	2	do	0
100	0	4	5% surface stain; pebbly black.	4
100	0	8	50% surface stain; blue-black.	6
50	50	0.5	No stain	0
50	50	1	Mottled dark stain	0
50	50	2	do	0
50	50	4	do	0

The results in Table I show that samples treated in baths containing even as much as 22% calcium nitride can be improved by adjustment of the chimney gas composition (see for example the results of the 4-minute hold).

As a control to show results in the absence of nitrogen addition similar steel samples were coated in a bath containing 2300 grams of calcium, 230 grams of —325 mesh chromium powder, 60 grams of nickel, and 22 grams of aluminum. The bath was at 1150° C. The chimney was at 850° C. and the samples were held in fairly pure argon (0.2% oxygen) in the chimney for 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75 and 3.0 minutes before the oil quench. The coatings after the final oil quench all had 30% chromium at the surface and were about 1.3 mils thick. All of the samples were stained with an intensely dark blue coloration suggestive of an oxide stain. It is noted that only a few tenths of a percent of oxygen need be present in the argon for such a stain to form on unprotected steel. The samples were mildly buffed with a polishing wheel so as to remove about 0.1 mil of the coating. The stain was no longer present after buffing however, the corrosion resistance was far inferior in all cases to samples only transferred through air to oil in two to three seconds. After 16 CASS hours all samples had general, light-surfaced rust. The sample held in the chimney for the shortest time was the best. The samples were cleaned and again returned to the CASS test; however, after 40 CASS hours, the samples again had widespread surface rusting.

EXAMPLE 2

A bath of 2300 grams of calcium, 60 grams of nickel and 230 grams of —325 mesh chromium powder was heated to 1150° C.; analysis showed 7% Ca_3N_2. Pieces of 5" x 2" x 0.02" steel were placed in the melt for 2 minutes, then raised into the cold chimney and cooled for 3 minutes. They were then removed into the air, the upper and lower 0.5" end pieces were removed and the remainder bisected horizontally to give two 2" x 2" panels (denoted "top" and "bottom") which were quickly weighed, cleaned of dragout, and reweighed.

	Chimney atmosphere [1] (grams)	
	Pure argon	Pure nitrogen
Frozen Bath (top) [2]	1.65	4.89
Frozen Bath (bottom) [2]	2.11	6.15

[1] This gas was passed through the 4 sq. in. cross section chimney at about 4 liters/min. to ensure fast cooling.
[2] In grams per square foot of exposed surface.

While the same amount of bath was dragged out of the bath by the samples, more was retained when the atmosphere was pure nitrogen; less vaporized from the samples as also borne out by the following qualitative observation. When argon was the chimney atmosphere, flaming and spitting continued for 30 seconds at the small annular space at the chimney top where the 4 liters/min. of gas escaped. The pyrotechnics were due to reaction of air with the hot calcium metal vaporized from the surface of the cooling sample. When nitrogen was the chimney atmosphere there was absolutely no flaming or spitting.

EXAMPLE 3

Experiment 2 was repeated on coated 90 mil steel and an 868° C. chimney.

Chimney atmosphere (liters/min. of gas)		Length of time (sec.) of flaming at gas exit
Argon	Nitrogen	
4	0	30
3	1	15
2	2	7
1	3	9
0	4	0

EXAMPLE 4

A 30 cu. ft. bath contained 91% Ca, 5% Ca_3N_2, 1.6% Ni, and 2.4% Cr. The argon atmosphere had less than 0.1% O_2 and the N_2 level was varied. Automotive bumper samples with 5 sq. ft. front surfaces were coated for about 15 minutes near 1150° C. and transferred through the atmosphere in 25 seconds to a sodium quench. After clean-up, polishing (0.1 mil coating removal) and passivation (4 min. at 165° C. in HNO_3 (20%)—$Na_2Cr_2O_7$ (2%)), the bumpers were CASS tested.

Percent N_2 in atmosphere:	Coating corrosion defects per sq. ft. in 160 CASS hrs.
0	1.0
63	1.4
90	1.2

No deterioration of corrosion performance was caused by the presence of large quantities of N_2 in the atmosphere.

The corrosion results cited above can be considered identical within experimental error. The beneficial result from this test points out another advantage of controlling the gas composition of the cooling atmosphere. Production of metallic dust comprised mainly of transfer metal presents an operational hazard. The dust originates from transfer metal vapors emitted from the surface of the coating bath and, more importantly, because of the larger surface area involved, from transfer metal evaporating from the surfaces of coated articles cooling following their removal from the coating bath. The presence of nitrogen in the cooling environment, as previously discussed, allows the conversion of a portion of the transfer metal dragout to calcium nitride which markedly decreases the rate of vaporization of transfer metal from the sample surface. Consequently, a decrease in the amount of generated dust was observed when the nitrogen containing atmospheres were employed. The dust which was formed and which contained calcium nitride in addition to metallic calcium, while still hazardous, was somewhat less reactive than dust containing lesser amounts of calcium nitride.

What is claimed is:

1. In an alloy diffusion coating process wherein a metal article is contacted 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 and at least one metal diffusing element, the improvement comprising removing the coated article from the bath into a gaseous atmosphere having a nitrogen content of at least about 25% and up to 75% of an essentially inert gas.

2. The process of claim 1 wherein the transfer agent is calcium.

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

4. The process of claim 1 wherein the essentially inert gas is argon having an oxygen content of less than 1%.

5. The process of claim 4 wherein the coated article is held in the gaseous atmosphere for about 0.25 to 5 minutes.

6. In an alloy diffusion coating process wherein a metal article is contacted 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 and at least one diffusing element selected from the group consisting of chromium, nickel, manganese and cobalt, said bath maintained at a temperature above about 800° C., the improvement comprising removing the coated article from the bath into a gaseous atmosphere having an oxygen content of less than 1%, a nitrogen content of at least about 25% and up to 75% of argon having an oxygen content of less than 1% and holding the coated article in the atmosphere for about 0.25 to 5 minutes.

7. The process of claim 6 wherein the transfer agent is calcium and the diffusing element is chromium.

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