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PROCESS OF COOLING DIFFUSION COATED METAL ARTICLES IN LIQUID SODIUM METAL

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ABSTRACT OF THE DISCLOSURE

In an alloy diffusion coating process wherein a metal article is immersed in a molten bath containing a metal transfer agent such as calcium, strontium, barium, magnesium and lithium and at least one metal diffusing element, the coated article is quenched in molten sodium below 300° C. An inert gaseous atmosphere can be used throughout the process.

This invention relates to a process for applying coatings to metal surfaces. More particularly, this invention relates to an improvement in a liquid-to-solid diffusion coating process in which the coated article is rapidly quenched from an elevated temperature.

In U.S. Patents 3,184,292, 3,184,330 and 3,184,331 there are described diffusion coating processes in which metal articles are alloyed at the surface by contacting them with a molten bath containing a transfer agent and one or more metallic diffusing elements. In these processes, the article to be coated is immersed in a molten metal bath for a predetermined time, thereafter removed from the bath, cooled and cleaned. Diffusion coatings having outstanding properties are provided. It is often desirable to rapidly cool or quench the coated metal articles. This is particularly true of unstabilized ferrous articles with chromium-containing coatings for superior corrosion resistance. Such articles require quenching in order to prevent migration of carbon to the surface of the article and a resulting reduction in corrosion resistance.

The usual quenching procedures have not proved to be entirely satisfactory since the articles, when removed from the molten coating bath, have superficial coatings of the molten transfer agents adhering to their surfaces. The transfer agents which are useful in the diffusion coating processes react violently with water at the temperatures used for quenching. Also, when water is used as a quenching medium, there is a tendency for the surfaces to become stained. Oils have been disclosed as quenching materials; however, the oils tend to pyrolize at the elevated temperatures which are used. Oils also tend to stain the surfaces and cause severe carburization of the coating with resulting loss of corrosion resistance. Furthermore, it has been found that quench media which contain carbonaceous substances or potentially volatile hydrocarbons contribute materially to the carbon content of the coatings. High velocity gas streams and fluidized solids beds have proved to be marginally effective and, in order to achieve sufficiently rapid cooling, require the use of expensive and complex equipment. Also, the fluidized solids methods of quenching require handling and recovery of large volumes of expensive inert gases if staining is to be avoided.

It is, therefore, an object of this invention to provide a process which permits quenching of alloy diffusion coated metal articles which have quantities of transfer agent on their surfaces without explosion hazards. It is another object to provide a process whereby the quenching medium does not rapidly degrade and does not contribute carbon to the coating. It is a further object of the invention to provide a process whereby the coated article can be rapidly cooled without producing stains on

the surface. A still further object of the invention is to provide a quenching stystem which will not impair the corrosion resistance of the coatings.

These and other objects are accomplished by a process in which a diffusion coated metal article is removed from a molten coating bath with a coating of the bath material on its surface and immersed, while at a temperature above the boiling point of liquid sodium, in a quenching bath containing liquid sodium metal. The liquid sodium metal rapidly quenches the coated article. Surprisingly, the sodium metal remains stable with little or no reaction with the transfer agent which adheres to the article to be quenched and with little vaporization of the sodium metal which might be expected at the elevated temperature of the coated article. It is indeed surprising that sodium oxide and sodium hydroxide, either or both of which is always found floating on the surface of molten sodium which has been handled without extreme measures being taken to exclude air, does not react violently with the transfer agent. In addition, the article when cleaned of sodium and transfer agent is essentially free of stains.

In carrying out the process of this invention a coating bath containing a transfer agent and one or more diffusing elements is heated to the desired processing temperature. This temperature will be between about 900° C. and the melting point of the article to be coated. A second bath containing liquid sodium metal is prepared and preferably maintained at a temperature between about 100° C. and 300° C. although higher temperatures may be used. The metal article to be coated is immersed in the molten coating bath for a predetermined period of time during which the diffusing element alloys with the base metal. The coated metal article is then removed from the coating bath and quickly transferred to the quenching bath. The time of transfer is so controlled that the article remains at a temperature above the boiling point of sodium metal until the moment of immersion in the quenching bath. The optimum temperatures and time of transfer to the quenching bath will depend on such factors as the relative size (mass) of the article and the amount of material in the quenching bath. Preferably, the transfer time is not greater than about 60 seconds, with about 10–30 seconds generally being preferred. The amount of quenchant in the bath should be sufficient to cool the coated article to a temperature below about 350° C. before any significant migration of undesirable elements, such as carbon, occurs within the coated article. The time of quenching should generally be in the range from about 1 to 3 seconds.

As disclosed in U.S. Patent 3,184,331, the transfer agents, particularly calcium, remove carbon from the alloyed portion of the coated article. By rapid quenching in the sodium containing bath, migration of carbon from the substrate to the diffusion coating is prevented. In addition, it is found that by maintaining a coating of the transfer agent on the metal during transfer and immersion of the article in the sodium-containing quenching bath, the surface of the coated metal remains free from staining which is commonly experienced when using other quenching media. It has been found that in cases where the surface of the article is not completely covered by transfer agent during the transfer step, staining is prevented by using a sodium quenching bath and surrounding the coated article and quench vessel with an inert gaseous atmosphere, e.g., argon, or a mixture of argon and nitrogen.

Articles coated and quenched by the process of this invention may be readily cleaned after removal from the quenching bath. The use of organic solvents and abrasives is not required. Residual sodium remaining on the quenched article may be removed by steam or high velocity water sprays. Any transfer agent remaining on the surface is then easily removed by washing with water or dilute acid solutions such as 10–20% nitric acid or 1–5% acetic acid. In selecting the agent for cleaning the treated and quenched articles, consideration should be given to possible corrosive attack on the coating or on uncoated parts of the substrate. Such effects are well known to those skilled in the art of cleaning metals.

In carrying out the process of this invention it is desirable to maintain a non-oxidizing or inert atmosphere around both the coating and quenching baths. An inert atmosphere of argon is preferred; however, other gases such as helium, hydrogen, and an argon-nitrogen mixture may be used. The operation may, of course, be carried out in air; however, if air is used, the process should be carefully monitored to detect any unusual build-up of sodium oxide or sodium hydroxide in the quenching bath.

The preferred quenching bath used in this invention is liquid sodium metal. However, combinations of the sodium metal with other alkali metals such as potassium, cesium and rubidium may be used. If combinations of the metals are used, it is preferred that sodium constitute a major portion of the bath.

The process is particularly suitable for quenching the diffusion coated low and medium carbon steels as well as various alloys which contain, for example, zirconium, titanium, vanadium, columbium, etc. Suitable substrates are disclosed in the U.S. patents previously mentioned. In addition, a wide variety of diffusing elements are disclosed, including such elements as nickel, manganese, cobalt, zinc, molybdenum, niobium and aluminum which may be present alone or in combination in the coating bath. Also, various diluents for the transfer agent may be used in the coating bath.

It is essential that the transfer agent represent a significant liquid phase in the coating bath. A preferred transfer agent is calcium, however, barium, strontium, magnesium and lithium may be used. The transfer agent must be present in an amount sufficient to wet the surface of the article in order to effect diffusion of the diffusing element into the surface of the article and to provide a superficial coating of the transfer agent on the article as it is removed from the coating bath. A practical lower limit for most coating operations will be about 10% by weight of the coating bath. Preferably, 60% to about 97% by weight of one or more of the transfer agents is used.

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 were determined by standard metallographic examination or in the case of chromium-containing coatings on iron by dissolving away the substrate with concentrated nitric acid and measuring the unsupported coating film with a suitable micrometer. The composition of the surface coatings was determined by X-ray fluorescence and, in the case of carbon, by a combustion/conductimetric method. This latter analysis was made with a Leco condimetric carbon analyzer, manufactured by the Leco Corp., St. Joseph, Mo. This apparatus and method of using it is well known to those skilled in the art. The CASS test (copper/acetic acid salt spray test) referred to in the examples was carried out in accordance with the ASTM B368–61T procedure.

EXAMPLE I

A molten bath was prepared in a heated iron crucible. The bath contained about 93% calcium, 1.5% calcium nitride, 4.5% chromium and minor amounts of calcium oxide, nickel, aluminum and other elements commonly found in commercial calcium. The crucible was positioned in an enclosure into which argon gas was introduced. Panels, 2.5" x 5", prepared from low carbon, cold rolled basic oxygen furnace steel, 100 mils thick, (nominal 0.05%–0.08% carbon content) were immersed in the coating bath for nine minutes with the bath being maintained at a temperature of 1140° C. At the end of the nine minute period, they were removed from the coating bath. A coating of the transfer agent was present on the panels. The panels were transferred through the argon atmosphere to quenching tanks which were maintained at temperatures in a 60–160° C. range. The time of transfer varied from 2 to 40 seconds with the temperature of the panels being about 900–1100° C. at the time they were immersed in the quenching bath, depending on the length of transfer time.

In one set of experiments, the quenching medium was liquid sodium at a temperature of 150–160° C. In another series of experiments, a hydrocarbon oil at 78–130° C. (Holden Clear Quench Oil, A. F. Holden Co., Milford, Mich.) was used, and in still another set of experiments, a silicon oil at 60–120° C. (Silicon Oil #710, Dow-Corning Co., Midland, Mich.) was used. After quenching, the panels were cleaned by one of the following methods:

(a) The sodium quenched panels were first washed in cold methyl alcohol to remove the sodium present, and were then cleaned in dilute (13–20% by wt.) nitric acid solution;

(b) Panels quenched in the other media were first washed in running hot water (140° F.), then further cleaned by the nitric acid treatment described above.

In all cases the cleaned panels were buffed lightly to develop a satisfactory surface luster and were then passivated by treating them for about 4 minutes at 155° F. in a 20% by weight nitric acid solution containing 2% by weight of $Na_2Cr_2O_7$. The panels were then subjected to the CASS accelerated corrosion test. The coating were analyzed for chromium content by X-ray fluorescence. The coating thicknesses were measured by observing a metallographically polished and etched cross-sectioned sample with a metallograph fitted with a calibrated micrometer eyepiece. Examination of the coatings after cleaning showed the panels quenched in sodium to be bright and free from stains whereas those quenched in silicon oil and hydrocarbon oil had stains ranging from gray to black. The data relating to coating characteristics and CASS test results for the samples are set forth in Table 1 which follows:

TABLE 1

Sample No.	Quench Medium	Coating Characteristics		CASS Test, Rust Spots Developed	
		Sur. Percent Cr.	Thickness, in.	16 hours	112 hours
1	Sodium	39.9	0.001	0	0
2	do	39.0	0.001	0	0
3	do	39.3	0.001	1	1
4	do	39.6	0.001	0	2
5	do	39.4	0.001	0	0
6	Hydrocarbon oil	38.2	0.001	>100	N.d.[a]
7	do	40.6	0.001	>50	N.d.[a]
8	do	39.2	0.001	30	N.d.[a]
9	do	38.7	0.001	60	N.d.[a]
10	do	38.0	0.001	40	N.d.[a]
11	Silicone oil	39.0	0.001	10	17
12	do	40.6	0.001	>25	N.d.[a]
13	do	37.0	0.001	>25	N.d.[a]
14	do	38.7	0.001	>30	N.d.[a]
15	do	37.3	0.001	3	10

NOTE.—Entries marked ([a]) signify "not determined". These data would have been meaningless if determined.

EXAMPLE II

The experiments of Example I were repeated except that the panels were removed from the coating bath and transferred through air to the quenching baths. The time of transfer from the coating bath to the quenching baths was varied. Liquid sodium and the hydrocarbon oil described in Example I were used as the quenching media. The average chromium content and coating thickness for the two groups of panels were as follows:

TABLE 2

	Oil Quenched	Sodium Quenched
Average percent Cr	31.5	30.8
Coating, in	0.00094	0.00092

The results of the CASS test are set forth in Table 3 which follows:

TABLE 3

Transfer Time To Quench Seconds	CASS Test, Rust Spots Developed			
	Qil Quenched		Sodium Quenched	
	At 16 hrs.	At 112 hrs.	At 16 hrs.	At 112 hrs.
5	15	20	0	1
10	0	0	0	1
15	1	3	0	0
20	1	1	0	0
25	3	7	0	0

EXAMPLE III

Panels of mild steel (nominal 0.05%–0.08% carbon content) 2.5" x 4" x 0.1" thick were heated in a calcium bath and quenched using the quench systems described in Table 4 which follows. The time required to cool the interior of the sample was measured by embedding a thermocouple in a hole drilled into the interior of the sample.

TABLE 4

Quench Medium	Time (Seconds) to Reach the Indicated temperature from 1,000° C.			
	900° C.	800° C.	700° C.	300° C.
Sodium	0.2	0.3	0.6	1.2
Helium Blast I [1]	0.6	1.5	3.5	8.0
Helium Blast II [2]	1.5	4.5	14.5	34.5
Oil	1.0	1.8	4.0	9.0
Fluid Bed	1.7	4.3	13.5	24.5

[1] Blast at 134 c.f.m.

[2] Blast at 25 c.f.m.

EXAMPLE IV

A coating bath, prepared in an iron crucible, contained 150 grams of barium and 5 grams of cobalt powder. The bath was stirred and surrounded by an argon atmosphere. An iron sample (0.0025% carbon) 3" x 4" x .02" was immersed in the bath for one hour at 1100° C. The sample was removed from the bath and quickly transferred through the argon atmosphere to a sodium quenching bath which was maintained at about 125° C. After cooling, the sample was removed from the bath and cleaned with water containing dilute (10%) nitric acid. The surface of the sample was bright and the sample contained about 30% cobalt at the surface.

EXAMPLE V

A coating bath was prepared in a molybdenum crucible containing 90 grams of strontium and 10 grams of powdered nickel. The bath was stirred and surrounded by an argon atmosphere. A sample of iron (0.0025% carbon) was immersed in the bath for 15 minutes at 1100° C. The sample was removed from the bath and quickly transferred through the argon atmosphere to a sodium quenching bath which was maintained at 110° C. After cooling, the sample was removed from the bath and cleaned with water containing dilute (10%) nitric acid. The surface of the sample was bright and the sample contained about 55% nickel at the surface.

EXAMPLE VI

A coating bath was prepared in an iron crucible containing 100 grams of magnesium and 10 grams of chromium. The bath was heated to 1100° C. and agitated by a mechanical stirrer. The bath was protected by an argon atmosphere. A mild steel coupon (0.05% carbon) 4" x 1" x .06" was immersed in the bath for two hours. The coupon was withdrawn and quickly transferred to a sodium quenching bath which was maintained at 130° C. After cooling, the coupon was cleaned with water containing dilute (10%) nitric acid. The surface of the coupon was bright and contained 22% chromium.

EXAMPLE VII

A coating bath containing 100 grams of lithium and one gram of chromium was prepared in a carbon steel crucible. A mild steel coupon (0.05% carbon) was immersed in the bath for 30 minutes at 1100° C. The coupon was withdrawn from the bath and quickly transferred to a sodium quenching bath. After cleaning with water containing dilute (10%) nitric acid, the surface was shiny and bright and had a concentration of 28 to 30% chromium. The coating was stripped from its substrate in concentrated nitric acid and found to be highly ductile.

EXAMPLE VIII

A coating bath containing calcium, calcium nitride and chromium powder was prepared in a heated iron crucible and protected from atmospheric contamination by a loose-fitting lid and a continuous purge of argon gas fed into the top of the crucible. The calcium nitride of the bath was varied from 2% to 24% during the tests, and the chromium content of the bath was maintained at a suitable level by replenishing additions made immediately after the treatment of each panel.

The coating bath temperature was maintained at 1140–1150° C. during the tests, and the test panels of 2.5" x 5" x 0.090" thick low carbon, basic oxygen furnace steel (0.08% nominal carbon content) were coated for nine minutes. At the end of the coating period the panels were transferred to the quench medium through air with the time of transfer varying from 5 to 25 seconds.

Alternate pieces were quenched in the hydrocarbon oil previously described in Example I at 25–40° C. and in sodium metal at 100–190° C. as reported in the table below. Use of this alternating sequence eliminated variations in test results due to changes in bath composition or uncontrolled variables.

Following the quenching operation, the panels were cleaned as described in Example I and examined for coating composition, coating thickness and corrosion resistance. The experimental data are presented in Table 5 which follows:

TABLE 5

Number of Panels Tested in each Medium	Transfer Time to Quench (Seconds)	Average Coating Composition				Thickness (Mils)		Corrosion Resistance as Rust Spots per Panel at 112 hrs. CASS Test	
		Surface % Cr		p.p.m. Carbon					
		Oil Quench	Sodium Quench	Oil Quench	Sodium Quench	Oil Quench	Sodium Quench	Oil Quench	Sodium Quench
1	5	30	30	153	145	0.93	0.87	>14	1
4	10	32	33	203	201	0.90	0.93	>13	0.75
1	15	31	28	181	150	1.01	0.88	3	0
3	20	34	35	246	169	0.94	0.94	>11	0
1	25	34	31	293	175	0.93	0.95	7	0

The above table clearly shows the advantages of sodium quenching over oil quenching under essentially equivalent conditions as exemplified by the comparative corrosion resistance of the test panels. The data also shows that the carbon content of the coatings is substantially higher when oil is used as the quenching medium.

EXAMPLE IX

In an alloy coating bath of molten calcium and chromium metal powder of the type described in Example I, panels of low carbon steel (commercially designated as SAE 1008) 2" x 5" x 0.020" thick were coated at 1140° C. for nine minutes, then quenched with short transfer times in the range of 3 to 8 seconds in hydrocarbon oil, silicon oil, or sodium as described in Example I. The data obtained are reported in Table 6 which follows:

TABLE 6

Panel No.	Transfer Time (Seconds)	Average Coating Composition		Quench Medium	Coating Thickness (Mils)	Corrosion Resistance in CASS Test, Rust Spots/Panel at 112 hrs.
		Surface	p.p.m.			
		Percent Cr	Carbon			
1	3	33	226	Hydrocarbon oil	1.1	[1] F
2	4	38	489	do	1.2	[1] F
3	8	36	194	Silicone oil		2
4	5	34	65	Sodium	1.1	0
5	5	33	103	do	1.2	2
6	3	38	72	do	1.0	0

[1] The values recorded as "F" indicate complete failure or general rusting of the panels.

The data reported in Table 6 show the advantages of sodium quenching over oil quenching with respect to both corrosion performance and coating carbon content.

EXAMPLE X

An alloy coating bath of molten calcium and powdered chromium metal was prepared as described in Example I, and steel panels were treated in this bath at 1140° C. for nine minutes. SAE 1008 steel panels, 90 mils thick by 2.5" x 4.25" were coated. The panels were transferred through an argon atmosphere to the quench medium in times varying from 3 to 60 seconds as reported in Table 7. All of the test panels were mechanically buffed before treatment in the coating bath. After coating and quenching, they were cleaned as described in Example I, mechanically buffed to heighten the luster of the finish, passivated as described in Example I, and then subjected to tests for determination of the properties of the coatings. One set of samples was quenched in sodium, and another in the hydrocarbon oil described in Example I. The data obtained are set forth in Table 7.

TABLE 7

Panel No.	Transfer Time (Seconds)	Coating Composition		Quench Medium	Coating Thickness (Mils)	Corrosion Data, Rust Spots/10 sq. in. After 112 hrs. in CASS Test
		Surface Percent Cr	P.p.m. Carbon			
1	5	36	182	Sodium	1.2	[1] 0
2	12	35	65	do	1.1	0
3	15	38	67	do	1.2	0
4	20	36	131	do	1.1	0
5	25	33	137	do	1.1	0
6	30	35	119	do	1.1	0
7	35	36	84	do	1.2	0
8	45	34	128	do	1.1	0
9	60	38	399	do	1.1	30
10	3	38	1,800	Oil	1.0	[2] 100
11	30	38	619	Oil	0.9	[2] 20
12	60	36	548	Oil	0.9	[2] 60

[1] Tested for 64 hours only.
[2] Tested for 16 hours only.

The data of Table 7 show clearly that irrespective of transfer time, other factors being equal, the amount of carbon in the coating of oil quenched samples was 2 to 30 times greater than that in sodium quenched samples, while the corrosion resistance of the soduim quenched samples was, for similarly prepared samples, far superior to that of the oil quenched samples.

After coating and cleaning the samples described above, it was observed that the sodium quenched samples were free of stains but the oil quenched samples were stained black in many places. These stains could not be completely removed by mechanical buffing.

EXAMPLE XI

A molten bath was prepared in a heated stainless steel crucible containing chromium and about 92% calcium. The crucible was positioned in an enclosure into which argon gas was introduced. Steel panels were immersed in the coating bath for nine minutes with the bath being maintained at 1140° C. The panels were removed from the bath and immersed in a sodium quenching bath which was positioned in the enclosure. The panels were removed, then cleaned in cold methanol and then cleaned in a 30% by weight nitric acid solution. The data obtained are reported in Table 8 which follows:

TABLE 8

Panel No.	Transfer Time to Quench (Seconds)	Coating Thickness (Mils)	Coating Composition				CASS Test Rust Spots Developed (hrs.)				
			Percent Cr	Percent Ni	Percent Cr	Percent A	4	20	50	90	114
32	5	1.18	32.5	1.8	29.0	0.8	0	0	2	3	2
33	5.8	1.18	32.6	1.8	30.6	0.8	0	0	1	2	2
34	15	1.18	35.1	1.9	29.2	0.8	0	[2] 20	[2] 20	[2] 20	[2] 20

[1] Cr and Al after 4 seconds, 4 amps. electropolishing.
[2] Spots localized.

In addition to the uses described in the foregoing examples, the process of this invention may be advantageously used in other diffusion coating applications where coatings or properties of the coated articles are improved by rapid quench. By using this process, bright, stain-free surfaces are obtained. The hazards of explosion due to violent reaction of the transfer agents with water are avoided. Also, surface staining and the tendency to carbonize the diffusion coated surface resulting from the use of oils is avoided.

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 a metal transfer agent selected from the group consisting of calcium, strontium, barium, magnesium and lithium and at least one metal diffusing element, the steps comprising:

(a) removing said article from said molten bath with a coating of said transfer agent adhering to the surface thereof,

(b) immersing said article while at a temperature above the boiling point of sodium metal in a quenching bath containing liquid sodium metal at a temperature below about 300° C., and

(c) rapidly cooling said article in said quenching bath.

2. A process of claim **1** wherein said molten bath is maintained at a temperature between about 800° C. and the melting point of said article, said quenching bath is maintained at a temperature between about 100° C. and 300° C., and said article is rapidly cooled to a temperature below about 350° C.

3. The process of claim **1** wherein the temperature of said article when removed from said molten bath is above 1000° C.

4. The process of claim **1** wherein said transfer agent is calcium, said diffusion element is chromium, and said process is carried out in the presence of an inert gaseous atmosphere.

5. The process of claim **2** wherein said article is immersed in said quenching bath within a period from about 10 to 30 seconds after removal from said molten bath.

6. The process of claim **5** wherein said article is cooled in said quenching bath to a temperature below about 350° C. within a period of from about 1 to 3 seconds.

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