

1

3,497,379

PROCESS FOR IMPROVING THE CORROSION RESISTANCE OF ALLOY DIFFUSION COATED METAL ARTICLES

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ABSTRACT OF THE DISCLOSURE

This invention comprises a novel method of improving the corrosion resistance and other properties of alloy diffusion coated metal articles. More particularly it comprises a process whereby the coated article is quickly reheated in contact with a molten metal transfer agent for a short period, and then quenched by suitable means. The result is an improvement in the corrosion resistance and other properties of the coated article. The process is particularly useful in treating continuous strips which cannot be effectively quenched following the initial coating process.

BACKGROUND MATERIAL

The coating of various metals and alloys to protect the surface and improve corrosion resistance or other properties is well known. The most common coating is chromium, but other coating elements such as nickel, manganese, cobalt, silicon, and aluminum are also used. When the coating is applied to a ferrous substrate by a diffusion process such as that described in U.S. Patent 3,184,331 issued to Giles F. Carter on May 18, 1965, good corrosion resistance is obtained due to the fact that the carbon concentration in the coating is less than that in the substrate. However, when the alloy coated articles are removed from the diffusion coating bath and quenched in oil, particularly at temperatures of 1125° C. and above, black stains often occur on the surfaces of the articles. These black stained areas are unsightly and also less resistant to corrosion than the remainder of the coating. Poor corrosion resistance also results when the coated articles are allowed to fall below 900° C. before quenching, or are not quenched at all.

In addition to the poor appearance and reduced corrosion resistance of the coating that occurs when black spots are formed and the poor corrosion resistance that results when the article is not properly quenched, another problem is encountered—the formation of a condition leading to undesirable surface texture after mechanical deformation. Coated and quenched steel strips will ordinarily be formed into articles of commerce such as trim moulding on automobiles and exteriors for home appliances such as toasters. During forming of the moulding, a surface texture known in the trade as "orange peel" is most apparent in the region of severe deformation. If orange peel is excessive, the coating material may be unsuitable for certain uses.

DESCRIPTION OF THE INVENTION

It has been discovered by the process of this invention that corrosion resistance can be improved, the un-

2

sightly black stains removed, and/or orange peel reduced on alloy coated metals.

According to the present invention there is provided the process of contacting alloy coated metal articles at an initial temperature of less than about 850° C. with a molten bath, said bath being maintained at a temperature between about 900° C. and the melting point of said articles. The bath contains at least about 50% by weight of a molten metal transfer agent selected from the group consisting of calcium, barium and strontium, and the articles are maintained in contact with the bath for about 1 to 120 seconds. The articles are then quenched before the temperature of the articles drops below 900° C.

In practice, a molten coating bath is prepared containing a diffusing element and a transfer agent, along with diluents, if any. If, for example, a chromium is used as the diffusing element, and calcium as the transfer agent, the calcium concentration may vary from about 10 to 99% by weight of the coating bath. Preferably, 60% to about 99% by weight calcium is used. Suitable diluents which can be used to reduce the amount of transfer agent required and to modify the transfer properties of the diffusing element are copper, lead, tin, and calcium nitride. After the coating bath has been prepared, the metal articles to be coated are placed in the bath and coated as explained in U.S. Patent 3,184,331 cited previously. After the articles have thus been coated and cooled, it is possible to further improve the corrosion resistance and also to improve the undesirable surface texture (orange peel) of the coated metal articles by practicing this invention.

In addition to metal articles that are alloy coated in the manner described above, the invention described herein can be used to improve the corrosion resistance and other properties of metal articles that are alloy coated by means of a gaseous diffusion process.

In one form the present invention may be practiced by re-treating the coated articles in the original coating bath, provided the bath contains at least about 50% by weight transfer agent. The length of time the article is kept in the re-treating bath depends on the result desired (improved corrosion resistance, or improved orange peel), the temperature at which the process is carried out and, to a lesser extent, the thickness of the coating and the thickness of the substrate. If the chosen temperature of the re-treating bath is close to the lower limit of 900° C., for example from 925 to 1000° C., the optimum time for the maximum improvement in orange peel is near the maximum of from 60 to 120 seconds; longer times can be used if corrosion resistance or stain removal is the desired result. At bath temperatures in the range 1000 to 1100° C., the time required in the bath is reduced to preferably from 10 to 30 seconds. After the coated articles have been removed from the re-treating bath, they should be quenched as quickly as possible and from a temperature higher than 900° C. Therefore, the bath should be maintained at such a temperature above 900° C. that the coated articles will not fall below 900° C. before quenching. For example, 925° C. may be selected as the lowest effective bath temperature. The temperature of the bath is limited only by the melting point of the substrate or the vaporization temperature of the bath; it could even be as high as 1300° C. If quenching re-treating is to be done in oil, it is advisable to allow the

3

article to cool to about 1125° C. or lower (but not below 900° C.) before quenching in order to prevent oil stain from forming. As a practical matter, the coated articles are placed in the re-treating bath, removed, and quenched all within a period of about 3 minutes.

In another form, the present invention may be practiced by carrying out part of the molten coating bath (containing at least about 50% by weight transfer agent) on the articles as "bath dragout," i.e., with a coating of transfer agent adhering to the surface of the articles, permitting the coating of transfer agent to solidify in an inert atmosphere, and then heating the articles to melt the frozen layer of transfer agent, thereby providing the necessary article-to-molten transfer agent contact. The layer of bath dragout is melted by heating the articles in an inert gaseous atmosphere such as argon at a temperature ranging from about 900 to 1300° C. The articles are then quenched as before. Any transfer agent remaining on the surface after quenching (there will usually be some transfer agent remaining, whether the invention is practiced by dipping in the coating bath or by melting frozen bath dragout) is easily removed by washing with water or dilute acid solutions such as 10 to 20% nitric or 1 to 5% acetic acid. Before re-treating, it is generally not necessary to remove bath dragout that may have remained on the articles from the coating process.

In still another form the invention may be practiced by dipping alloy coated metal articles in a molten bath containing from about 50 to 100% transfer agent, the process conditions being the same as those described above.

Although hydrocarbon or silicone oils are useful when the sample is in the 1125° C. temperature range, the preferred quenching bath for use in this invention is liquid sodium metal which is useful over the wider range of from 900° C. to the melting point of the substrate. Combinations of the sodium metal with other alkali metals such as potassium, cesium and rubidium may be used. Other quenching mediums such as water, brine, high velocity gas streams, and fluidized solid beds are also suitable.

In carrying out the process of this invention it is desirable, especially when the invention is practiced by melting frozen bath dragout, to maintain a non-oxidizing or inert atmosphere around both the re-treating and quenching baths. This is necessary when frozen bath dragout is melted to prevent chemical reaction from reducing the concentration of transfer agent in the dragout to below about 50%.

A wide variety of diffusing elements are suitable for use in the re-treating bath, although chromium is preferred. Other suitable elements include nickel, manganese, cobalt, zinc, molybdenum, niobium, silicon, and aluminum. These diffusing elements may be present alone or in combination in the bath. It should be pointed out, however, that in practicing this invention it is not necessary to have a diffusing element present in the re-treating bath, only the transfer agent is required.

A preferred transfer agent is calcium, but barium and strontium may also be used. The lower limit of transfer agent concentration in the bath of the invention is about 50 weight percent of the bath. Various diluents that may be used with the transfer agent in concentration up to about 50 weight percent are copper, lead, tin, and a nitride of a transfer agent. Calcium nitride in concentrations up to about 50 weight percent of bath has been found to be a particularly suitable diluent.

Although from a practical standpoint it may be desirable to practice the invention by re-treating the coated articles in the coating bath or by melting frozen coating bath dragout on the coated articles, as previously indicated, the invention may also be practiced by dipping the coated articles in a separate bath containing at least about 50% by weight transfer agent, the remainder being diluents and/or diffusing elements. While it is desirable to stir the coating bath while coating the articles, the bath

4

of the present invention need not be stirred, since the alloyed article-bath contact time is so short. Stirring is not harmful, however.

The transfer agent used in the molten bath of this invention acts to remove carbon from the surface of the alloy coating. Thus, in order to achieve the best improvement in corrosion resistance of the alloy coated articles, the molten bath should be substantially free of carbon which would be free to diffuse into the alloy coating. However, some carbon may be present in the bath, as long as it is present in a state so that it does not readily diffuse into the alloy coating.

A better understanding of the invention will be gained from the following examples illustrating the preferred methods of carrying out the invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

This example illustrates the effect of re-treating on stains, corrosion resistance, and orange peel developed on coated ferrous articles. Samples 5" x 2" x 0.02" were cut from Jones and Laughlin aluminum-killed steel (0.04% carbon) and degreased in trichloroethylene. The samples were then placed in a mechanically stirred vessel initially containing 2300 grams calcium and 115 grams chromium (-325 mesh powder) with 5-gram additions of chromium before each sample treatment. Nickel and aluminum also were present as shown in the table below. A close fitting cover was in place over the bath and argon was introduced over the bath to reduce its reaction with air, the cover being removed only to introduce and remove samples from the bath. The bath temperature in each test is shown in the table below. After coating for 9 minutes, the samples were quenched by transfer through air in 2 seconds into an oil bath at a temperature of about 30 to 50° C. (Holden Clear Quench Oil, A. F. Holden Company, Milford, Michigan). The samples were cleaned overnight in water and then cleaned for 10 to 15 seconds in 30% HNO₃ at 20° C., rinsed in water, and dried.

After coating in the manner described above, certain of the samples had black stains on the surface. These stains were removed by re-treating the sample in the same bath at a lower temperature, approximately 1100° C., for a period of from 15 to 30 seconds, followed by quenching as before by transferring the samples through air in 2 seconds into a Holden Clear Quench Oil bath. The temperature of the oil bath ranged from 30 to 50° C. In all cases the stain was eliminated by this treatment.

In addition to the removal of the black stains, the re-treated samples were improved over identical nonre-treated samples in that the re-treated samples showed improved corrosion resistance and also when deformed developed less objectionable texture ("orange peel") in the region of deformation.

The orange peel was measured on 250 mil Olsen cups and the rating was against standard reference panels.

The results are tabulated in the following Table I.

Temperature (°C.) of Coating Operation	Percent Metal Added to Bath		Orange Peel Rating*		Improvement (In Orange Peel Units) by Re-treat- ing
	Ni	Al	Not		
			Re-treated	Re-treated	
1,140	0	0	7	8-9	1.5
1,140	0	3	6-7	6-7, 7	0, 0.5
1,140	2	0	6-7	8	1.5
1,140	2	0.5	7-8	8	1.5
1,140	4	1	6-7, 7	8	1, 1.5
1,175	2	0	7, 7-8	8	1, 0.5
1,175	2	1	7	8-9	1.5
1,175	4	0	6	6-7	0.5
1,175	4	0.25	6-7	8	1.5
1,175	4	0.5	6-7	7	0.5
1,175	4	1	6-7	8	1.5

*A rating of 10 is perfect, i.e., no increase in roughness upon deformation.

It can be seen that the comparisons in the above table show an average improvement of about one orange peel

5

unit. Thus, re-treating substantially improved the appearance of the subsequently deformed samples by reducing objectionable orange peel.

The improvement in corrosion resistance of re-treated samples was determined by CASS testing similar samples in groups of three. (The CASS test, copper/acetic acid salt spray test, was carried out in accordance with the ASTM B368-61T procedure. Prior to testing, the samples were degreased, rubbed with an aqueous slurry of magnesium oxide and dried.) Group I contained one re-treated and 2 nonre-treated samples. Group II contained two re-treated and one nonre-treated sample. The effectiveness of re-treating on corrosion resistance was rated as follows:

Group I

2 points—the re-treated sample was best.

1 point—the re-treated sample was intermediate.

0 points—the re-treated sample was worst.

Group II

0 points—the nonre-treated samples was best.

1 point—the nonre-treated sample was intermediate.

2 points—the nonre-treated sample was worst.

The comparison covered chromium-iron coatings containing various nickel (from 0 to 7%), aluminum (from 0 to 4%), and nickel-aluminum concentrations. Twenty-four sample trios (72 samples) were used for comparison. If re-treated samples were no better than nonre-treated samples, they would receive an average score of 1.0; the maximum average score is 2.0. The average was actually found to be 1.6, which clearly shows the beneficial effect of re-treating on corrosion resistance.

Similar results in the improvement of orange peel and corrosion resistance as obtained in Example 1 are obtained when either calcium, barium, or strontium, or a combination thereof is used as the transfer agent in the re-treating process.

EXAMPLE 2

This example illustrates the effect of the re-treating time, i.e., the time the coated sample is left in the re-treating bath, on the reduction of orange peel on samples coated only on one side. Several samples were made by welding together two pieces of .020 inch thick Jones and Laughlin aluminum-killed oxygen furnace steel (.04% carbon). The samples were then coated for 9 minutes at 1140° C. in a mechanically stirred bath initially containing 2300 grams calcium, 115 grams chromium, (—325 mesh powder), plus approximately 2% nickel and 10% Ca_3N_2 . After coating, the samples were removed from the bath, allowed to air cool to room temperature, then cleaned by brief exposure to acidified hot water. Before re-treating, the samples were cut apart and trimmed to 3" x 4" so that sheets with allow coating on one side only were re-treated. The re-treating bath contained 2200 grams calcium, 88 grams chromium (—325 mesh), 44 grams nickel and 11 grams aluminum. Calcium nitride (Ca_3N_2) was present in a concentration ranging from 6% at the beginning to 13% at the end of the run.

The data is summarized in Table II below:

TABLE II

Temperature (° C.)	Number of Samples	Average Orange Peel*
1,025	7	7.9
1,050	16	8.0
1,075	17	7.6

*A rating of 10 is perfect, i.e., no increase in roughness upon deformation. All ratings were done by a surface examination of standard 300 mil Olsen cups.

6

One particularly good sample re-treated at 1050° C. for 60 seconds attained an orange peel rating of 8+ to 9+ after deformation to a 300 mil Olsen cup.

EXAMPLE 3

This example illustrates the improvement in corrosion resistance obtained by re-treating samples that were air cooled after coating. Samples can be cooled in air or argon after coating, but the corrosion resistance thus achieved is poor. Excellent corrosion resistance can be restored by re-treating the samples in a calcium, or preferably a calcium-chromium bath.

Fifteen 4" x 8" x .020" thick Jones and Laughlin aluminum-killed basic oxygen furnace steel (.04% carbon) samples were coated in an argon padded calcium-chromium mechanically stirred bath initially containing 2300 grams calcium, and 115 grams chromium at 1140° C., cooled in air, and then re-treated at 1050° C. in the same bath and transferred in about 2 seconds to an oil quench. All 15 samples were cleaned, lightly polished and then passivated in HNO_3 — $\text{Na}_2\text{Cr}_2\text{O}_7$. They were then CASS tested for 64 hours and afterwards compared with nonre-treated samples. The results are given in Table III below:

TABLE III

Coating Time (min.)	Re-treating Time (sec.)	CASS Defects per 32 in. ² at 64 hrs.	
		Nonre-treated	Re-treated
15	15	100, 100+, 100+	0, 0, 0, 2, 2
9	8	100+, 100+, 100+	0, 1, 1, 2

The six slow cooled nonre-treated samples showed more than a hundred defects each, while the nine re-treated samples averaged less than one defect each, clearly showing the improvement in corrosion resistance obtained by re-treating.

EXAMPLE 4

This experiment illustrates that there is a temperature dependent, optimum re-treatment time for the reduction of orange peel. A two-side-coated piece of 0.04% carbon steel was coated for 10 minutes in a stirred, argon padded bath of calcium-chromium containing 2% Ni+1% Al and then rapidly oil quenched, cleaned, and then cut into 22 identical 2½" x 2½" samples. One was saved as a control and the remaining 21 were re-treated in a bath of 2300 grams calcium+115 grams chromium+46 grams nickel. Each sample was oil quenched following re-treatment, cleaned, and a 300 mil Olsen cup formed. The cup was then rated for orange peel. Results are shown in Table IV below:

TABLE IV.—ORANGE PEEL (300 MIL OLSEN CUPS) VS. TEMP/TIME

Re-treatment Temp. (° C.)	Time of Re-treatment in Seconds												
	1	2	4	8	16	32	48	64	80	128	256		
1,140	7	7-8	*8	7-8	7-8								
1,100	7	7-8	7	7-8	*8	7		7					
1,050				7	7-8		*8	*8	7	7-8			
1,000								7		*7-8	7		

*Best results.

The above cupped samples plus the nonre-treated control then were CASS tested for 16 hours. The control exhibited gross failure, as it was fully rusted. All the above re-treated samples were improved. The series at 1140° C. illustrates the results:

Time of re-treatment, seconds (0=control):	CASS defects on each cup (gross failure)
1	8
2	5
4 ¹	11
8	0
16	0

¹ Best orange peel (8) as noted above.

A change in either coating time or substrate thickness has also been noted to affect the optimum re-treating time. However, the changes thus caused are generally small, less than a factor of two. Although the optimum re-treating times as a function of temperature are tabulated above, it should be pointed out that some improvement in orange peel will accrue over a time range of approximately 1 to 100 seconds.

EXAMPLE 5

An important process variation of the invention is illustrated in this example. Rather than re-treating the samples in the coating bath, a thin film of the bath is frozen on the samples during quenching and then heated. Similar results are obtained as when the samples are re-treated in the bath. The experiment was carried out as follows:

A bath was prepared of 2300 grams calcium plus 230 grams chromium (—325 mesh powder) plus 60 grams nickel plus 22 grams aluminum. It was padded with argon, heated to 1140° C., and stirred mechanically. The furnace was fitted with an argon-filled chimney above the coating bath. A second furnace at 1150° C. was fitted with an empty steel liner filled with argon. Twenty-four 6" x 2" x 0.020" panels of Jones and Laughlin aluminum-killed, basic oxygen furnace steel (0.04% carbon) were treated at two coating times. Five different types of quench were used to terminate the coating operation as follows:

(A) 2 second transfer through air into oil quench.

(B) 90 second cool in argon-filled chimney, then air cool to room temperature.

(C) 25 second cool in argon chimney (then samples were about 500° C. after 25 seconds cooling. At the end of this time they were uniformly covered with a thin protective layer of frozen bath), then 1 second air transfer into argon-filled pot, 8 second hold in the argon-filled pot at 1150° C. Then 2 second air transfer to oil quench.

(D) Like (C) but 20 second hold in argon-filled pot.

(E) Like (C) but 45 second hold in argon-filled pot. The samples were then cleaned, passivated, and CASS tested for 16 hours with the following results:

Coating Time (min.)	Type of Quench	Defects After 16 hrs. in CASS Test
8	A	1, 7
8	B	100, 100
8	C	2, 6
8	D	2, 4
8	E	1, 6
4	A	11, 100
4	B	100+, 100+
4	C	17, 20
4	D	6, 7
4	E	5, 22

For each coating time it can be seen that the argon cool (B above) destroyed corrosion resistance, but that the short heating (C, D, E above) of the dragout-covered samples restored the original level of good corrosion resistance.

In the variation of the invention as shown in Example 5, it is seen that the coated article need not be physically dipped into a large volume of liquid bath. Instead, the relatively small amount of bath intentionally frozen on the article as bath dragout can be quickly melted to provide the liquid metal environment which must surround the article to effect decarburization. Using this technique, it is of course necessary that the bath composition and coating process be adjusted so that the dragout will be continuous and sufficiently thick. Experience suggests that dragout coverage of as little as 0.01 lbs. per sq. ft. is adequate.

EXAMPLE 6

The following example illustrates the improvement in corrosion resistance obtained by re-treating samples followed by quenching in a sodium bath. The original samples were argon cooled after coating.

A stainless steel container having a bath prepared from 2000 grams calcium, 60 grams chromium (—325 mesh), 15 grams aluminum, and 40 grams nickel was heated to 1140° C. The bath was agitated by a mechanical stirrer and was covered by an inert atmosphere of argon (~0.05% nitrogen). The melt had been used for some time and was found to contain 79% calcium, 18% calcium nitride, 2.2% nickel and 0.2% aluminum by analysis. A series of low carbon steel specimens 0.020 and 0.090 inch thick) were introduced for a coating time of 9 minutes followed by cooling to room temperature in the argon atmosphere. The diffusion coatings applied in this manner were typically 0.8 mils thick with a surface composition of 26% chromium, 3% nickel and 0.3% aluminum. A portion of these samples was then re-treated in the same bath for 1 minute at 1050° C. followed by a 7 second transfer in argon to a sodium quenching bath whose initial temperature was about 120° C. The samples were cleaned, lightly polished, passivated and exposed in the CASS test for 16 hours with the results shown in Table V below:

TABLE V

Group (Sample Numbers)	Steel Thickness, inch	Re-treated	CASS Defects at 16 hrs.
A—2 Samples	0.090	No	+100, +100
B—3 Samples	0.090	Yes	0, 0, 10
C—2 Samples	0.020	No	+100, +100
D—3 Samples	0.020	Yes	0, 0, 2

It will be apparent from the foregoing examples that the treatment of alloy coated metals in accordance with this invention will result in stain removal, improved corrosion resistance, and less objectionable "orange peel" as well as other advantages.

What is claimed is:

1. A process for improving alloy diffusion coated metal articles which comprises contacting said articles having an initial temperature of less than about 850° C. with a molten bath, said bath being maintained at a temperature between about 900° C. and the melting point of said articles, said bath containing at least about 50% by weight of a molten metal transfer agent selected from the group consisting of calcium, barium, and strontium, maintaining said articles in contact with said bath for about 1 to 120 seconds, followed by immediately quenching while the temperature of said articles is not less than about 900° C.

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

3. The process of claim 1 wherein the molten bath contains up to about 50 weight percent calcium nitride.

4. The process of claim 1 wherein said articles are maintained in contact with said bath for about 10 to 30 seconds while said bath is at a temperature of about 1000–1100° C.

5. The process of claim 1 wherein said articles are maintained in contact with said molten bath for about 60 to 120 seconds while said bath is at a temperature of about 925 to 1000° C.

6. The process of claim 1 wherein the articles are quenched in liquid sodium metal.

7. A process for improving the corrosion resistance of alloy coated metal articles which are coated in a diffusion coating bath containing a diffusing element and at least about 50 weight percent transfer agent selected from the

9

group consisting of calcium, barium, and strontium, which comprises removing said articles from said bath with a coating of said transfer agent adhering to the surface thereof, permitting said coating to solidify in an inert atmosphere followed by heating said articles to melt said layer of transfer agent, and thereafter quenching said articles.

8. The process of claim 7 wherein said articles having a coating on the surface thereof are heated at a temperature of about 900 to 1300° C. in an inert gaseous atmosphere.

9. The process of claim 7 wherein said diffusing element is chromium and said transfer agent is calcium.

10. The process of claim 7 wherein said articles are quenched in liquid sodium metal.

10

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