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METHOD OF CHROMIZING IN A FUSED SALT BATH

Filed March 2, 1971

FIG. 1

x200

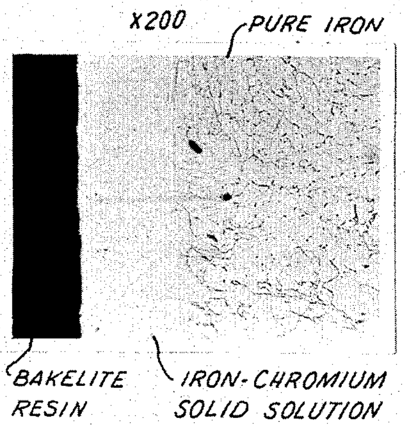


FIG. 2

x400

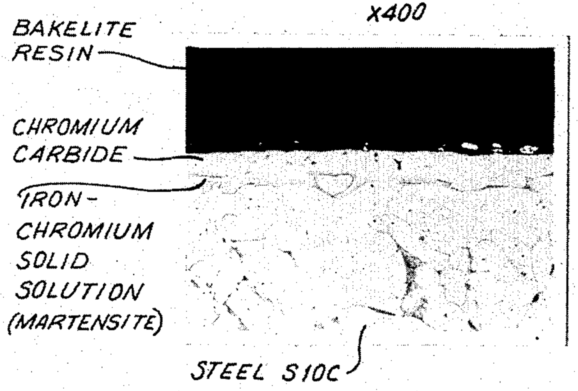


FIG. 3

x400

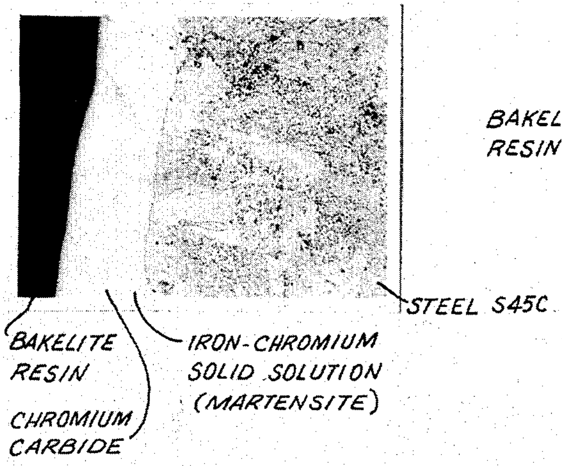


FIG. 4

x400

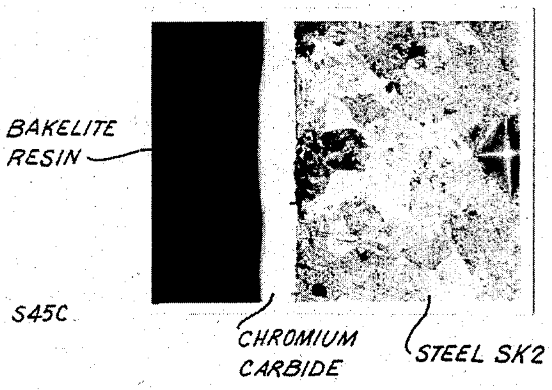
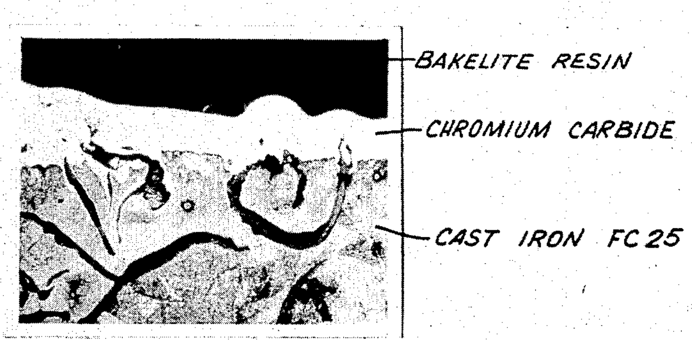


FIG. 5

x400



3,671,297

METHOD OF CHROMIZING IN A FUSED SALT BATH

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Int. Cl. C23c *9/10*
U.S. Cl. 117—113 18 Claims

ABSTRACT OF THE DISCLOSURE

A method of treating metals and alloys in which a fused salt bath consisting of at least one boron-containing salt such as boron oxide (B_2O_3) or borax ($Na_2B_4O_7$), and a chromium-containing material is prepared and a material to be treated is immersed in the fused salt bath as a result of which a chromium-impregnated layer with fine structure and with excellent resistance to corrosion, oxidation and wear is formed at the surface of the metal.

BACKGROUND OF THE INVENTION

Heretofore, coating or diffusion-impregnation with chromium at a metal surface has been used as a means for improving the corrosion resistance and oxidation resistance of ferrous materials. Recently, the technique has been modified so that it is applicable to non-ferrous materials such as the heat resistant alloys used in the space industries.

The conventional techniques for coating or diffusion-impregnation of chromium on a metal surface are electrochemical plating, pack cementation and vapor-phase plating. However, the corrosion resistance of deposits prepared by electrochemical plating is unsatisfactory owing to the presence of pin holes; moreover adhesion between the plated coating and the substrate is inadequate due to the lack of a diffusion layer between the coating and the substrate, so that the coating is apt to peel.

Pack cementattion and vapor-phase plating are superior to electroplating so far as adhesion of the coating is concerned due to the fact that the chromium diffuses into the substrate in the process, forming a layer of intermediate composition.

Pack cementation, however, is unsuitable for continuous operation so that it cannot attain high production; moreover the protection against oxidation which it affords is inadequate. Vapor-phase plating is also unsuitable for continuous operation, and requires complex and expensive equipment.

Attempts have been made to impregnate chromium into the surface of a metal by dipping the metal into a fused salt bath containing chromium. The only method of this type known calls for dipping the metal substrate into a mixed salt bath of chromous chloride, barium chloride, sodium chloride and metallic chromium. However, the method is impractical and has not been used because it requires heating in an argon atmosphere to prevent oxidation of the substrate and also requires an expensive zirconia crucible because of the strong corrosiveness of the salt.

SUMMARY OF THE INVENTION

This invention relates to the diffusion-impregnation of chromium into the surface of a substrate by dipping and maintaining the material to be treated within a salt bath comprising at least one boron-containing salt and a chromium-containing metal or alloy. This type of bath is non-corrosive to the vessel, and the impregnation can be carried out in air. Moreover, the surface layer produced is structurally fine rather than porous and has excellent resistance to corrosion, oxidation and wear. The reason why a non-oxidizing atmosphere is unnecessary for this process is that the boron oxide or borate forms a fused bath at relatively low temperature in which the chromium dissolves; also the boron oxide or borate dissolves any oxide on the surfaces of the substrate or the vessel so that the surfaces remain clean. Naturally, if desired, the method of the present invention may be carried out in an inert atmosphere.

Accordingly, a primary object of the present invention is to provide a method for forming a chromium-impregnated layer with excellent resistance to corrosion, oxidation and wear and with fine structure in the surface of metals and alloys.

Another object of the present invention is to provide a method for forming a chromium-impregnated layer of sufficient thickness in the surface of metals and alloys, which does not require complex apparatus and which can be carried out in air. A further object of the present invention is to provide an economic, simple method for forming a chromium-impregnated layer in the surface of metals and alloys which is suitable for mass production.

Yet another object of the present invention is to provide a method for forming a chromium-impregnated layer in the surface of metals and alloys in a fused salt bath which does not corrode the vessel containing the bath.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the method hereinafter disclosed, and the scope of the invention will be indicated in the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photomicrograph of chromized pure iron;

FIG. 2 is a photomicrograph of chromized JIS S10C (structural carbon steel);

FIG. 3 is a photomicrograph of chromized JIS S45C (structural carbon steel);

FIG. 4 is a photomicrograph of chromized JIS SK2 (carbon tool steel); and

FIG. 5 is a photomicrograph of chromized JIS FC25 (grey cast iron).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention is carried out by immersing a specimen in a fused bath which includes at least one compound containing baron-containing salt and a source of chromium metal. As the boron-containing salt, boron oxide, or borates of the alkali metals such as lithium borate, sodium borate, potassium borate or mixtures thereof may be employed. As the source of chromium metal, metallic chromium may of course, be used; another source is ferro-chromium (Fe-Cr). It is economically advantageous to use the ferro-chromium compound. In order to achieve a sufficiently chromized layer to yield the desired oxidation and corrosion resistance of the substrate, at least about one percent of the chromium source must be present. In general the optimum amount is about 5% or more. As the amount of chromium added is increased, the viscosity of the salt bath mounts until it is so high that dipping of the specimen becomes difficult so that a suitably impregnated layer of uniform thickness cannot be obtained. In view of this limitation it is undesirable in practice to add more than 60%.

Either stainless steel or graphite may be used for the vessel containing the bath. When stainless steel is used as the vessel, a very small amount of the chromium may be dissolved out during the operation; however, the chromium removed in this way eventually diffuses into the substrate specimen without causing any damage. The loss of chromium from the stainless steel vessel by this process is negligible and stainless steel vessels are suitable for industrial use.

The temperature of operation ranges from that at which the salt bath composition melts to the melting point of the substrate. In practice, the temperature of treatment ranges from 700° C. to 1100° C. depending on the rate of formation of the chromized layer, the desired thickness of the layer, and the material of which the vessel is made. When steel having a low transformation point is to be treated, materials are added to the bath in order to lower its melting point and thus prevent the strains resulting from the transformation. The melting point of borax, for example, is nearly 740° C.; where a steel having a transformation point lower than 740° C. is to be treated, alkali halides such as NaCl, KCl, and NaF, or oxides such P_2O_5, or hydroxides such as NaOH and KOH or sulfates, carbonates or nitrates may be added. However, it must be noted that effective chromizing does not take place at temperatures lower than 600° C.

The time of treatment depends upon the thickness of the chromized layer desired. The minimum time of treatment is about one hour, the actual time depending on the temperature of the treatment. Although the thickness of the impregnated layer increases as the time of treatment increases, in general it is not necessary to prolong the treatment beyond 30 hours, since the desired thickness can usually be achieved within this period.

Following are examples of the method of the present invention:

EXAMPLE 1

A bath consisting of 300 grams of borax (67%) and 150 grams of ferro-chromium (67% chromium) in a graphite crucible was heated to 1000° C. A specimen of pure iron, 14 mm. in diameter and 10 mm. in length was immersed for eight hours in this salt bath, removed, air cooled and immersed for 2 hours in boiling water to remove residual traces of the fused salt bath. Specimens of other types of steel were also prepared. The data are given in Table 1.

TABLE 1

Specimen	Composition	Bath temp., ° C.	Immersion time, hrs.	Figure number	Thickness, microns
Iron	Pure iron	1,000	8	1	100
JIS S10C	Structural carbon steel.	1,000	4	2	20
JIS S45C	do	1,000	8	3	30
JIS SK2	Carbon tool steel	800	24	4	15
JIS FC25	Grey cast iron	1,000	8	5	25

NOTE.—JIS=Japan Industrial Standards.

As is clearly evident from the figures, impregnated layers were formed on all of the specimens, and in all cases the layers were non-porous and the surfaces were smooth.

X-ray analysis of the impregnated layers showed that the alpha-phase (Fe-Cr solid solution) was formed in pure iron and in S10C and that the carbides M_7C_3 and $M_{23}C_6$, in addition to the alpha-phase, were formed in S45C, SK2 and FC25. Examination of the element distribution by means of the electron probe microanalyser showed that the chromium content at the surface portion exceeded 50% in S45C and SK2, and exceeded 20% in pure iron. These results demonstrate that when a substrate is dipped into a mixed bath of borax and ferro-chromium a substantial amount of chromium enters the surface layer and that when carbon is present in the substrate as is the case with S45C, SK2 and FC25, chromium carbides are also formed in the surface layer.

EXAMPLE 2

500 grams of a mixed powder consisting of 95% borax and 5% ferro-chromium (the ferro-chromium containing 67% of chromium was used in all the examples) were heated to 1100° C. in a stainless steel vessel and a specimen SK2 was immersed for six hours in the fused salt bath, removed, air cooled, and immersed in boiling water to remove the bath residue. Microphotography showed that the impregnated layer was about 20 microns thick. There was no visible corrosion on the inner surface of the stainless steel vessel. It follows that satisfactory impregnation with chromium can be achieved with a ferro-chromium content of 5% in a bath and that a stainless steel vessel is satisfactory for industrial use.

EXAMPLE 3

500 grams of a mixed powder consisting of 80% anhydrous boric acid and 20% ferro-chromium were heated to 1000° C. in a graphite crucible. A specimen of SK2 was immersed for 8 hours therein, removed and immersed in boiling water to remove bath residue. Examination by microscope showed that a chormium-impregnated layer about 15 microns thick had been produced.

EXAMPLE 4

500 grams of a mixed powder containing 73.2% borax and 20% ferro-chromium and 6.8% sodium fluoride to lower the melting point of the bath, were heated; the bath was completely molten at 700° C. A specimen of S10C was immersed for 24 hours in the bath, removed, air cooled and immersed in boiling water to remove the bath residue. Examination by microscope showed a chromium-impregnated layer about 8 microns thick. It is therefore evident that the method can be carried out at a temperature below the melting point of the borax.

EXAMPLE 5

A bath consisting of 70% borax and 30% ferro-chromium was prepared in a graphite crucible. Specimens of tungsten, molybdenum, tantalum, niobium, nickel and cobalt measuring 5 mm. in diameter and 10 mm. in length were dipped therein. For the tungsten, molybdenum, tantalum and niobium, the bath temperature was 1000° C. and the time of immersion was 8 hours. For the nickel and the cobalt, the bath temperature was 900° C. and the time of immersion was 8 hours. After immersion and removal, the bath residue was removed by boiling water. Microscopic observation of cross sections of the above samples showed that impregnated layers ranging from eight to twenty microns were produced. Fluorescent X-ray analysis showed that all of the surfaces were impregnated with chromium. It is therefore evident that the method of the present invention is effective with non-ferrous metals as well as with ferrous metals.

EXAMPLE 6

500 grams of a mixed powder containing 70% borax and 30% ferro-chromium were brought to 1000° C. in a graphite crucible. Two specimens each of S10C and S45C were dipped into the crucible for 8 hours, removed and air cooled and cleaned of bath residue with boiling water.

Oxidation resistance of the treated specimens was compared with that of untreated specimens of S10C, S45C and SUS27 (stainless steel) of the same size and shape as the treated specimens, where all were maintained for two hours in a furnace heated to 700° C.

Noticeable oxide scale appeared on the surfaces of the untreated specimens of S10C and S45C, part of which peeled off. On the other hand, there was virtually no scale on the treated specimens of S10C and S45C and in fact the weight gain due to oxidation was in no case greater than that of the specimen of SUS27 as shown in Table 2.

TABLE 2

Specimen	Weight gain due to oxidation, mg./cm.^{2} Treated	Weight gain due to oxidation, mg./cm.^{2} Untreated
JIS S10C	0.02	0.12
JIS S45C	0.09	0.62
JIS SUS27		0.09

The corrosion resistance of the various specimens was tested by dipping them for 4 hours into an aqueous solution of 10% HCl at room temperature. The untreated specimens of S10C and S45C were severely corroded and developed rough surfaces; the surfaces of the treated materials S10C and S45C were almost unaffected, and the weight loss due to the immersion in the HCl approximately that of the SUS27 as shown in Table 3.

TABLE 3

Specimen	Weight loss due to corrosion, mg./cm.^{2} Treated	Weight loss due to corrosion, mg./cm.^{2} Untreated
JIS S10C	0.30	36.7
JIS S45C	0.12	22.7
JIS SUS27		0.25

These data show that the oxidation resistance and corrosion resistance of carbon steels are remarkably improved by means of the chromizing treatment of the present invention.

EXAMPLE 7

500 grams of a mixed powder of 70% borax and 30% ferro-chromium were heated to 900° C. in a graphite crucible. A specimen of SKD 1 (alloy tool steel) of 5 mm. thickness, 15 mm. width and 70 mm. length was immersed for 24 hours in the fused salt bath, removed, air cooled, and cleaned of bath residue by boiling water. Microscopic observation of a cross section showed an impregnated layer 25 microns thick, and X-ray analysis showed carbides of $M_{23}C_6$ and M_7C_3 types.

The treated specimen of SKD1 and a control specimen of SKD1 having the same size and shape were subjected to a wearing test of Ogoshi type where the control specimen had been quenched and tempered in a salt bath furnace. In the test, normalized S45C was used as the opposing sliding material, at a sliding distance of 600 m., under a load of 3.3 kg. and without lubrication.

The amount worn from the treated specimen of SKD1 was from one half to one fifth that of the comparative sample as is shown in Table 4.

TABLE 4

Specimens	Wear amount (mm.^{3} under load of 1 kg. after sliding distance of 1 m.) At sliding velocity of 0.105 m./sec.	Wear amount (mm.^{3} under load of 1 kg. after sliding distance of 1 m.) At sliding velocity of 4.5 m./sec.
Treated	4.7×10^{-5}	3.8×10^{-5}
Untreated	10.6×10^{-5}	17.3×10^{-5}

It is evident from these data that the wear resistance of a high carbon steel is remarkably enhanced by the formation of a chromized layer containing a carbide.

As is evident from the above examples, the method of the present invention wherein the surfaces of both ferrous and non-ferrous metals are treated by dipping and holding in a fused salt bath containing chromium and boron oxide or borate are remarkably improved with respect to oxidation and corrosion resistance and with respect to wear resistance. Moreover both the intensity and the depth of chromizing can be controlled by choice of the operating temperature and time of immersion. The method is broadly applicable for treatment of machine parts where resistance to corrosion, oxidation and wear resistance is required.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method of chromizing a metal work-piece comprising the steps of preparing a fused salt bath consisting essentially of at least one boron-containing salt and a chromium-containing metal and immersing said metal work-piece in said fused salt bath until a diffusion layer containing chromium is formed on the surface of the work-piece.

2. A method as defined in claim **1**, wherein said boron-containing salt is selected from the group consisting of B_2O_3 and borates.

3. A method as defined in claim **2**, wherein said borates are selected from the group consisting of $Li_2B_4O_7$, $Na_2B_4O_7$ and $K_2B_4O_7$.

4. A method as defined in claim **1**· wherein said chromium-containing metal is metallic chromium.

5. A method as defined in claim **1**, wherein said chromium-containing metal is ferro-chromium.

6. A method as defined in claim **1**, wherein said bath comprises from 1 to 60% by weight of said chromium-containing metal.

7. A method as defined in claim **1**, wherein the temperature of the salt bath during immersion of said work-piece lies between 700° C. and 1100° C.

8. A method as defined in claim **1**, wherein the duration of said immersion lies between about 1 and 30 hours.

9. A method as defined in claim **1**, wherein said fused salt bath is formed by heating and fusing at least one boron-containing salt and adding thereto one chromium-containing metal.

10. A method as defined in claim **1**, wherein said fused salt bath is contained in a graphite crucible.

11. A method as defined in claim **1**, wherein said fused salt bath is contained in a stainless steel vessel.

12. A method as defined in claim **1**, wherein said metal work-piece is of a ferrous material.

13. A method as defined in claim **12**, wherein said ferrous material is selected from the group consisting of iron, structural carbon steel, carbon tool steel, grey cast iron, stainless steel and alloy steel.

14. A method as defined in claim **1**, wherein said metallic work-piece is of a non-ferrous material.

15. A method as defined in claim **14**, wherein said non-ferrous material is selected from the group consisting of W, Mo, Ta, Nb, Ni and Co.

16. A method as defined in claim **1**, wherein said fused salt bath includes a material which lowers the melting point of said bath.

17. A method as defined in claim **15**, wherein said material is selected from the group consisting of NaCl, KCl, NaF, P_2O_5, NaOH, KOH and mixtures thereof.

18. A method as defined in claim **1**, wherein said method is carried out in air.

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U.S. Cl. X.R.

106—1; 117—118, 130 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,671,297 Dated June 20, 1972

Inventor(s) Noboru Komatsu, Tohur Arai, and Masayoshi Mizutani

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claims priority, application Japan, Mar. 6, 1970, 19437/70

Second Inventor: Tohru Arai

Signed and sealed this 24th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents