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METALLIC DIFFUSION PROCESSES

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In the specification of our copending application Serial No. 801,995 there is described a process for promoting a more efficient rate of deposition, with or without diffusion, of one element on a metal, in which there is used in the required proportion two or more halides of the diffusive metal, with or without the addition of a third element, which is preferably a metal or metalloid, in combination with one or more halides which will, in certain concentrations, increase the rate of the surface reactions, said reactions being of interchange, reduction or thermal dissociation and being either simultaneous i.e., combined in one process, or effected in successive steps.

The process according to the said application Serial No. 801,995 is usually carried out by packing the articles to be treated in a powder or composition of the diffusion metal or metals, the latter being present in high concentration in relation to the surface of the articles to be treated.

The present invention is concerned with a metallic diffusion process which can be carried out in cases where the reacting atmosphere cannot be easily controlled or where only small quantities of the diffusion metal or metals are available for the reaction. Such processes are particularly convenient for the economic treatment of large surfaces, such as sheets, where close packing and regularity of surface reaction is essential. The process according to the present invention is also applicable when there is used a rapid method of heating, such as direct flame impingement, resistance heating and, more particularly, induction or high-frequency heat.

In such cases, economic and practical considerations show that, when solid compounds are used, it is preferable to utilize small quantities of diffusion agent which are discarded after each operation, rather than a large quantity of compound capable of being reactivated over a long period of time, as would be the case when conventional methods of processing are used.

The following indicates a flow sheet diagram of steps embodying and for practicing this invention:

Mixture of coating metal and halide thereof and reducing reactant applied to metal article

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Heating article in contact with mixture

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Coating metal diffused into article as reducing reactant reduces halide thereof

We have found that the essential requirements of compounds capable of reacting under the conditions described above are, first, a halide or dissociable compound of the coating metal must be present at or at close proximity to the surface to be treated, secondly, the vapor pressure of this compound at the processing temperature must be sufficiently low to avoid rapid volatilization, thirdly, the coating metal, in powder form, should preferably be present at or near the surface to be treated and, fourthly, other elements, preferably metallic, capable of reducing the diffusion metal compound should be incorporated in order to provide a source of diffusing metal in an active and highly divided condition.

According to the particular requirements, this reducing metal may, on the one hand, be chosen to react with the surface of the article in order to provide an additional alloying element, or, on the other hand, it may be selected from a group of metals or other elements which cannot take part in a surface reaction with the material of the article to be coated. The following examples are given for the purpose of illustrating the invention:

Example 1

Specimens of steel sheeting were coated with a compound comprising 10% by weight of chromium chloride ($CrCl_2$), 20% by weight of chromium metal, 60% by weight of magnesium oxide and 10% by weight of magnesium metal, this compound being applied by spraying onto the surface of the degreased steel sheets to a thickness of approximately 0.010 inch.

Several hundred coated steel sheets were stacked on top of each other and placed inside a steel container which was sealed to prevent any excessive leakage during treatment. This steel container was then heated for a period of 4 hours in a furnace at a temperature of 1020° C. After cooling, the steel sheets were removed from the box. The caked compound could easily be removed to give surfaces which were uniformly bright.

Sections of the treated steel sheets showed that their surface layers consisted of an alloy of chromium and iron containing an average of about 25% by weight of chromium. Micro-examination showed that the diffused layer extended to an average depth of 0.0025 inch. This chromium-iron alloy was ductile and was resistant to all concentrations of nitric acid.

Example 2

The process described in Example 1 was repeated but using a compound comprising 10% by weight of chromium fluoride, 20% by weight of chromium metal, 65% by weight of fine 320 mesh aluminum and 5% by weight of aluminum powder. After treatment it was found that a certain amount of aluminum had diffused into the steel and that a coating thickness of 0.0035 inch was obtained. If the aluminum content of the compound used is increased to 10% by weight or more, coating of at least 0.005 inch thickness are obtained but the resistance of such coatings to nitric acid is lowered.

Example 3

A half inch diameter, 1 inch long steel rod was coated with a compound comprising 30% by weight of chromium powder, 5% by weight of chromium chloride, 60% by weight of magnesia and 5% by weight of calcium metal. By spraying the compound onto the oily surface of the specimen, a loosely adhering crust of about 0.005 inch thickness was formed. The specimen was then introduced inside the coil of a high frequency generating apparatus and a frequency of 1.5 megacycles was induced in order to raise the surface temperature of the specimen to about 1100° C. for 90 seconds. On cooling, the compound could easily be removed from the surface of the specimen by washing in water.

Examination of this specimen showed a diffused coating thickness of 0.0015 inch containing an average of 35% by weight of chromium.

The calcium in the compound used may be replaced by the same amount of powdered aluminum.

Example 4

The process described in Example 3 was repeated but using a compound comprising 30% by weight of chromium powder, 5% by weight of chromium fluoride, 60% by weight of magnesia and 5% by weight of silicon powder. In this case, the diffusion layer had a thickness of about 0.0025 inch and, in addition to chromium contained up to 5% by weight of silicon.

Example 5

The process described in Example 3 was repeated using a composition comprising 30% by weight of chromium powder, 5% by weight of chromium fluoride, 15% by weight of nickel powder, 5% by weight of nickel fluoride, 40% by weight of magnesia and 5% by weight of silicon powder.

The resulting coating, which had an average thickness of about 0.0015 inch, contained a significant amount of nickel, in addition to chromium and silicon.

In carrying out the process described in Examples 3, 4 and 5, it is advantageous to place a quartz tubular container between the inductor coil and the articles to be processed. In this way, it is possible to maintain a reducing or inert atmosphere around the article to be coated which favors the efficiency of the surface reaction and prevents the possibility of oxidation taking place at any stage. Such an atmosphere is suitably provided by gases such as helium, argon, hydrogen, nitrogen or ammonia. In some cases, in which sealed containers are used, it is possible to introduce reacting gases into the induction chamber. Thus, for example, iodine, chlorine and most easily volatilized halides can be used. Quartz, however, should not, of course be used in the presence of fluorine or a fluoride.

Although the above examples are limited to the treatment of steel it is, nevertheless, possible with some modification, to use the same type of process for the coating of other metals, such as nickel, cobalt, molybdenum, tungsten, titanium, zirconium, columbium and tantalum.

Furthermore, in addition to the metals exemplified, other metals can also be diffused onto any of the above metals. Examples of such diffusable metal are chromium, aluminum, manganese, nickel, cobalt, copper, zinc, cadmium, columbium, tantalum, vanadium, titanium, zirconium, beryllium and thorium. Non-metallic elements, such as silicon and boron, may also be used.

I claim:

1. In a process of the character described for the diffusion coating of a metallic substance into the surface of a metal article, the steps which comprise applying to the surface of said metal article to be coated a mixture of said metallic substance for said coating and a halide thereof and a different metallic component for reducing said metallic substance and said halide thereof into diffusible

elemental form, said different metallic component being selected from the group consisting of aluminum, calcium, magnesium, silicon, and mixtures thereof, and being present in said mixture in an amount at least one-half that of said halide of said metallic substance, and heating said metal article with said mixture in contact with the surface thereof for the diffusion coating of said metallic substance into said metal article.

2. A process as recited in claim 1 in which said mixture applied to said metal article includes a plurality of different metallic substances for said coating and a halide of each thereof.

3. A process as recited in claim 1 in which said mixture applied to said metal article also includes inert refractory filler material.

4. A process as recited in claim 1 in which said different metallic reducing component is present in said mixture in an amount substantially equal to the amount of said halide of said metallic coating substance.

5. A process as recited in claim 1 in which at least a portion of said different metallic reducing component is also diffusion coated into said surface of said metal article during said heating thereof in contact with said mixture.

6. A process as recited in claim 1 in which the metal articles to be coated are large sheets, rods, and the like having extensive surface areas and in which said mixture is applied to said surface areas as a relatively thin layer.

7. A process as recited in claim 1 in which said metal article to be coated comprises a metal selected from the group consisting of iron, nickel, cobalt, molybdenum, tungsten, cadmium, zirconium, columbium, tantalum, and alloys thereof.

8. A process as recited in claim 1 in which said metallic substance for said coating is selected from the group consisting of chromium, aluminum, manganese, nickel, cobalt, copper, zinc, cadmium, columbium, tantalum, vanadium, titanium, zirconium, beryllium, thorium, silicon, boron, and mixtures thereof.

9. A process as recited in claim 1 in which said metallic substance for said coating is chromium and in which said halide thereof is selected from the group consisting of chromium chloride and chromium fluoride.

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