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METALLIC DIFFUSION

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The present invention is concerned with improvements in or relating to metallic diffusion, and, more particularly, with the deposition of a metallic layer by means of diffusion or partial diffusion of one metal into another metal.

Most metallic diffusion processes from the gaseous phase depend upon the reaction at elevated temperatures of a halide of one metal on the surface of another metal, well-known examples of such processes being siliconising and chromising.

The formation of a diffusion coating results from one or both of two distinct and often simultaneous factors: first the surface reaction relating to the deposition of the diffusing metal (solute) and, secondly, the gradual diffusion of the deposited metal into the parent metal, the nature and extent of which depends upon the respective characteristics of the two metals in question.

Considering the general case of a solute metal A and a solvent metal B, if X is halogen atom, three types of general reactions are normally possible:

(*a*) Interchange reaction of the type:

$$B+AX_m=BX_m+A \text{ (deposited)}$$

(*b*) Reduction reaction of the type:

$$AX_m+\frac{m}{2}H_2=mHX+A \text{ (deposited)}$$

(*c*) Thermal dissociation of the type:

$$AX_m \leftrightarrows \frac{m}{2}X_2+A \text{ (deposited)}$$

In the above equations it has been assumed that the metals A and B have the same valency *m*. The possibility of the occurrence of these reactions can, to a large extent, be determined by considering the free energy of formation of the respective halides. The close approximation of the possibility of the occurrence of reactions *a*, *b* or *c* is given by considering the curves relating to $\log_{10}$ of the equilibriums constant for $M+X_2 \rightleftarrows MX_2$ as a function of temperature, M being a metallic atom.

For any given temperature, the difference of −1 to −2 units represents a conversion of halide to coating metal varying from approximately 10% to 1% of the vapour of the coating halide. It can, therefore, be stated that operable limits will exist between 0 and −2 units in the appropriate curve.

If the standard is taken in relation to the solvent metal halide, then the possibility is that reaction (*a*) will occur (interchange); alternatively, in the case of a hydrogen halide the possibility is that reaction (*b*) will occur (hydrogen reduction).

If any given system of metals, such as chromium diffusion of steel, be considered, the relevant information will be obtained by comparing the curves representing the $\log_{10}$ of $Cr+X_2 \rightarrow CrX_2$ with $Fe+X_2 \rightarrow FeX_2$ and $H_2+X_2 \rightarrow 2HX$, the last equation assuming that hydrogen is present during the processing operation.

Comparison of these curves will show that appreciable differences in behaviour will be found, according to the halogen used as "carrier" and depending on the amount of hydrogen present during the processing operation. It will, therefore, be possible to arrive at a preliminary

selection of suitable halogen and hydrogen concentration according to the results required at any given temperature. This selection can, however, only operate within comparatively narrow limits but, following the general principle set out above, it will, of course, be possible profoundly to influence the nature of the reaction by introducing small concentrations of other metallic or non-metallic elements, the purpose of which is to shift the reaction in the desired direction.

The method can be applied generally to most systems of metallic diffusion from halides and, although considerable information can be derived from consideration of theoretical data, it is not possible to formulate a general principle to cover the numerous combinations of pairs of metals. The reason for this is that the important influence of respective vapour pressures of the halides must be considered at the same time as other fundamental thermodynamic data. It follows, therefore, that considerable part of the investigational work must, of necessity, rest on empirical selection of the precise conditions of treatment.

According to the invention there is provided a process for promoting a more efficient rate of deposition, with or without diffusion, of one element on a metal, which process is characterised in that there is used in the required proportion either two or more volatile halides or a third element, which is preferably a metal or metalloid, in combination with one or more volatile 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 following indicates a flow sheet diagram of steps embodying and for practicing this invention:

Metal article embedded in coating pack with additional reactant therein

↓

Heating article in pack in closed retort

↓

Coating metal diffused into article while additional reactant inhibits interfering reactions

It will be understood that the process is carried out in a chamber and that this chamber may contain a filler gas which may be inert, such as argon or helium, or which may react with one or all of the metals present by reduction or nitriding, such as hydrogen, nitrogen or a combination thereof.

The effect achieved by the addition of one or more halogens appears to be due to the fact that the presence of small quantities of volatile halides inhibit the formation of stable halides which, in the course of time, would tend to form a film on the surface of the chromium particles and the surfaces to be coated. As a consequence, these minor additions of volatile halides promote an efficient surface reaction.

The following examples are given for the purpose of illustrating the invention:

Example 1

To a mixture comprising 70 parts by weight of alumina and 30 parts by weight of chromium metal powder, there is added 0.2% by weight of ammonium fluoride, said fluoride acting as a carrier compound. Iron or steel articles are packed in contact with this powder mixture and heated to a temperature of between about 800 and 1200° C. under conditions which will ensure freedom from oxidation. Heating at 1020° C. for 4 hours under these conditions will result in the formation of a chromium-rich coating on a low carbon steel specimen of approximately 0.003" thickness, the chromium content being of the order of about 25%. Repeated use of the powder mixture shows that after a few operations, care being taken to renew the carrier compound and to adjust the chromium concentration after each use, the results deteriorate until, after about 8 to 10 consecutive runs, the compound no longer gives results comparable to its earlier performance.

According to the present invention, however, the addition of small concentrations of chemically combined chloride, such as ammonium chloride or any suitable volatile chloride, ensure a satisfactory performance of a powder mixture of the above combination even after prolonged use. Thus, a compound comprising 70 parts by weight of powdered alumina and 30 parts by weight of powdered chromium metal to which is added 0.2% by weight of ammonium fluoride and 0.01% by weight of ammonium chloride will give a satisfactory performance for long periods of time.

Example 2

Silicon is an example of a suitable third element which may be added, according to the invention, to the reacting system in order to bring about the above described improvements. Silicon can, for example, be used in concentrations of from 0.5 to 2% when used in an elemental form but even higher amounts may be used if the silicon is combined with a metal, such as iron.

A compound comprising 70 parts by weight of alumina powder and 30 parts by weight of chromium metal powder together with 0.2% by weight ammonium fluoride and 1% by weight silicon powder, gives a performance equal or superior to that obtained by the composition described in Example 1. The reason for this improved performance is readily deducible from the thermodynamic data mentioned above.

Initially, while the reaction temperature is still comparatively low, silicon tetrafluoride is formed and reacts with the steel surface to be treaed according to the equation:

(*a*) $SiF_4+2Fe\rightarrow 2FeF_2+Si$ (depositing)

As the temperature increases, the following reaction also takes place:

(*b*) $SiF_4+2Cr\rightarrow 2CrF_2+Si$ (depositing)

In addition, the normal chromising reactions also take place:

(*c*) $Fe+CrF_2\rightarrow Cr+FeF_2$

(*d*) $FeF_2+H_2\rightarrow Fe+2HF$

The effect of the silicon is, therefore, twofold: first it reacts with both the chromium and the steel surface and, secondly, prevents the formation of stable fluoride films. As a result, chromium diffusion proceeds at an increased rate whilst a very small percentage of silicon from reaction (*a*) remains in the coating. The presence of a small percentage of silicon in the chromised coating does not adversely affect the general properties of the coating and substantially improves the resistance of such coatings to oxidation at elevated temperatures.

The further addition of small amounts of chlorides, bromides or iodides to the silicon compound results in still further improvements in performance.

Example 3

The importance of experimental adjustment of the conditions to suit the metal being coated is exemplified by the application of the powder described in Example 2 to the treatment of nickel. A deep chromium-rich layer is obtained under the conditions described but the surface of the treated nickel object is taken up in sufficient quantity to form, with the chromium and nickel, a phase that melts at the processing temperature.

If the amount of silicon in the powder mixture is reduced to 0.1%, the surface of the nickel is not roughened and the chromium-rich layer is noticeably deeper than that obtained in the absence of silicon.

Example 4

The siliconising of mild steel and other metals may be brought about by a number of methods, where a silicon tetrahalide reacts with the metal surface. Usually, the silicon-rich layer is porous, and the surface rough. We have found that the activity of the silicon tetrahalide can be conveniently controlled, when a powder processing mixture is used, by adding a proportion of another metal which can be diffused into the base metal.

For example, mild steel parts were packed in a powder mixture consisting of 4 parts by weight silicon powder, 5 parts of chromium powder, 91 parts of alumina and 0.5 part of ammonium fluoride. The mixture was heated in a sealed box at 1100° C. for 6 hours. The steel was smooth after treatment; there was produced a silicon-containing surface layer, 0.008" deep. The "coating" was substantially free from pores and contained a small amount of chromium.

Example 5

We have found that zirconium can be chromised by methods similar to those used for steel if a suitably modified powder is used. Since zirconium reacts with nitrogen and hydrogen, an atmosphere free from these gases is required. A suitable powder mixture has the following composition:

	Parts
Chromium powder	25
Beryllium powder	2
Zirconium oxide	73
Iodine	0.1

Zirconium packed in this mixture and heated at 1050° C. for several hours became coated with an adherent layer containing an average of 15% chromium. Beryllium was not detected.

In the absence of beryllium, there was a considerable loss of zirconium due to the formation of volatile zirconium iodide, the surface was deeply pitted and the coating became detached from the zirconium surface on cooling.

The above remarks have shown the use of the hereinbefore defined general principle for a single processing operation. However, these principles can also be used in conjunction with successive diffusion treatments. Thus, molybdenum can be chromium diffused by heating the metal at an elevated temperature in the presence of a chromium halide and hydrogen, the reaction which takes place being one of reduction or chemical dissociation. Molybdenum can also be silicon-diffused by heating in the presence of a silicon tetrahalide and hydrogen, the reaction being illustrated by the equation:

$$Mo+2SiX_4+4H_2\rightarrow MoSi_2+8HX$$

Thus, in both cases, chromising and siliconising take place by deposition only, without the removal of atoms of the solvent metal, i.e. without an interchange type of reaction taking place.

Interchange and reduction reactions are not always effective since they rely largely on the distribution of reacting gases and on the physical conditions prevailing at the surface of the solvent metal. It has been found that more satisfactory results can be achieved if an interchange type of reaction can be incorporated into the process in sequence. Thus, a depositing reaction of the type:

$$SiX_4+2Cr\rightarrow 2CrX_2+Si$$

is possible. Thus, the preferred method of siliconising molybdenum or other metals where silicon can only be deposited by a reduction reaction or by thermal dissociation consists, therefore, in first chromising the molybdenum surface by any suitable method, for example, by heating to a temperature to 1200° C. for 6 hours in the presence of a compound comprising 50 parts by weight of chromium metal powder, 50 parts by weight of alumina powder and 0.1% by weight of an ammonium halide, and then siliconising the chromised molybdenum by any suitable method, for example, by heating at a temperature of 1200° C. for 4 hours in the presence of silicon tetrachloride and hydrogen.

Since siliconising of chromium can proceed by means of an interchange reaction, it is possible to reduce the concentration of hydrogen at the second stage to a minimum and it is, therefore, also possible to control the silicon uptake and, consequently, the composition of the resulting coating to within relatively close limits.

The above given example merely illustrate particular applications of the invention but the general principles are not limited to the solvent metals and solute metals specifically exemplified. Thus, other suitable solvent metals, are iron, nickel, cobalt, molybdenum, tungsten, titanium, copper, niobium, tantalum, platinum and alloys thereof and examples of solute or diffusing metals are chromium, aluminium, manganese, nickel, cobalt, copper, zinc, cadmium, niobium, tantalum, vanadium, titanium, zirconium, beryllium, thorium and their alloys. Furthermore, elements such as silicon and boron may also be used.

I claim:

1. In a process for diffusion coating of a coating metal into the surface of a metal article embedded in a coating pack containing a powdered source of said coating metal and a powdered refractory oxide filler material and a volatile halogen carrier for reaction with said coating metal and said metal article during said diffusion coating thereof, the steps which comprise heating said article embedded in said powdered coating pack in a closed retort for reaction of said halogen carrier and said coating metal and said metal article forming both desired diffusion coating products and undesired by-products interfering with said diffusion coating and tending to diminish the coating activity and utility of said powdered coating pack materials after prolonged use and reuse thereof, maintaining in said coating pack during said heating step a halide of a halogen different from that of said halogen carrier as an additional reactant in said pack for inhibiting said formation of said interferng by-products, said additional halide reactant being present in said pack in an amount less than said volatile halogen carrier.

2. A process as recited in claim 1 in which said volatile halogen carrier is a fluoride and in which said additional halide reactant is a volatile choride.

3. A process as recited in claim 1 in which said volatile halogen carrier is an ammonium fluoride and said coating metal is chromium, and in which said additional halide reactant is ammonium chloride.

4. In a process for diffusion coating of a coating metal into the surface of a zirconium metal article embedded in a coating pack containing a powdered source of said coating metal and powdered refractory zirconium oxide and a volatile halogen carrier for reaction with said coating metal and said zirconium article during said diffusion coating thereof, the steps which comprise heating said zirconium article embedded in said powdered coating pack in a closed retort for reaction of said halogen carrier with said coating metal and said zirconium article forming both desired diffusion coating products and undesired by-products and reactions interfering with said diffusion coating, maintaining in said coating pack during said heating step beryllium as an additional reactant for reaction with gaseous components in said retort and inhibiting said interfering reactions and formation of said by-products, said beryllium being present in said coating pack in a concentration less than that producing reaction thereof with said zirconium oxide refractory.

5. A process as recited in claim 4 in which said concentration of beryllium in said coating pack is less than about 2% by weight thereof.

6. A process as recited in claim 4 in which chromium is said coating metal for diffusion into said zirconium article.

7. In a process for diffusion coating of a coating metal into the surface of a metal article embedded in a coating pack containing a powdered source of said coating metal and a powdered refractory oxide filler material and a volatile halogen carrier for reaction with said coating metal and said metal article during said diffusion coating thereof, the steps which comprise heating said article embedded in said powdered coating pack in a closed retort for reaction of said halogen carrier and said coating metal and said metal article forming both desired diffusion coating products and undesired by-products interfering with said diffusion coating and including interfering halide reaction products of said halogen carrier and said metal article, maintaining in said coating pack during said heating step elemental silicon as an additional reactant for reaction with said halogen carrier to inhibit formation of said interfering halide by-products, said silicon being present in an amount not exceeding a maximum concentration of about 1% by weight of said pack.

8. A process as recited in claim 7 in which said halogen carrier is a fluoride reacting with both said coating metal and said metal article during said heating step for forming undesired fluoride films thereon, and in which said silicon is reacted with said fluoride carrier and said metal article for inhibiting said formation of said undesired fluoride films.

9. A process as recited in claim 8 in which said metal article to be coated comprises nickel and said coating metal is chromium, and in which the concentration of said additional silicon reactant in said pack is no more than about 0.1% for inhibiting said formation of fluoride films and also for avoiding the formation of low melting mixtures in the coated surface of said nickel article.

10. A process as recited in claim 7 in which said coating metal is chromium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,219,004	Daeves et al.	Oct. 22, 1940
2,811,466	Samuel	Oct. 29, 1957
2,903,106	Wrotnowski	Mar. 29, 1960

FOREIGN PATENTS

787,958	Great Britain	Dec. 18, 1957