

[54] **VAPOUR DEPOSITION COATING PROCESS**

3,356,528 12/1967 Gibson et al. 117/107.2

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[58] **Field of Search** **117/107.2 P, 107.2 R, 22,**
117/48, 71 M

[56] **References Cited**

UNITED STATES PATENTS

3,619,232 11/1971 Nakamo et al. 117/22

3,585,068 6/1971 Holker et al. 117/107.2

1,312,716 8/1919 Wise 117/107.2

[57]

ABSTRACT

Metal substrates may be chromised by subjecting them to a diffusion heat treatment in which the substrate is placed in contact with a flexible carrier sheet having adherent thereto or incorporated therein chromium metal or an alloy thereof or a reducible compound of chromium. Particularly suitable flexible carrier sheets are made from asbestos paper. If chromium metal or an alloy thereof is employed it is necessary that a halide is also present. This may be present either on the surface of the substrate itself, on the flexible carrier sheet bearing the chromium or its alloy or on a separate sheet of flexible carrier material.

14 Claims, No Drawings

VAPOUR DEPOSITION COATING PROCESS

The present invention relates to diffusion coatings wherein a chromium containing layer is formed on a metal substrate. Such coatings are formed by the thermal decomposition of a chromium compound on the substrate, the displacement of chromium by iron from its halides at the surface of the substrate or by the reduction of a chromium compound to chromium metal at the surface of the substrate followed by diffusion of the chromium so deposited on the surface into the substrate to form what is in effect a stainless steel surface coating on it.

The methods of accomplishing the formation of chromium/iron diffusion layers on ferrous metal work pieces are varied. One method introduces into a heated furnace containing the ferrous metal work piece, chromous halide vapour where upon reaction between the surface of the work piece and the vapour takes place. Another method is to pack the work piece in a powder mixture containing a source of chromium and the container is then heated. The ingredients of the mixture interact to yield chromous halide which then reacts with the surface of the work piece. Yet another method involves compacting on the surface of the ferrous substrate, a chromium-containing source which is allowed to react at temperature with the halide which is introduced into the furnace. The resulting products then react with the ferrous work piece. A further method similar to the last uses an adhesive to bind the chromium to the substrate rather than compaction of the powder on to it.

All of these processes have disadvantages of varying degrees of seriousness. Processes in which a gas stream is passed into the furnace pose problems in ensuring that no part of the substrate to be coated is shielded from the stream, since this would cause a non-uniform deposition. Moreover in processes in which displacement reactions occur processes of this type tend to be wasteful of materials, since an atom of halogen is required per atom of element deposited and this halogen atom is blown from the furnace in the form of the halide of the substrate metal. There is also a wastage of material in that not only is the chromium deposited on the surface of the substrate but it is also inevitably deposited in substantial amounts on the inside of the furnace. So far as processes in which the articles are embedded in a pack are concerned, a problem is that they are time-consuming in that it is necessary in packing the container in which the process is carried out to ensure that adjacent surfaces of the articles being treated do not come into contact otherwise uniform coatings will not result. Also, there is a tendency for the mixture in the pack to sinter strongly to the surface of the work piece thereby seriously affecting the appearance. Compaction processes are satisfactory for flat surfaces such as steel strip and sheet but are not suited for the treatment of irregularly shaped objects. In processes in which an adhesive is employed the chromium particles sometimes tend to sinter together on the surface, thereby detracting from its appearance, if the carbon content of the substrate is low.

The essence of the present invention, which mitigates these disadvantages, is to apply to a flexible carrier sheet, such as an asbestos sheet or paper or a plastic sheet either chromium metal or an alloy thereof or a compound of chromium capable of depositing the ele-

ment on the substrate by thermal decomposition or by reduction and to put this coated sheet into contact with the substrate for a heat treatment. In the first instance a halide will also need to be present and this can be applied either to the substrate or to the carrier sheet bearing the chromium or to a separate carrier sheet before the necessary heating is carried out, so that this can react with the element to produce its halide which actually participates in the displacement reaction.

Accordingly the present invention provides a process for producing a diffusion coating of chromium on a metal substrate, which comprises (1) Placing in contact with at least part of the surface of the substrate a flexible carrier sheet which has adhering to it or incorporated in it particles of chromium metal or an alloy thereof or a reducible compound of chromium, when chromium metal or an alloy thereof is present there also being present in the assembly a halide capable of reacting with the chromium and (2) subjecting such an assembly to a heat treatment to cause chromium to diffuse into the substrate.

Metal substrates which may be chromised to the present invention are normally ferrous. We have found that the technique may be particularly useful for chromising ferrous metal articles or sheets having a low free carbon content as these are particularly liable to the sintering problem which is mitigated by this technique. A low free carbon content substrate is one which has been decarburised or has its carbon bound by a carbide-forming element — such as titanium stabilised steels. Such steels normally have a free carbon content of no more than 0.02 percent frequently less than 0.01 percent.

The flexible carrier sheet should desirably not produce any harmful products which are likely to interfere with the production of the desired coating. If it does so, however, it is desirable that any decomposition occurring should take place at a low temperature so that the products can be purged from the furnace before any harmful effects can occur. Suitable carrier sheets include sheets of cellulosic paper especially those sheets such as air mail paper, woven fabrics for example of cotton or wool, plastic fibres such as polyvinyl chloride, or polyethylene, or woven or knitted fabrics made from synthetic materials such as nylon, polyesters or acrylics. Most preferred, however, is asbestos "paper". This paper may be from 2 to 10 thou thick, although we have found it is most preferable to use paper of 6 – 7 thou thickness.

The chromium or alloy thereof or reducible compound of the chromium can be applied to the flexible sheet in any convenient manner. For example elemental powders can be compacted onto the sheet by applying them in loose powder form and then passing the material through a roller or by electroless plating or plasma spraying. Alternatively the sheet may be pretreated with a binder which will not give rise to appreciable amounts of harmful products which may interfere with the coating process such as ethyl silicate or polyvinyl pyrrolidone and the element applied to this. In cases where a halide is required to be present as well as chromium metal or an alloy thereof, we have found that this halide may be employed as the binder. In this case the halide is applied to the sheet from solution and the chromium containing metal powder then sprinkled onto the sheet while it is still wet and the whole is subsequently dried. Alternatively a suitable sheet can be

prepared from a pulp containing asbestos, cellulosic fillers and other binders and chromium by normal paper making techniques. In such a sheet the chromium or chromium containing metal is impregnated into the material itself.

Accordingly, from a further aspect the present invention provides a process for forming asbestos paper sheets suitable for use in chromising as previously described, which comprises incorporating chromium metal or a chromium alloy powder as previously described, in a pulp suitable for the manufacture of asbestos paper prior to production of the paper. It also provides coated asbestos sheets produced by such a process.

It is also possible to form a sandwich of two suitable sheets and chromium metal or alloy and employ this to be interposed between surfaces to be coated or wrapped around articles to be coated.

In such a case it may be desirable to preform this sandwich, possibly using a binder to secure both sheets to each other and to the chromium or alloy powder. In the case of a decomposable or reducible compound being applied this can if soluble in a suitable solvent be applied from it and then dried. Other methods such as roller coating or spraying may be employed if desired, however.

We believe that flexible carrier sheets coated with such elements or reducible compounds are novel and accordingly they provide the second aspect of the present invention.

Suitable sources of chromium metal which may be employed include pure chromium and alloys thereof such as ferrochrome. Ferrochromes which may be employed include both the conventional material containing 50-70 percent chromium and the more recently developed materials containing from 75-90 percent chromium. They may also contain other elements, such as aluminium, silicon, titanium, molybdenum, niobium, tantalum, vanadium which it may be desired to have present in the chromium diffusion alloy for various purposes, for example to combine with freed carbon from the paper to prevent it from being incorporated in the coating, to produce specific effects such as abrasion resistance or high temperature oxidation resistance in the diffusion layer. Such additional elements if present will normally be present in amounts of from 2-20 percent preferably 5-10 percent by weight of the chromium. The additional elements may be present either as a separate powder or as a suitable alloy with the chromium, iron or any of the other named elements.

If a reduction technique is employed then the paper should be coated with a reducible halide, such as chromic chloride. The reduction may be carried out by hydrogen gas, if the sheets used are permeable to hydrogen, or by the use of the reducing agents which do not form products to interfere with the diffusion process.

The amount of chromium or compound employed will depend upon the thickness of the desired coating. The best amount for a given application can be fairly readily determined by simple experimentation and we have found that for chromium metal or ferrochrome alloys amounts of about 30-40 g of chromium per square foot of flexible carrier are suitable. However, it may be that less amounts are suitable for particular circumstances.

As previously stated if chromium metal or an alloy is applied to the sheet it is necessary that a halide also be

present. This halide can be applied either to the substrate or to the carrier sheet bearing the metal or to a separate sheet which is also interposed between or wrapped around surfaces of the substrate. Suitable halides are those which will react with the element at a reasonable temperature and we have found that ferrous halides such as ferrous chloride are normally particularly suitable. Other halides such as magnesium, aluminium, nickel and manganese halides, naturally occurring halides such as cryolite and in particular the alkali metal halides such as sodium and potassium chlorides and fluorides can also be employed if desired, however some of these although satisfactory in the process are hygroscopic and pick up water from the atmosphere thus rendering the storage of the treated asbestos paper difficult. We have found that of particular use in this technique are oxy halides such as magnesium oxy chloride as these facilitate the storage and transportation of treated asbestos paper in normal ambient humidity without the use of any special precautions. During processing, such halides also leave a residual inert harmless oxide which assists in mitigating problems which may occur as a result of sintering together of the chromium containing particles.

The halides can be applied simply by passing either the substrate or the flexible sheet through a solution of the halides and then drying it or as in the case of the oxy chloride by applying the dry powder to the flexible sheet with the chrome source or incorporating it in the asbestos pulp prior to the paper making. As previously mentioned the wet halide layer can act as a binder for subsequently applied chromium containing powder. It will normally be possible to employ considerably less halide than is required to react with all of the element employed, roughly 2-10 percent preferably about 5 percent of that required will normally be suitable although lesser amounts may be used if desired.

It is of course highly desirable that the solution used to apply the halide is not so acid as to result in attack on the sheet substrate. We have found that this may occur if the halide employed is aluminium chloride. In such cases satisfactory solutions can be obtained by incorporating sufficient basic material which does not itself affect the chromizing reaction to raise the pH to more than 1.2. We have found the addition of magnesium carbonate a suitable method for this purpose and that solutions of aluminium chloride containing it having a pH in that range 1.2-2.5 preferably from 1.7-2.3 are particularly suitable.

Chromium or reducible chromium compound-bearing flexible sheets may be employed as the source of chromium deposited on the substrate during heat treatment either being wrapped around the substrate or by being interposed between adjacent surfaces thereof, for example in a stack or in a close coil. In the latter case the flexible sheet will be fed into the coil as it is being formed. It is normally desirable that they should be interposed between adjacent surfaces since this cuts down a wastage. However, if complex shaped articles are to be treated it is possible simply to wrap the sheet around them. We have also found, when the sheet employed is porous that it may be advantageous to employ a "sandwich" of chromium between two sheets for the heat treatment.

Normally the substrate having its element or reducible compound-coated sheet in contact with it will be subjected to a heat treatment in a furnace. Thus it will

normally be desirable to arrange the substrate in the furnace in any convenient manner. However, especially in the case where a decomposable compound is being employed other techniques may be employed. For example if only one side is to be coated a sandwich of two sheets of substrate and the coated flexible sheet can be used.

It is often desirable to carry out a purge of the furnace for example at a temperature of 400°C before raising it to the operating temperature which is normally, when using chromium metal or a ferrochrome as the chromium source between 800°C and 1,000°C, preferably at least 920°C since the process of the invention is liable to produce unsatisfactory products if any impurity is present. Most desirably the process is carried out in a pure hydrogen atmosphere but argon may also be used.

The process of the invention is illustrated by the following examples:

EXAMPLE 1

0.007 in thick asbestos paper was coated on one side with an alloy powder containing 80% Cr and 20% Fe at a rate of 40g of powder per sq.ft. of paper. The paper was then passed between the rolls of the 2 high compaction mill to compact the powder on to the paper.

Cleaned and pickled mild steel panels (6 in. \times 3 in. \times 0.036 in.) of 0.05% C content were coated with an aqueous solution of ferrous chloride and dried. The rate of application was such that after drying 4g of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ remained per sq.ft. of steel surface. The steel panels were then stacked alternately in a pile with pieces of the treated asbestos paper which had been cut to the same size as the steel panels. The complete pack was then bolted between end plates of heavy gauge steel. The oxygen was purged from the furnace using argon and the temperature was raised to 400°C. The argon was then displaced with hydrogen and the temperature was held at 400°C for 6 hours during which time the water of hydration was removed from the ferrous chloride. The flow of gas through the furnace was then ceased and the temperature raised to 950°C where it was retained for 16 hours. After this time the furnace was allowed to cool whilst being purged with argon.

On removal from the furnace, the panels were separated from the pack, the excess powder brushed from their surfaces and then washed. The panels were attractive in appearance and on being exposed to salt fog and to 100 percent humidity, displayed excellent corrosion resistance. On cutting up one of the panels and boiling the pieces in 30 percent nitric acid solution, the mild steel substrate dissolved leaving that part of the chromised panel which contained more than 13% Cr. The chromised coatings were 0.002 inch thick and subsequent analysis showed them to contain an average of 25.3% Cr 74.5% Fe and 0.15% C.

EXAMPLE 2

A piece of 20 gauge steel strip (0.05% C) was degreased in a solvent degreasing bath, pickled in 10 percent v/v nitric acid for 30 seconds, and washed with water. A solution was applied to the strip, consisting of ferrous chloride tetrahydrate (1 part) and water (1 part), and the strip was dried under an infra-red heater to give a pick up of 4 grammes/sq.ft. of steel.

A stack of such sheets was constructed, each sheet being interleaved with two layers of 0.015 inch thick

asbestos sheet which had been impregnated with 18 gms/sq. ft of 83 percent chromium ferrochromium powder (200 BS mesh) during manufacture, giving a total ferrochromium concentration of 36gm/sq. ft. of steel.

The sheets were held between tightly bolted steel plates and placed in a suitable furnace. After purging for 16 hours at 400°C in flowing hydrogen, the gas flow was stopped and the temperature was raised to 950°C over a period of 8 hours and held at that temperature for a further 16 hours. After cooling the sheets were removed from the furnace and washed with water to remove excess halide. The surfaces of the sheets were silver grey in colour and metallographic examination of a section of a sheet showed a chromised coating had formed of thickness 0.002 inch. A portion of the coating was separated by treatment in boiling 40 percent aqueous nitric acid. Analysis of the coating after dissolution in hydrochloric acid showed a chromium content of 22.5 percent.

EXAMPLE 3

Pieces of 20 gauge steel strip (0.05% C) was degreased in a solvent degreasing bath, pickled in 10 percent v/v NH_3 for 30 seconds and washed with water. A paste was made consisting of magnesium chloride hexahydrate (1 part), lightly calcined Magnesium oxide (1 part) and water (1 part). To this was added 6 parts of 83 percent chromium ferrochromium powder (200 BS mesh). The mixture was spread evenly onto both sides of a sheet of asbestos paper, 0.009 inch thick, and dried in an oven held at 130°C, to give a pick-up of 15 gms/sq.ft. of ferrochromium on each side of the asbestos sheet.

A stack was constructed consisting of alternate sheets of 20 gauge steel and coated asbestos, prepared as described. The stack was held between tightly bolted steel plates and placed in a suitable furnace. After purging in flowing hydrogen for 16 hours at 250°C the gas flow was stopped and the temperature was raised to 950°C over a period of 10 hours and held at that temperature for a further 16 hours.

After cooling the steel sheets were removed from the furnace and washed with water to remove the residues. A chromised coating had formed on the surfaces of the sheets which was found by metallographic examination to be 0.0015 inch thick. A portion of the coating was stripped in boiling 40 percent aqueous nitric acid and analysis after dissolution in hydrochloric acid showed a chromium content of 20.0 percent.

We claim:

1. A process for producing a diffusion coating of chromium on a ferrous metal substrate which comprises (1) placing in contact with at least part of the surface of the substrate a flexible carrier sheet containing particles of a chromium source material selected from the group consisting of chromium metal, an alloy thereof, and a reducible compound of chromium, where if said chromium source material is chromium or an alloy thereof, a halide capable of reacting with the chromium metal or alloy thereof is also present, said chromium source material being the source of the chromium in said diffusion coating of chromium on said ferrous metal substrate; and (2) subjecting said carrier sheet in contact with said substrate to a heat treatment to cause chromium to diffuse into the substrate.

2. A process according to claim 1 wherein the flexible carrier sheet is plastic sheet.

3. A process according to claim 1 wherein said chromium source material is an iron chromium alloy; and wherein said flexible carrier sheet is selected from the group consisting of asbestos sheet or paper, cellulosic paper, and plastic sheet.

4. A process according to claim 3 wherein the free carbon content of said substrate is no more than 0.02 percent by weight.

5. A process according to claim 1 wherein chromium metal or an alloy thereof is employed and the halide employed is applied to the surface of the substrate prior to placing the flexible carrier sheet in contact with it.

6. A process according to claim 1 wherein said flexible carrier sheet contains (i) chromium metal or an iron-chromium alloy, and (ii) said halide.

7. A process according to claim 1 wherein chromium metal or an alloy thereof is employed and the halide employed is a ferrous halide.

8. A process according to claim 5 wherein chromium

metal or an alloy thereof is employed and the halide employed is a ferrous halide.

9. A process according to claim 5 where an iron chromium alloy is employed.

10. A process according to claim 3 wherein said substrate is arranged prior to the heat treatment in the form of a coil with said flexible carrier sheet interposed between adjacent laps of the coil.

11. A process according to claim 3 wherein said flexible carrier employed has thereon from 30 to 40 grams of chromium in the form of chromium metal or an alloy thereof, per square foot.

12. A process according to claim 5 wherein said halide is present in an amount of from 2 to 20 percent by weight based on the chromium.

13. A process according to claim 6 where said halide is present in an amount of from 2 - 10 percent by weight based on the chromium.

14. A process according to claim 3 wherein the heat treatment is carried out at a temperature in the range of 800°-1,000°C.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,804,665 Dated April 16, 1974

Inventor(s) Robert David CHAPMAN

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

Column 7, line 1, replace "1" with --3--.

Column 8, line 14, replace "20" with --10--.

Signed and sealed this 24th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents