METHOD OF PRODUCING A METALLIC LENGTH

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ABSTRACT OF THE DISCLOSURE

A method is provided for producing a continuous sintered ferrous metal length having at least one metallic chromium-containing surface from powdered metallic materials. Unsupported ferrous metal powder is passed through the nip of a first pair of compaction rollers to produce a continuous length of ferrous metal. At least one surface of the length of ferrous metal is coated with a metallic chromium-containing powder and the metallic chromium-containing powder is compacted thereto by passing the coated length through the nip of a second pair of compaction rollers. Thereafter, the coated length of ferrous metal is heat treated to effect sintering thereof in the presence of a halogen-containing material which, during the heat treating, promotes the fusion of the metallic chromium into the coated surface of the length of ferrous metal. The method is especially useful in producing a length of a stainless iron, or a length of stainless steel foil, which is corrosion resistant throughout.

This invention concerns a method of producing a ferrous metal length at least one surface of which is constituted by an alloy and, although the invention is not so restricted, it is more particularly concerned with a method of producing a length of a stainless iron or stainless steel foil, which is corrosion resistant throughout.

According to one important variant of the present invention, there is provided for a producing a continuous sintered ferrous metal length having at least one metallic chromium-containing surface from powdered metallic materials. Unsupported ferrous metal powder is passed through the nip of a first pair of compaction rollers to produce a continuous length of ferrous metal. At least one surface of the length of ferrous metal is coated with a metallic chromium-containing powder and the metallic chromium-containing powder is compacted thereto by passing the coated length through the nip of a second pair of compaction rollers. Thereafter, the coated length of ferrous metal is heat treated to effect sintering thereof in the presence of a halogen-containing material which, during the heat treating, promotes the fusion of the metallic chromium into the coated surface of the length of ferrous metal. The method is especially useful in producing a length of stainless iron, or a length of stainless steel foil, which is corrosion resistant throughout. Preferably, the coated length, after passing through the nip of the second pair of compaction rollers and prior to the said heat treating, has the said halogen-containing material applied thereto.

Preferably, after the application of the halogen-containing material and before the said heat treating, the coated length of ferrous metal is formed into a coil. Preferably also at least the initial part of the said heat treating is carried out in a reducing atmosphere.

The halogen-containing material may be a powdered material but is preferably in the form of an aqueous solution. The halogen-containing material preferably comprises ferrous chloride and/or ammonium chloride, although it may alternatively comprise ammonium iodide, or sodium chloride, or a mixture of a chloride and an iodide such as a mixture of sodium chloride and ammonium iodide.

The length of ferrous metal may be formed by passing wetted ferrous metal powder through a dryer, in which it is substantially dried, and then through the nip of the first pair of compaction rollers. The wetted ferrous metal powder may be supplied to an endless belt, it being carried by the latter through the dryer and thence to the said first pair of compaction rollers.

Moreover, the said length of ferrous metal leaving the said first pair of compaction rollers may be heated. The sintered ferrous metal length thus produced may be a length of metallic ferrous metal foil, which may be corrosion resistant throughout.

If a stainless steel is to be produced, the ferrous powdered material may have nickel admixed therewith, or the chromium-containing powdered material may also contain nickel, or nickel may be electroplated onto the said pre-compactd length prior to the application thereto of the chromium-containing powdered material.

The invention also comprises a metallic length when made by the method set forth above.

The invention is illustrated by the following examples.

EXAMPLE I

An aqueous slurry containing powdered low carbon mild steel particles together with an inhibitor and a binder, such as sodium carboxy methyl cellulose, was "cast" onto a moving endless belt and carried by the latter through a dryer, in which the slurry was substantially dried, and thence to the nip of a pair of compaction rollers, the said binder giving the slurry (which contained little water) sufficient strength to bridge the small gap which was provided between the endless belt and the compaction rollers.

Immediately after leaving the said compaction rollers, the ferrous length, which was pre-compactd thereby, was passed for a producing a metallic length of ferrous metal. The length of ferrous metal was then passed through a furnace which was heated to a temperature of 800°C so as to strengthen the said ferrous length and to burn off the binder.

Chromium powder was then applied (e.g. electrostatically) to both sides of the said ferrous length so as to form 18% of the total weight thereof, the ferrous length having been previously wetted, if desired, with a sodium or potassium silicate solution, or with a 0.05—0.25% solution of sodium carboxy methyl cellulose, or with a suspension of a gelatinous metal hydroxide, e.g. Ni(OH)₂ or Al(OH)₃, which assists in retaining the chromium powder on the said ferrous length, and which solution or suspension was dried off after the application of the said powder. The ferrous length was then passed through the nip of a pair of compaction rollers which compacted the chromium powder thereto, and which produced a length of foil formed of compacted unsintered material having a thickness not exceeding 0.010".

This length of foil then had applied to each side thereof a halogen-containing material which may be a fluoride, chloride, bromide or iodide, and which was employed in an amount of 15 to 25% by weight of the amount of chromium powder applied to the ferrous length. The halogen-containing material may, for example, be an aqueous solution into a coil of ferrous chloride tetrahydrate and 1 part by weight of ammonium chloride. The said solution, if employed, was dried by passing the length of foil through an infra-red heater.

The length of foil was then passed to a furnace which was purged with hydrogen or a mixture of hydrogen and argon (e.g. 90—95% argon...
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and 5–10% hydrogen) during heating to 400°C, e.g., over 10 hours, after which the flow of gas was stopped and the temperature gradually raised to 950°C over a period of 10 to 20 hours and retained at this temperature for 15 to 20 hours. After cooling, the coil was removed from the furnace and washed with water to remove excess halide. Final tempering of the coil could then be effected if desired.

The treatment of the coil in the furnace caused sintering of the compacted, unsintered material of the coil so as to produce a stainless iron alloy foil (e.g., 0.005” thick), the addition of the halogen-containing material promoting substantial diffusion of the chromium into the iron by an interchange mechanism arising from the fact that both the chromium and the iron react with the halogen. Thus the halogen-containing material reacts with the chromium to form chromium halide CrX₂.

The interchange then proceeds as follows:

1. The chromium is thus deposited on the iron of the ferrous length and the ferrous halide reacts with the chromium powder.

2. The iron is thus deposited on the iron of the ferrous length.

A chromium-rich layer is thus built up on each surface of the ferrous length, which thus becomes chromised.

The ammonium chloride mentioned above as forming a possible part of the halogen-containing material dissociates into gaseous products at about 350°C, thereby purging any water formed in the convolutions of the coil by the dehydration of the above-mentioned ferrous chloride trihydrate.

As will be appreciated, the various different powdered materials which are employed in the formation of the coil respectively contain the various elements of the stainless iron alloy.

The foil so produced will be corrosion resistant throughout but, as indicated in the graph constituting the accompanying drawing, will have a chromium concentration which is at its maximum at the two surfaces of the coil, and which is at its minimum at the centre thereof. As can be seen from the graph, which was obtained by examining the foil by an electron probe micro analyser, the surface layers of the foil are very rich in chromium, probably by reason of a very small amount of substantially pure chromium which has sintered during the heat treatment in the furnace. The centre of the coil has the lowest chromium content, but provided that the foil is not too thick, or the diffusion time too short, the foil will be corrosion resistant even at its centre.

If desired, the chromium powder could be replaced by ferrochrome powder, or alternatively, by a mixture of chromium and nickel powders such as to produce a stainless steel foil having an average composition of 18% chromium and 8% nickel by weight. The chromium powder could also be mixed with titanium, molybdenum, aluminium, vanadium, or silicon-containing powders.

If a ferrochrome powder is employed, it may have a composition of 80% chromium and 20% iron by weight. As will be appreciated, the total weight of ferrochrome powder applied to the ferrous length to achieve the said average composition of 18% chromium would need to be adjusted according to the chromium content of the ferrochrome powder.

It is not essential to apply the chromium (or chromium-containing) powder to both surfaces of the ferrous length, since it could quite satisfactorily be applied to one surface only thereof. This is possible because the diffusion heat treatment in the presence of the halogen-containing material actually takes place in the vapour phase. In the convolutions of the coil in the furnace, the surface of the ferrous length coated with the compacted chromium will be in contact with the uncoated surface of the ferrous length. The interchange reaction indicated above can readily occur between the coated and uncoated surfaces.

If a stainless steel, as opposed to a stainless iron, foil is to be produced, the necessary nickel may be introduced by mixing it with the mild steel (or iron) powder in the slurry, or, as suggested above, by mixing it with the chromium powder, or by replacing the latter by a nickel-chromium alloy powder, or by electroplating nickel onto the ferrous length prior to the application thereto of the chromium or ferrochrome powder.

**EXAMPLE 2**

A mixture of iron powder (or mild steel powder) and of ferrochrome powder (together with any other ingredients of the final stainless iron alloy to be produced) was wetted to form an aqueous slurry containing an inhibitor and a binder. This slurry was then "cast" onto a moving endless belt which carried the length of material so formed through a dryer, in which the slurry was substantially dried, and thence to the nip of a pair of compaction rollers, the said binder giving the slurry (which contained little water) sufficient strength to bridge the small gap which was provided between the endless belt and the compaction rollers. The said length of material, which was now constituted by a length of compacted, unsintered material, was heated to a temperature of 800°C so as to strengthen it and burn off the binder.

The said length then had halogen-containing material applied to each side thereof, the remaining steps in the process by which it was formed into stainless iron foil, e.g., of homogeneous composition throughout, being the same as described above in Example 1.

Instead of employing the endless belt mentioned in Example 1, or Example 2, the materials to be compacted may be supplied to a hopper disposed immediately above the nip of a pair of compaction rollers, which are arranged horizontally, the compacted material being fed downwardly, by a "flooded nip" technique to a furnace to impart strength.

I claim:

1. A method of producing a sintered ferrous metal length having at least one metallic chromium-containing surface comprising passing unsupported ferrous metal powder through the nip of a first pair of compaction rollers to produce a length of ferrous metal, coating at least one surface of the said length of ferrous metal with a metallic chromium-containing powder and compacting the metallic chromium-containing powder thereto by passing the coated length thus prepared through the nip of a second pair of compaction rollers, applying halogen-containing material to said coated length, forming said coated length having the halogen-containing material applied thereon into a coil, and thereafter heat treating the said coil of the coated length to effect sintering thereof in the presence of the halogen-containing material, the halogen-containing material, during the said heat treating, promoting diffusion of the metallic chromium into the coated surface of the said length of ferrous metal.

2. A method as claimed in claim 1 in which at least the initial part of the said heat treating is carried out in a reducing atmosphere.

3. A method as claimed in claim 1 in which the halogen-containing material is in the form of an aqueous solution.

4. A method as claimed in claim 1 in which the halogen-containing material comprises at least one substance selected from the group consisting of ferrous chloride and ammonium chloride.

5. A method as claimed in claim 1 in which the said length of ferrous metal is formed by passing wetted ferrous metal powder through a dryer, in which it is substantially dried, and then through the nip of the said first pair of compaction rollers.

6. A method as claimed in claim 5 in which the wetted ferrous metal powder is supplied to an endless belt, it
being carried by the latter through the dryer and thence to the said first pair of compaction rollers.

7. A method as claimed in claim 5 in which the said length of ferrous metal leaving the said first pair of compaction rollers is strengthened by heating.

8. A method as claimed in claim 1 in which the sintered ferrous metal length is a length of ferrous metal foil.

9. A method as claimed in claim 1 in which the ferrous metal powder has metallic nickel admixed therewith.

10. A method as claimed in claim 1 in which the metallic chromium-containing powder also comprises metallic nickel.

11. A method as claimed in claim 1 in which metallic nickel is electroplated onto the said length of ferrous metal prior to the application thereto of the metallic chromium-containing powder.