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CHROMISING OF FERROUS METAL SUBSTRATES

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ABSTRACT OF THE DISCLOSURE

A process for chromising ferrous metal workpieces and particularly sheet and plate, which is carried out while the ferrous metal is coiled or stacked in the furnace. The ferrous metal workpiece is first coated with an adherent porous chromium metal containing surface. Subsequently a metal halide-containing coating is applied to the porous chromium-containing surface. A coil or stack is formed wherein the coated workpiece or workpieces have surfaces in contact with one another and the workpieces are then chromised in a furnace at elevated temperatures.

The present invention relates to the chromising of ferrous metal workpieces which have been given an adherent porous surface layer containing chromium metal in metal to metal contact with the workpiece and which are in contact with one another, especially, but not exclusively, closed coils of steel strip.

In the chromising of a ferrous metal workpiece a chromous halide vapour is presented to the surface of the workpiece at a high temperature. The chromous halide interacts with the iron at the surface of the workpiece to yield chromium metal, which then diffuses into the surface of the workpiece forming an iron/chromium diffusion alloy surface.

One method of carrying out the chromising process comprises introducing chromous halide vapour into a furnace containing the workpiece to be chromised which is heated to a temperature of the order of 1000° C. The chromous halide vapour is usually formed by action of a halogen or halogen acid upon a chromium source which may be provided within the furnace.

Another method for achieving chromising is to pack the workpiece in a powder mixture containing a source of chromium. The packed workpiece is then heated, usually in a sealed furnace, to a temperature of at least 900° C. At this temperature the ingredients of the pack interact to yield chromous halide which then brings about chromising of the workpiece. However, this type of method is very wasteful of chromium since only about 40% of the chromium present in the pack actually appears in the iron/chromium surface alloy produced on the workpiece.

These methods rely upon the free circulation of gas over the surface of the workpiece in order to enable the halide to reach all parts of the workpiece. However, where the workpiece is in contact with another article, the halide is not able, even upon application of considerable pressure, to penetrate between the surfaces in contact to bring about a uniform and acceptable extent of chromising of such surfaces. Thus, whilst the chromising of metal workpieces has been known and practised for many years, no practical method has yet been devised for the satisfactory chromising of surfaces which are in contact with one another and it was not envisaged that such a process could in fact be possible.

It has been proposed to vary the chromising processes in which the workpiece is placed in a powder pack containing the chromium and halogen sources by applying the chromium and halogen reagents together in powder form to the surface of steel strip during coiling of the strip. In this proposal the powder was entrapped between convolutions of the coiled strip, which was then heated directly to the temperature required to bring about chromising. However, such a process is not commercially practicable since appreciable amounts of powder may be lost from between the convolutions of the coil during handling. This may result in uneven chromising during heating, unless special precautions are taken to minimise this loss, for example by the welding of end plates over the open ends of the coil. As with other processes involving the use of a packed powder, only a small proportion of the chromium in the powder coating will be used.

Another method by which chromising has been achieved is based upon the fact that when a chromium coated article is heated to a temperature of about 1000° C. thermal diffusion of the chromium into the substrate takes place unaided by any chemical reaction. In a proposed example of this method the workpiece was coated with chromium powder which was then compacted upon the surface of the workpiece by a rolling technique. The coated workpiece was then heated in a furnace through which a stream of hydrogen was passed. It was proposed to include some halogen in the gas stream in order to remove any oxide present in the powder coating. The proposal is restricted in its description to articles which are not in contact with one another, and it is stated that, in order to ensure that any halogen which may have been incorporated into the gas stream is effective, it is necessary to have sufficient space between adjacent surfaces of the workpieces which are being chromised to permit free circulation of the gases over those surfaces. Furthermore, it is stated that separation of the surfaces is necessary in all cases to avoid welding of adjacent surfaces.

We have now discovered a method by which surfaces in contact with one another may be chromised successfully. In many cases the process of the invention also permits better utilisation of both the chromium and halogen present in the chromising furnace than had hitherto been considered possible. Surprisingly no welding between adjacent surfaces occurs. The process of the invention also has the commercially attractive advantage that it may successfully be used to chromise steels which have not been subjected to a decarburisation process and which have not received special additions of materials, such as titanium, which minimise the migration of carbon in the steel. This is in contrast with other methods of chromising where it has been considered necessary to use such specially treated steels.

Accordingly, the present invention provides a process for the chromising of ferrous metal workpieces. The process is considered in two parts, the first part consisting of applying two coatings to at least one surface of the workpiece, and the second part consisting of furnace operations, as follows:

(1) Applying an adherent porous chromium metal-containing surface layer onto a ferrous metal workpiece, wherein said chromium metal is in metal to metal contact with said workpiece; subsequently applying an adherent metal halide-containing coating onto said porous chromium metal-containing surface layer, said metal halide being one that will react with iron to form ferrous halides at the temperature and in the atmosphere which it is intended to use during the heating of the coated workpiece to bring about formation of the diffusion alloy, forming a stack or coil of the coated ferrous workpieces or workpiece,

respectively with surfaces in contact with one another; and

(2) Heating said stack or coil in a furnace in a protective atmosphere to a temperature above about 750° C. and maintaining said stack or coil at a temperature above about 750° C. for a time sufficient to chromise the ferrous workpieces or workpiece comprising the stack or coil, respectively, a purging gas being passed through said furnace during at least the early stages of heating.

The present invention also provides novel products which are manufactured during the first part of the process. These novel products are ferrous metal workpieces having an adherent porous chromium metal-containing surface layer in metal to metal contact with at least one surface of said workpiece, and having an adherent metal halide-containing coating on said porous chromium-metal containing layer, said metal halide being one selected from the group consisting of iron halides, nickel halides, cobalt halides, and manganese halides. The workpiece may be formed into a tight coil, or may be cut into lengths and stacked for the chromising operation.

The workpieces which are to be chromised according to the invention are ferrous metal articles which have been given all adherent chromium surface layer on one or more faces. With steel strip or sheet it is preferred to coat both sides. Somewhat surprisingly we have found that coating of the edges of the strip or sheets is usually not required since adequate chromising of the edges is achieved without it. The surface layer is one which contains metallic chromium in direct metal to metal contact with the surfaces of the workpiece. In order that the initial surface layer may contain sufficient chromium to form the desired final diffusion alloy layer on the surface of the workpiece and yet not be so thick as to lose its porosity, it is desirable that the layer contain at least 20%, preferably at least 50% chromium. Preferably it is in the form of comparatively pure chromium metal or an alloy thereof, for example, a chromium/iron alloy. The surface layer may also contain other metals for example nickel, which it may be desired to incorporate in the surface alloy finally produced on the substrate.

As indicated above, the process of the invention is comparatively insensitive to the carbon content of the ferrous metal. Whilst steels which have had added thereto ingredients, such as titanium, which minimise the migration of the carbon in the steel may be used in the process of the invention, it is possible and preferred to use normal commercially available steels, for example, rimmed or capped mild-steels which have not been decarburised; aluminium killed steels and stainless steels. It will be appreciated that the nature of the workpiece influences the nature and thickness of the coating obtained. The nature of the substrate may therefore be varied in order to produce a product having the optimum properties for the intended use.

The term "adherent" is used herein to mean that the chromium surface layer, and the coating applied subsequently, must be sufficiently attached to the surface of the workpiece to enable it to be handled during transfer from the application operation to the furnace, or in the case of steel strip, to permit the strip to be coiled without the chromium surface layer or the coating becoming detached. The chromium-containing surface layer may be deposited upon the surface of the workpiece by known methods. Such methods include electrolytic deposition of chromium from conventional chromium plating solutions, plasma or flame spraying of a chromium-containing powder or wire and the compaction by a rolling technique of a powder containing chromium which has previously been distributed over the surface of the workpiece.

The amount of chromium which is initially applied as the surface layer on the workpiece depends upon the final use to which the treated workpiece is to be put and the properties desired for such an end use. For example, where mild steel is being chromised to produce a corrosion-resistant surface, it is usual to provide a chromium/iron diffusion alloy layer on the surface of the mild steel which layer is 0.002 to 0.003 in. thick. In applications where mild steel is to be drawn or formed after chromising, it is desirable that the diffusion alloy layer should not have too high a chromium content. For such applications a diffusion layer containing not more than 30% chromium is desirable. To obtain such a diffusion layer 0.002 to 0.003 in. thick the initial surface layer applied to the workpiece contains from 11 to 17 gms. of chromium per sq. ft. of the surface of the workpiece. However, as indicated earlier, the initial surface layer of chromium must be porous, in order to permit diffusion of vapours therethrough. The porosity depends to a large extent on the thickness of the surface layer and the method by which it is applied to the workpiece. Thus, if the chromium is electrolytically deposited by conventional chromium plating techniques upon the workpiece, the maximum thickness which may be deposited without serious loss of porosity is of the order of 0.001 in. Where the chromium is applied as a powder of size 200 mesh B.S. and this powder is compacted upon the workpiece by a rolling operation, the surface layer may be up to 0.003 in. thick. Thus, where a particular amount of chromium per unit area of the surface layer is required, the method used to achieve this surface layer is determined by whether or not the particular method produces a surface layer which is porous enough to facilitate diffusion of the vapours subsequently formed therethrough. However, we have found that in general the application of a surface layer which is from 0.0001 to 0.001 in. thick provides a satisfactory result with a variety of application techniques.

The coating which is applied to the chromium coated workpiece in the above referred to part (1) of the process of the invention is one which contains a metal halide The preferred metal halide is an iron halide, especially a ferrous halide. Nickel halides are the metal halides of second choice. Whilst mixtures of iron halides and other metal halides may be used, it is preferred to use solely the iron halide. The metal halides used in this chromising process, other than ferrous halides, are those metal halides which react with iron to yield ferrous halides, when heated to the temperature and in the atmosphere which it is intended to use during the heating of the coated workpieces to bring about formation of the diffusion alloy. Whether any particular metal halide is suitable may be readily determined by a simple test in which a solution of the metal halide is coated onto a steel sheet, or powders of the metal halide and iron are mixed together, to form test samples. The samples are heated to the temperature at which it is intended that chromising will take place, that is to at least 750° C., and held at this value for several hours. For convenience we have found that heating to about 800° C. provides a satisfactory indication of the suitability or otherwise of the metal halide for use in the chromising process. During the heating of the samples a stream of the purging gas, such as hydrogen which it is intended to use as the protective atmosphere during diffusion is passed over them until such time as the temperature reaches 400° C. Once this value has been reached the gas stream is stopped and the temperature raised further to the desired limit. If a metal halide is to be suitable for use in the present invention, ferrous halide will have been formed during the heating and can be detected either in the atmosphere surrounding the test sample, or upon the surface of the sample, when the heating has been completed.

The preferred halide is ferrous chloride or a hydrated ferrous chloride. In place of the ferrous halide there may be used other iron/halogen compounds which upon heating decompose or interact with themselves or the coating of any iron of the workpiece to yield the desired ferrous halide. Obviously, such other iron/halogen compounds should not produce volatilisation of decomposition products which would cause appreciable harm to the coating

or substrate at the temperature at which they are liberated as specified in greater detail hereinafter. Suitable iron/halogen compounds include ferric halides and hydrates thereof. The compounds may form ferrous halides by an oxidation/reduction reaction with the coating and possible also with the surface layer. Particularly suitable ferrous halides and iron/halogen compounds include: ferrous chloride, ferrous bromide, ferrous iodide, ferrous fluoride, ferrous chloride dihydrate, ferrous chloride tetrahydrate, ferrous fluoride tetrahydrate, ferrous fluoride octahydrate, ferrous iodide tetrahydrate, ferric chloride, ferric bromide, ferric fluoride, ferric chloride hexahydrate and ferric bromide hexahydrate. Ferrous halides and iron/halogen precursors thereof are to be considered as being equivalent to one another in the process of the invention. These are herein collectively denoted by the term iron halides.

Other suitable metal halides for present use include those of cobalt, nickel or manganese, especially the chlorides thereof. As with the iron halides, there may be used other metal/halogen compounds which interact with themselves, the chromium surface layer and/or the iron of the workpiece during heating to yield the metal halides and/or the ferrous halide active chromising ingredient directly. Other metal/halogen compounds are considered the equivalent of the metal halides if they yield ferrous halides during the chromising process in accordance with the criteria set-forth hereinbefore, and are collectively denoted by the term metal halide. Suitable other metal/halogen compounds include hydrates of the metal halides, such as $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, and $CoCl_2 \cdot 6H_2O$.

It will be appreciated that the chromising process of the present invention may give rise to surface alloys on the workpiece which contain a proportion of the metal originally present in the metal halide coating applied to the workpiece, e.g., nickel halides result in a nickel-containing alloy surface.

Although the metal halide and metal halide coating which is applied on the porous chromium metal-containing coating may be any of the metal halides as aforedescribed, the chromising process in the remaining portion of the Specification is largely described in connection with a coating containing the preferred metal halides, i.e., the iron halides and ferrous chloride in particular. It is to be understood that the disclosure equally applies to the other metal halides referred to herein.

In addition to the ferrous chloride or other metal halide, the coating applied to the workpiece may also contain other ingredients such as fillers and ingredients which aid the adhesion of the coating to the workpiece. However, we prefer to use no ingredients other than the metal halide and, as described below, a gas-forming compound. The use of fillers and adhesion aids may lead to the introduction of harmful materials into the system and their use is often unnecessary since satisfactory adhesion of the coating is achieved in their absence.

The coating containing the iron halide is applied to the workpiece in known manner, for example by roller coating, brushing, spraying or dipping. The coating may be applied to all exposed surfaces of the workpiece. However, when strip or sheet workpieces are treated, it is possible to achieve satisfactory results by coating only one of the sides of the workpiece and then stacking or coiling them so that the iron halide-coated surfaces contact surfaces which have not been so treated. The iron halide then acts not only on the chromium-coated surface to which it has been applied, but also on the adjacent non-iron halide-coated surface. The methods for applying the coating usually require that the coating medium be in fluid form and solutions or suspensions or the coating ingredients may be prepared in known manner. Whilst organic solvents or diluents may be used, it is preferred to use water in the preparation of the coating medium and we have found that the use of water may in some cases assist the adhesion of the coating to the workpiece. Where the coating has been applied in fluid form, it is of course necessary to dry, and perhaps set, the coating to render it adherent before stacking or coiling. The pretreatment usually takes the form of a preheating. The duration and temperature of the preheating depend upon the composition of the coating and the solvent or diluent used during its application to the workpiece. We have found that the use of temperatures of up to 300° C. preferably not more than 150° C., for periods of up to about 1 minute is satisfactory.

An especially preferred coating for present use consists of hydrated ferrous chloride and (as a gas-forming compound to be described below) ammonium chloride in a weight proportion of 3 to 10 parts ferrous chloride and 1 part ammonium chloride. Such a coating is sufficiently adherent to the workpiece when it is applied in a solution or slurry in water to obviate the use of binders or fillers.

The coating is applied to the workpiece in sufficient amount to provide the desired amount of halogen to ensure that chromising occurs at a reasonable rate upon heating the coated workpiece. We have found that if sufficient of the coating is applied to provide from 1 to 50%, preferably from 5 to 30%, of the theoretical amount of halogen to react with all the chromium in the surface layer on the workpiece to form chromous halides, satisfactory rates of chromising are achieved. Where the coating is applied to only one surface of the workpiece, allowance must be made for the fact that about half the halogen therein will be required to bring about chromising of the uncoated surface with which it is in contact.

Once an adherent coating containing the iron halide has been formed on the workpiece, this is treated according to part (2) of the process of the invention. It will be appreciated that up to this point in the process, the articles to be chromised do not have surfaces in contact with one another. However, once the iron halide coating has been applied to the workpieces these may then be stacked, rolled, coiled or otherwise put in contact with one another for placing in the chromising furnace. Since the coating is adherent, the coated articles may be stored for some time before being chromised if desired.

The diffusion operation occurs at temperatures in excess of about 750° C. and is carried out in a protective atmosphere, which is an atmosphere composed substantially of hydrogen, which is preferred, or one of the noble gases such as argon or helium, or any mixture of these gases. The atmosphere will also contain any reactant halides evolved from the coating. For effective chromising, the furnace environment should be substantially free of substances which will cause harm, e.g. oxidation, carburisation and/or nitriding, to the workpiece, the chromium containing surface layer, and/or the coating. Substances which will cause these harmful effects include oxygen, vapour, and air. Although it is theoretically desirable that such substances (which are referred to herein as undesirable and/or harmful) should not be present in the furnace at any time during the process, this is not a practical possibility since these substances are, to some extent, present in or formed from components of the furnace, such as refractories. They also enter the furnace during shut-down periods between cycles, or through leaks. Moreover, they are introduced in many cases as a component of the metal halide-containing coating or at air entrapped between contacting surfaces of the coated workpieces. The presence of appreciable amounts of such undesirable substances may be tolerated in the furnace provided they are substantially removed from the furnace before the furnace reaches a temperature at which they cause harm. This is accomplished by passing a gas through the furnace. The furnace is purged during at least the early stages of the heating process and, preferably, also before heating.

This necessity for purging to remove undesirable substances from the furnace permits greater flexibility in the selection of components of the metal halide-containing

coating. The coating may contain substances which will volatilise or decompose to form undesirable substances, so long as such volatilisation or decomposition occurs sufficiently early in the heating cycle that the undesirable substances are substantially removed during the purge. Specifically, advantage is taken of the purging gas in this fashion to utilise hydrated metal halides which are often available at lower cost than the non-hydrated metal halides. Similarly ammonium halides may be utilised in the coating as described in more detail hereinafter.

Hydrogen, argon or helium and the other noble gases may be used for the entire purge, and also to form the protective atmosphere during the subsequent chromising at elevated temperatures. Gases of commercial purity may be employed. Nitrogen containing gases, such as cracked ammonia, may be used to purge the furnace at low temperatures, e.g., below about 400° C. and preferably at temperatures below about 200° C. Where an initial purge with a nitrogen-containing gas is used, the purge is in two stages with either hydrogen or one of the noble gases being used in the later stages of purging. Since the initial purging of air from the furnace requires large volumes of purging gas, we prefer to carry out the initial purge using a nitrogen-hydrogen mixture, such as 95 parts of nitrogen and 5 parts of hydrogen. This preference results from economic and safety factors.

During the heating of the furnace any volatile materials evolved from the coating, together with entrapped air, are largely removed from between the surfaces of the coated workpieces, particularly when the areas of the surfaces in contact are small, by expansion of these volatile materials. The evolved materials, together with this evolved from the furnace, and any air present are then removed from the furnace by the purging gas stream before they can cause appreciable harm to the coating or substrate. In this part (2) of the process of the invention, the passage of purging gas through the furnace is continued for at least a sufficient period to ensure that substantially all the harmful vapours have been removed from the furnace atmosphere. Whilst it is possible to continue the purging of the furnace throughout the heating of the coated workpiece to, and at, the chromising temperature, such operation is preferably avoided, since it may result in the removal of excessive amounts of reactant halides from the coating on the workpiece by evaporation. We therefore prefer to carry out part 2 of the process, in which the coated workpiece is heated, in two stages. In the first stage the coated workpiece is heated in a furnace to cause evolution of any harmful materials that may be present in the coating and from other sources within the furnace, which are then removed from the furnace by the purging gas; the purging gas stream is then stopped and in the second stage the temperature of the furnace is raised further to bring about chromising of the workpiece.

The temperature reached during the first stage should be sufficiently great to cause vaporisation of any harmful volatilisation and decomposition products which could be evolved from the coating but should of course not be so great that excessive quantities of reactant halides would be evaporated from the coating. The temperature at which appreciable quantities of reactant halides would be evaporated is usually within the range 350° C. to 700° C. Once substantially all the harmful materials have been vaporised and swept from the furnace by the purging gas stream, the gas stream is stopped, or at least reduced to the minimum flow required to ensure that the furnace is maintained under slight positive pressure. The heating of the furnace is then continued in the second stage to a temperature of at least 750° C. in order to bring about chromising.

Whilst it is possible to heat the furnace directly to the temperature at which reactant halides would be evaporated from the coating, it is preferred to carry out this heating in steps, especially where the areas of the surfaces in contact are of any appreciable size. Although it is possible to secure adequate chromising by the use of a coating which contains only the iron halide, it is preferred to have present in the coating a compound which decomposes or vaporises upon heating to yield a gas which does not cause appreciable harm at the temperature at which it is evolved or is present in appreciable amount. The presence of this compound is especially desirable where the coating gives rise to harmful materials and the areas of the surfaces in contact are large, since a proportion of the harmful materials evolved from the coating will be entrapped between the contacting surfaces. The evolution of the gas aids the removal, before they can cause any appreciable harm to the coating or substrate, of air or decomposition or volatilisation products from the coating which may be entrapped between the contacting surfaces and which might not otherwise be removed during this stage of the heating process. It is preferred that the decomposition or volatilisation temperature of the gas-forming compound be sufficiently high for the vaporisation of any harmful products from the coating to take place before the evolution of the gas from the gas-forming compound occurs. We have found that in general the use of ammonium halides, such as ammonium chloride, satisfy all the requirements for the gas-forming compound outlined above. Whilst such compounds may give rise to nitrogenous gases which would cause harm at high enough temperatures the latter are higher than those at which the gases are evolved and the amount of residual gas which remains between the contacting surfaces is too small to cause appreciable harm at the higher temperatures. The gas-forming compound may be present in up to 50%, preferably 10 to 30%, by weight based on the content of iron halide in the coating.

It follows from the foregoing description that stage (1) of part (2) of the process usually involves the following sequence of events:

(a) Decomposition or volatilisation products are evolved from the coating, at a temperature below that at which any gas is evolved from the gas-forming compound present in the coating. The coated workpiece remains below this latter temperature for a period sufficient to ensure substantially complete evolution of any harmful vapours, which are then swept from the furnace by the purging gas stream. We have found that in general the use of temperatures of from 100° C. to 300° C. for this first heating step provides satisfactory results. It will be noted that the temperatures employed in this first step are substantially the same as those employed to dry or set the coating after application to the workpiece. However, in the latter case heating was continued for only a short period, whereas heating in order to vaporise harmful materials may be carried out over prolonged periods.

(b) Once the furnace has been at the desired temperature for sufficiently long a period to ensure the evolution of substantially all the harmful materials from the coating, the temperature of the furnace is then raised to a temperature which is above that required to evolve gas from any gas-forming compound present in the coating and yet is not high enough to cause evaporation of excessive quantities of reactant from the halide coating. In this second step, the gas evolved from the gas-forming compound expels harmful vapours entrapped between contacting surfaces or retained in the coating on the workpiece. The expelled vapours are then swept from the furnace by the purging gas stream which is being passed through the furnace.

(c) When the harmful vapours, displaced from between contacting surfaces by the gases resulting from decomposition and/or volatilisation of the gas-forming compound, have been removed from the furnace by the purging gas stream, the flow of gases is stopped or reduced. The temperature at which the gas flow is stopped or reduced is below that at which excessive vaporisation of reactant

halides from the coating occurs and the temperature reached in the furnace when all the harmful vapours have been removed may in fact be well below this limit. We prefer to continue the passage of the purging gases until the temperature reaches approximately 400° C., though the temperature may vary from 350 to 700° C. depending upon the design of furnace used. It is desirable that the flow of gases be stopped or reduced in such a manner that the furnace is under a slight positive pressure and that this pressure be maintained during chromising in order to minimise the risk of any leakage of air into the furnace. Once the flow of gas through the furnace has been stopped or reduced, the temperature of the furnace is then raised to the temperature at which chromising takes place.

In the final stage of part 2 of the process the furnace temperature is raised to at least 750° C. and preferably at least 780° C., to chromise the workpiece. The furnace is held at this elevated temperature for the requisite period to ensure that chromising of the workpiece occurs. Such period depends upon the desired thickness and composition of the chromium/iron alloy to be achieved on the surface of the workpiece and is usually of the order of from 4 to 40 hours at temperatures which are generally between 800° C. and 1000° C. Whilst higher temperatures than these may be used if desired, the nature of the workpiece dictates the maximum temperature which may be used, since above a given temperature deformation and even melting of the workpiece occur. The maximum temperature which may be used may be determined by trial and error in each case.

Although the foregoing description of the process describes the heating in terms of distinct stages, it is to be understood that the temperature rise in commercial operations may be continuous, although not necessarily at a constant rate. This will most likely occur in the heating of large furnaces which require long heating periods and consequent by a slow rate of heating.

The invention will now be illustrated by the following examples, in which all parts are given by weight.

EXAMPLE 1

A piece of 20 guage steel strip (0.2% carbon) was degreased in a solvent degreasing bath, pickled in 10% v./v. nitric acid for 10 seconds and washed with water. Chromium metal powder (200 B.S. mesh) was applied to both surfaces of the steel strip at a rate of 12.3 g./sq. ft. and compacted by passing the strip between rolls. The chromium covered steel strip was then passed through a solution of ferrous chloride tetrahydrate (4.2 parts) and ammonium chloride (0.97) part in water (.5 part) and dried by passing the strip under an infrared drier to give a pick-up of 4 gms./sq. ft. of coating. A 20 ft. length of the treated strip was wound under a tension of 1000 lbs. onto a mandrel of 3½ inch external diameter and the free end clamped to retain the tension.

The coil was placed in a suitable furnace which was then purged with hydrogen for 3 hours at 250° C., after which time the temperature was raised to 400° C. over a period of 1½ hours. The flow of gas was continued through the furnace for 10 hours to ensure the complete removal of harmful products. The flow of gas was then stopped and the temperature raised to 800° C. over a period of 4 hours and retained at this temperature for 24 hours.

After cooling the coil was removed from the furnace and washed with water to remove excess halide. The surfaces were silver-grey in colour and were resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, even after bending. Removal of a portion of the coating by filing and treatment with boiling 50% aqueous nitric acid to dissolve the steel core revealed a coating 0.002 inch thick which was insoluble in nitric acid. Analysis of the coating after dissolution in hydrochloric acid showed an iron content of 69%.

EXAMPLE 2

A piece of 20 gauge steel (0.2% carbon) sheet was degreased by immersion in an alkali cleaner and then treated anodically in 50% sulphuric for 30 seconds at a current density of 400 a./sq. ft. The sheet was then transferred to a catalysed chromic acid plating bath and a current of 300 a./sq. ft. passed until a layer of chromium 0.0003 in. thick had been deposited. The chromium plated sheet was then washed, dried and dipped into a solution consisting of ferrous chloride tetrahydrate (4 parts) and ammonium chloride (1 part) in water (5 parts), and dried under an infra-red heater to give a pick-up of 4 gms./sq. ft. of coating. A stack of such sheets was then placed in a suitable furnace and subjected to a heat treatment similar to that used in Example 1. On removing the sheet from the furnace it was found that a chromised coating 0.001 in. thick containing 71% iron had been found.

EXAMPLE 3

A piece of 20 gauge steel strip (0.2% carbon) was degreased in a solvent degreasing bath, pickled in 10% v./v. nitric acid for 10 seconds and washed with water. Chromium metal powder (200 B.S. mesh) was applied to both surfaces of the steel strip at a rate of 17 gms. per sq. ft. and compacted by passing the strip between rolls. The chromium covered steel strip was then passed through a solution of ferrous bromide (6 parts) and ammonium chloride (1 part) in water (6 parts) and dried by passing the strip under an infra-red drier to give a pick-up of 4 gms./sq. ft. of coating. A length of the dried strip was wound under a tension of 800 lbs. onto a mandrel of 3½ inches external diameter and the free end clamped to retain the tension.

The coil was placed in a suitable furnace which was then purged with hydrogen for three hours at 250° C. after which time the temperature was raised to 400° C. for a period of 1½ hours. The flow of gas was continued in the furnace for 10 hours to ensure substantially complete removal of harmful products. The flow of gas was then stopped and the temperature raised to 900° C. over a period of 5 hours and retained at this temperature for 16 hours.

After cooling, the coil was removed from the furnace and washed in water to remove excess halide. The surfaces were silver-grey in colour and were resistant to corrosion by water, aqueous sodium chloride and aqueous nitric acid, even after bending. Removal of a portion of the coating by filing and treatment with boiling 50% aqueous nitric acid to dissolve the steel core revealed a coating 0.0026 inch thick, which was insoluble in nitric acid. Analysis of the coating after dissolution in hydrochloric acid showed an iron content of 71.1%.

EXAMPLE 4

Pieces of 20 gauge steel strips (0.2% carbon) were degreased in an alkaline degreasing bath, pickled in 10% v./v. nitric acid for 10 seconds and washed with water. Chromium metal powder less than 200 B.S. mesh) was applied to both surfaces of the steel strips at a rate of 15 gms./sq. ft. Compaction of the chromium onto the surface of the strips was achieved by passing the strips between rolls. The chromium covered steel strips were then dipped into a solution of ferric chloride hexahydrate (5.7 parts) and ammonium chloride (1 part) in water (7.2 parts), and dried under an infra-red drier to give a pick-up of 4 gms./sq. ft. of coating. The strips of steel were then stacked in a suitable furnace which was then purged with hydrogen for 3 hours at 250° C. after which time, the temperature was raised to 400° C. over a period of 1½ hours. The flow of gas was continued through the furnace for 14 hours to ensure the complete removal of harmful products. The flow of gas was then stopped and the temperature raised to 850° C. over a period of 4½ hours and retained at this temperature for 24 hours.

After cooling, the strips of steel were removed from the furnace and washed with water to remove excess halide. The surfaces were silver grey in colour and were resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, even after bending.

Removal of a portion of the coating by filing, and treatment with boiling in 50% aqueous nitric acid to dissolve the steel core revealed a coating 0.0032 in. thick which was insoluble in nitric acid. Analysis of the coating, after dissolution in hydrochloric acid, showed an iron content of 77%.

EXAMPLE 5

Pieces of 20 gauge steel strips (0.2% carbon) were degreased in an alkaline degreasing bath, pickled in 10% v./v. nitric acid for 10 seconds and washed with water. Chromium metal powder (200 B.S. mesh) was applied to both surfaces of the steel strips at a rate of 15 gm./sq. ft. Compaction of the chromium onto the surface of the strips was achieved by passing the strips between rolls. The chromium covered steel strips were then dipped into a solution of ferrous iodide (anhydrous) (4 parts) and ammonium iodide (1 part) in water (7.2 parts), and dried under an infrared drier to give a pick-up of 4 gms./sq. ft. of coating. The strips of steel were then stacked in a suitable furnace which was then purged with hydrogen for 3 hours at 250° C. after which time, the temperature was raised to 400° C. over a period of 1½ hours. The flow of gas was continued through the furnace for 14 hours to ensure the complete removal of harmful products. The flow of gas was then stopped and the temperature raised to 900° C. over a period of 4 hours and retained at this temperature for 24 hours.

After cooling, the strips of steel were removed from the furnace and washed with water to remove excess halide. The surfaces were silver grey in colour and were resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, even after bending.

Removal of a portion of the coating by filing and treatment with boiling 50% aqueous nitric acid, to dissolve the steel core, revealed a coating 0.0022 inch thick which was insoluble in nitric acid. Analysis of the coating, after dissolution in hydrochloric acid, showed an iron content of 70%.

EXAMPLE 6

A piece of 20 gauge steel strip (0.2% carbon) was degreased in a solvent degreasing bath, pickled in 10% v./v. nitric acid for 10 seconds and washed with water. Chromium metal powder (200 B.S. mesh) was applied to both surfaces of the steel strip at a rate of 12.2 g./sq. ft. and compacted by passing the strip between rolls. The chromium covered steel strip was then passed through a solution of nickel chloride hexahydrate (5.7 parts) and ammonium chloride (1 part) in water (7.2 parts), and dried by passing the strip under an infra-red dryer to give a pick-up of nickel and ammonium chlorides of 4 g./sq. ft. A 20 ft. length of the treated strip was wound under a tension of 750 lbs. onto a mandrel of 3½ inch external diameter, and the free end clamped to retain the tension.

The coil was placed in a suitable furnace which was then purged with a mixture of 10% v./v. hydrogen in argon for 2 hours at 200° C. The temperature was then raised to 400° C. over a period of 2 hours. The flow of gas was continued through the furnace for 10 hours to ensure the complete removal of harmful products. The flow of gas through the furnace was then stopped and the temperature raised to 900° C. over a period of 5 hours and retained at this temperature for 16 hours.

After cooling, the coil was removed from the furnace and washed with water to remove residual halide. The surfaces were silver grey in colour and were resistant to corrosion by water, aqueous sodium chloride and aqueous nitric acid, even after bending.

Removal of a portion of the coating by filing, and treatment by boiling in 50% aqueous nitric acid to dissolve the steel core revealed a coating 0.0025 in. thick which was insoluble in nitric acid. Analysis of the coating after dissolution in hydrochloric acid, showed an iron content of 76%.

EXAMPLE 7

Pieces of 20 gauge steel strip were degreased, pickled and washed as described in Example 6. The strips were coated with chromium metal powder at the rate of 16 g./sq. ft. and the chromium powder was compacted as in Example 6. The chromium covered steel strips were then dipped into a solution of manganous chloride tetrahydrate (80 parts) and ammonium chloride (14 parts) in water (100 parts) and dried under an infra-red dryer to give a pick-up of manganous and ammonium chlorides of 4 g./sq. ft. The strips of steel were stacked in a suitable furnace which was purged with hydrogen for 3 hours at 250° C. after which time the temperature was raised to 400° C. over a period of 1–2 hours. The flow of gas was continued through the furnace for 14 hours at this temperature. The gas flow was then stopped and the temperature raised to 900° C. and maintained at this temperature for 16 hours.

After cooling, the plates were removed from the furnace and washed with water. The surfaces were silver grey in colour and were resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, even after bending. Analysis of the chromium/iron alloy coating after dissolution of the steel core in nitric acid showed an iron content of 52%. The thickness of the alloy layer was 0.0015 in.

EXAMPLE 8

The experiment described in Example 7 was repeated using cobaltous chloride hexahydrate instead of the hydrated manganous chloride. Once again the steel strips after treatment had silver grey corrosion resistant surfaces. The chromium/iron alloy layer was 0.0013 in. thick and contained 40% iron.

Although the process utilises the purge, and particularly the later stage of the purging operation with hydrogen or one of the noble gases, to remove substances which are harmful to the chromising operation, the process is sufficiently flexible to tolerate such small amount of deleterious materials as may be present under practical operation conditions when using materials of commercial purity.

The process of the present invention has been illustrated in the examples in terms of a batch process, i.e., the workpieces which have been first surfaced with the chromium metal containing layer then coated with the halide-containing layer are coiled and/or arranged in a stack of workpieces, which are placed in a furnace and the furnace is then heated. The process is also adaptable to continuous furnace operation by conveying coils or stacks of the coated workpieces through a tunnel furnace having different temperature zones. Such a furnace would require provision for purging during the initial sections thereof followed by the use of the protective atmosphere in the remaining sections.

The process of the present invention is useful for chromising stacks or coils of ferrous metal. The coils are formed from continuous strip material which is most commonly sheet of relatively thin gauge. The process is also useful for producing chromised wire, and tubing by chromising coils thereof. The chromising operation is most usefully carried out by stacking those ferrous metal workpieces which are not readily coiled, such as heavier sheet material, and dished ferrous metal workpieces which form a nestled stack. Prior art processes have not been successful in chromising a tightly coiled workpiece or stacked workpieces, where adjacent workpieces are in direct contact with each other.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such

modifications and variations as come within the scope of the appended claims.

We claim:

1. A process for the chromising of ferrous metal work pieces which comprises

(i) applying an adherent porous chromium metal-containing surface layer onto a ferrous metal workpiece, wherein said chromium metal is in metal to metal contact with said workpiece;

(ii) subsequently applying an adherent metal halide-containing coating onto said porous chromium metal-containing surface layer, said metal halide being one that will react with iron, at the temperature and in the protective atmosphere which it is intended to use during chromising, to form ferrous halide;

(iii) forming a stack or coil of the coated ferrous workpieces or workpiece, respectively, with surfaces in contact with one another;

(iv) heating said stack or coil in a furnace;

(v) passing a purging gas through said furnace during at least the early stages of heating;

(vi) raising the temperature to above about 750° C. and maintaining said stack or coil at said temperature in a protective atmosphere for a time sufficient to chromise the ferrous workpieces or workpiece comprising the stack or coil, respectively.

2. The process of claim 1 wherein said metal halide is an iron halide, a nickel halide, a cobalt halide, or a maganese halide, and wherein the atmosphere during chromising is composed substantially of hydrogen, argon, or helium.

3. The process of claim 2 wherein said workpiece is a steel workpiece; wherein said chromium metal-containing surface layer is obtained by the use of chromium or ferrochromium and contains at least 20% chromium; wherein said halide is the chloride; wherein said metal chloride in the adherent metal halide-containing coating is present in an amount of between 1% and 50% of the stoichiometric amount of chlorine theoretically required to react with all the chromium in said chromium metal-containing surface layer to form chromous chloride; and wherein at least the later portion of the purge is carried out with hydrogen, argon, or helium.

4. The process of claim 3 wherein said chromium metal-containing surface layer is applied to both sides of a substantially flat workpiece; wherein said metal halide is ferric chloride or hydrate thereof, in an amount sufficient to provide between about 5% and 30% of the stoichiometric amount of chlorine theoretically required to react with all of the chromium in said chromium metal-containing surface layer to form chromous chloride; wherein the metal halide coating is applied to one or both of the two porous chromium surfaces; wherein hydrogen is used for at least a portion of the purging gas and as the protective atmosphere; and wherein chromising is carried out at a temperature above about 780° C.

5. The process of claim 3 wherein said chromium metal-containing surface layer is applied to both sides, of a substantially flat workpiece; wherein said metal halide is a ferrous chloride or hydrate thereof, in an amount sufficient to provide between about 5% and 30% of the stoichiometric amount of chlorine theoretically required to react with all of the chromium in said chromium metal containing surface layer to form chromous chloride; wherein the metal halide coating is applied to one or both of the two porous chromium surfaces; wherein hydrogen is used for at least a portion of the purging gas and as the protective atmosphere; and wherein chromising is carried out at a temperature above about 780° C.

6. The process of claim 5 wherein said metal halide-containing coating consists essentially of between about 3 parts and 10 parts of ferrous chloride or a hydrate thereof to 1 part of ammonium chloride; wherein said coating is applied on said porous chromium metal-containing surface layer in the form of an aqueous solution or aqueous suspension.

7. The process of claim 6 wherein the furnace is purged with a nitrogen-containing gas at a temperature below about 400° C., followed by a purge with hydrogen.

8. The process of claim 6 wherein said steel is selected from the group consisting of mild steel, rimmed steel, capped steel and stainless steel.

9. The process of claim 5 wherein the workpiece is heated to a temperature of up to 300° C., after step (ii) of the process and prior to step (iii); and wherein the purge is stopped at a temperature between about 350° C. and 700° C.

10. The process of claim 5 wherein said steel is selected from the group consisting of mild steel, rimmed steel, capped steel, and stainless steel.

11. The process of claim 3 wherein an adherent porous chromium surface is electrodeposited on said workpiece; and wherein said metal halide is selected from the group ferrous chloride, ferric chloride, hydrated ferrous chloride and hydrated ferric chloride and said metal halide coating is applied on said porous chromium surfaces as an aqueous solution or aqueous suspension.

12. The process of claim 11 wherein said metal halide-containing coating contains 1 part of ammonium chloride for each 3 to 10 parts of ferrous chloride or hydrate thereof.

13. The process of claim 3 wherein finely powdered chromium or ferrochromium is compacted on the surfaces of said workpiece to form said adherent porous chromium metal-containing surfaces; and wherein said metal halide is selected from the group ferrous chloride, ferric chloride, hydrated ferrous chloride and hydrated ferric chloride; and said metal halide coating is applied on said porous chromium metal containing surfaces in the form of an aqueous solution or aqueous suspension.

14. The process of claim 13 wherein said metal halide-containing coating contains 1 part of ammonium chloride for each 3 to 10 parts of ferrous chloride or hydrate thereof.

15. The process of claim 3 wherein said metal halide-containing coating contains an ammonium halide in an amount up to 50% by weight of said metal halide; and wherein a nitrogen-containing gas is used to purge said furnace at a temperature below about 400° C., followed by a purge with hydrogen, argon or helium.

16. The process of claim 9 wherein said metal halide-containing coating contains ammonium chloride in an amount between 10% and 30% based on the weight of said metal halide in said coating.

17. The process of claim 3 wherein said steel is selected from the group consisting of mild steel, rimmed steel, capped steel, and stainless steel.

18. The process of claim 1 wherein said metal halide-containing coating also contains an ammonium halide in an amount up to 50% of the weight of said metal halide.

19. The process of claim 18 wherein said steel is selected from the group consisting of mild steel, rimmed steel, capped steel and stainless steel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,585,068 Dated June 15, 1971

Inventor(s) KENNETH URMSTON HOLKER and COLIN PAUL ALBON

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

Column 1, lines 9-11 should read:
--Claims priority, application Great Britain, June 7, 1966, 25,415/66 (Provisional); and Nov. 29, 1966, 25,415/66 (Complete); Mar. 16, 1967, 12,455/67; April 11, 1967, 16,641/67--

Column 14, line 47, "claim 9" should read --claim 15--.

Signed and sealed this 25th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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