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CHROMISING OF FERROUS METAL SUBSTRATES

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13 Claims

ABSTRACT OF THE DISCLOSURE

This invention provides a process for chromising ferrous metal substrates. A porous adherent chromium-containing coating is applied to the surface of a ferrous metal substrate. The coated substrate is then heated in contact with a gaseous stream containing a hydrogen halide and also hydrogen and/or in inert gas to a temperature such that the hydrogen halide reacts with the surface of the coated substrate said temperature being below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation. The flow of the gas is then stopped and the coated substrate heated to a temperature of at least 750° C. for a period sufficient to alloy the chromium in the initial coating with the substrate and form an alloy coating of the desired thickness.

This application is a continuation of co-pending application Ser. No. 561,327, filed June 29, 1966, now abandoned.

The present invention relates to the chromising of ferrous metal substrates.

In the chromising of ferrous metal substrates a chromous halide vapor is presented to the surface of the substrate at a high temperature. The chromous halide interacts with the iron of the substrate to yield chromium metal and ferrous halide. The deposited chromium then diffuses into the surface of the substrate forming a chromium/iron alloy surface which is corrosion resistant.

In one type of chromising process used hitherto the article to be chromised is introduced into a furnace which is then purged of air by the passage therethrough of a non-oxidising gas and the temperature is raised to the operating temperature which is in excess of 840° C. and usually of the order of 1000° C. Once the operating temperature has been reached a hydrogen halide is incorporated into the gas stream passing through the furnace. The gases containing hydrogen halide are then passed over a source of chromium, which may be sited either in a separate furnace or in the furnace containing the workpiece, to form the chromous halide required for chromising. In an alternative method it has been proposed to apply a compacted coating of chromium powder to the workpiece which is then placed in a furnace, heated to the operating temperature and chromised by maintaining at this temperature, optionally in the presence of a hydrogen halide contained in the non-oxidising gas-stream which is again continuously passed through the furnace.

Another method for achieving chromising is to pack the workpiece in a powder mixture containing an ammonium halide and powdered chromium or an alloy thereof and to heat the loaded furnace to the operating temperature of at least 900° C. In this process the ammonium halide decomposes to yield a hydrogen halide which reacts with the chromium present to form the

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chromous halide required. It is usual to carry out this method of chromising in a sealed furnace and not to pass a gas stream therethrough.

In these methods the ferrous halide, which is liberated from the surface of the workpiece during chromising, vapourises and forms part of the furnace atmosphere. Where a non-oxidising gas is passed continuously through the furnace substantially all of this ferrous halide is removed from the furnace. This represents a considerable loss of halogen from the system which might otherwise have taken part in the chromising process. In order to overcome this loss it has been customary in the commonly used processes to recycle the furnace off-gases over the source of chromium again. Where this is done the ferrous halide interacts with the chromium source to yield chromous halide which is used in the chromising process. However, the source of chromium gradually accumulates iron therein. As the proportion of iron increases the rate of pick up of chromium therefrom decreases. Since the surface of a chromised ferrous metal substrate normally contains 30-40% chromium metal, it follows that, when the chromium available on the surface of the source has dropped to this level, chromising ceases. In practice it is necessary to discard the source before this stage is reached in order to secure an acceptable rate of chromising. Thus, such processes are compromises between wastage of halogen and usage of chromium and whilst permitting a more economic usage of halogen necessitate discarding a substantial proportion of the chromium employed.

In the chromising process wherein the workpiece is packed with a powder containing ammonium halide and chromium, substantially all the halogen fed to the furnace is utilised in the chromising process by reaction of the ferrous halide formed with the chromium in the pack forming more chromous halide, which in turn reacts with the substrate surface producing more ferrous halide. The halogen is thus used repeatedly in the reactions involving transfer of chromium from the pack to the substrate and iron from the substrate to the pack. However, the chromium source again becomes contaminated with iron. Therefore, in order to secure satisfactory chromising it is necessary to use an excess of chromium, this excess being removed with the powdered packing at the end of the process.

According to the present invention a chromium coated substrate is heated in a furnace through which is passed a stream of a non-oxidising gas containing a hydrogen halide to a temperature of the order of 600° C., which is below that at which chromising takes place. After sufficient of the halogen required for the chromising process has been fixed onto the surface of the substrate by reaction with the coating and exposed substrate, the gas flow is stopped. The substrate is subsequently heated to the temperature at which chromising takes place. We find that by using this procedure substantially all the halogen and chromium fed to the furnace are utilised in the chromising process. The process of the invention also has the important result that it makes it possible to carry out chromising at temperatures of the order of 800° C. which are substantially lower and the temperatures hitherto necessary.

Accordingly, the present invention provides a process for the chromising of ferrous metal substrates which comprises:

(1) Applying a porous adherent chromium-containing coating to a ferrous metal substrate;

(2) Heating the coated substrate in a stream of a non-oxidising gas containing a hydrogen halide to a temperature such that the hydrogen halide reacts with the surface of the coated substrate which temperature is below that at which any appreciable amounts of the resultant

metal halides would be removed therefrom by evaporation; and

(3) Subsequently stopping the flow of gas and heating the coated substrate to a temperature of at least 750° C. for as long a period as is required to alloy all the chromium in the initial coating with the substrate and form an alloy coating of the desired thickness.

We believe that the mechanism by which this process enables effective chromising to be achieved using substantially all the chromium in forming the coating and the minimum amount of halogen is as follows. During the period when the hydrogen halide is introduced into the furnace, this is fixed on the substrate surface as a mixture of chromous and ferrous halides. On raising the temperature some or all of these halides vapourise. The chromous halide reacts with exposed ferrous metal, chromising the ferrous metal and forming ferrous halide. The ferrous halide reacts with the chromium rich layer depositing iron in this layer and forming more chromous halide. Thus, the halogen is used repeatedly in the chromising process, as in the known pack process. However, since the source of chromium is already bonded to the substrate surface, the iron deposited in the chromium is not wasted, as in the pack process and those processes in which ferrous chloride is removed from the furnace, but forms an integral part of the final alloy layer on the substrate surface. The chemical "ferrising" of the original chromium layer in the process of this invention aids the thermal ferrising which is also taking place in the chromising operation, since it leads to more rapid formation of the chromium/iron alloy layer. If our belief as to the mechanism of the process is true, it is this factor which enables the process to operate at a lower temperature than the known processes. The role of ferrous chloride in bringing about chemical ferrising has not hitherto been appreciated and in the known processes where a non-oxidising gas is continuously passed through the furnace during chromising, such chemical ferrising is not possible and the advantages of the process of this invention cannot be realised.

In carrying out the invention, the ferrous metal substrate is first degreased and pickled and is then coated with a chromium-containing coating. The substrate may be mild steel, stainless steel or high carbon steel and may be in the form of shaped articles or, alternatively, in the form of sheet or strip material. The coating is one which contains chromium in a form which is capable of reacting with the halogen content of the vapor present in the furnace in stage 2 of the process. It may be in the form of chromium metal or an alloy thereof, for example ferro-chrome. The coating may also contain other metals which it is desired to incorporate in the coating of the substrate, for example nickel and aluminium. However, in order that an appreciable amount of chromium be incorporated into the substrate during chromising, it is desirable that the initial coating contain at least 20%, preferably 50% or more of chromium.

The term adherent is used herein to mean that the coating must be sufficiently adherent to the surface of the ferrous metal substrate to enable it to be handled during transfer from the coating operation to the furnace, or, in the case of steel strip, to permit the strip to be coiled without the coating becoming detached. The chromium-containing coating may be deposited upon the surface of the substrate by any well 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 chromium containing powder previously distributed over the surface of the ferrous metal.

The amount of chromium which is initially applied in the coating of the substrates depends upon the final use to which the treated substrate is to be put and the properties desired for such an end use. Whilst the process

of the invention may be used to incorporate very small amounts of chromium in the alloy coating of the substrate, it is of especial application in the formation of corrosion-resistant surface alloys which contain at least 13% chromium. Where mild steel is being chromised to produce a corrosion resistant coating, it is usual to provide a chromium/iron alloy layer on the surface of the mild steel which is 0.002 to 0.003 inch thick. In applications where the mild steel is to be drawn or formed after chromising, it is desirable that the coating should not have too high a chromium content. For such applications a layer containing approximately 30% chromium is desirable. To obtain such a layer 0.002-0.003 in. thick an initial coating must be applied to the substrate at a rate of from 11 to 17 grams of chromium per sq. ft. of the surface of the substrate. However, as indicated earlier, the initial coating of the substrate must be porous in order to permit diffusion of the chromous and ferrous halide vapours therethrough. The porosity depends to a large extent upon the thickness of the coating and the method by which it is applied to the substrate. Thus, if the chromium is electrolytically deposited upon the substrate the maximum thickness which may be deposited without serious loss of porosity is of the order of 0.001 inch. Where the chromium is applied as a powder of size 200 mesh BS and this powder is compacted upon the substrate by a rolling operation, the coating may be up to 0.003 inch thick. Thus, where a particular rate of deposition of chromium on the surface of the substrate is required, the method used to achieve this coating is determined by whether or not the particular method produces a coating which is porous enough to facilitate diffusion of the chromous and ferrous halides therethrough. However, we have found that, in general, the application of a coating which is from 0.0001 to 0.001 inch thick provides a satisfactory result with a variety of coating methods.

The coated substrate is then subjected to a first heating stage (stage 2) in a furnace having a non-oxidising atmosphere containing a hydrogen halide. In order to obtain the non-oxidising atmosphere, it is preferred to purge the furnace of oxygen before commencing the heating operation by passing therethrough a non-oxidising gas. The non-oxidising gas may be hydrogen, argon or other inert gases. The hydrogen halide may be introduced into the furnace atmosphere either directly as the anhydrous gaseous acid or by passing the non-oxidising component of the atmosphere through an aqueous solution of the acid and subsequently drying the gas stream before it enters the furnace. Alternatively the halogen may be introduced with hydrogen into the furnace. The hydrogen halide may on the other hand be generated by a compound which dissociates on heating to form a hydrogen halide. For example, there may be included in the furnace charge an ammonium or other halide which decomposes on heating to give the hydrogen halide. It is preferred that the hydrogen halide employed be hydrogen chloride or hydrogen bromide.

The temperature at which the first heating stage is carried out, as indicated above, is that at which reaction between hydrogen halide and the coating and/or exposed iron on the surface of the substrate would occur but below that at which any appreciable amount of the metal halides formed would be removed therefrom by evaporation. In practice we have found that this temperature usually lies within the range 400° to 700° C., preferably at about 600° C., though where aluminium is incorporated in substantial quantities in the initial coating, it may be necessary to employ temperatures as low as 180° C. to minimise the loss of aluminium halides from the furnace. The furnace is maintained at this temperature while the passage of non-oxidising gas is continued with the addition of a hydrogen halide. The amount of hydrogen halide in the gas stream and the rate of passing of the gas stream through the furnace are preferably ad-

justed so that there is little or no hydrogen halide in the furnace off-gases.

The incorporation of hydrogen halide in the furnace atmosphere is continued until sufficient halogen has been fixed on the surface of the substrate to ensure that a satisfactory speed of chromising in the stage 3 of the process of the invention is achieved. Although the speed of chromising in stage 3 of the process in general increases with an increase in the amount of halogen fixed on the surface of the substrate, the use of two great amount of halogen results in wastage of metals which would otherwise have formed part of the alloy coating since these metals are left as metal halides which are removed from the system at the end of the heating period. The amount of hydrogen halide incorporated into the chromium coating will therefore generally vary from about 30% to 60%, preferably 50 to 60%, of the theoretical amount of hydrogen halide required to react with all the chromium in the coating.

When the desired amount of halogen has been introduced into the furnace the flow of gases therethrough is stopped, preferably in such a manner that the furnace remains under a slight positive pressure in order to minimise the possibility of leakage in of air, which might cause oxidation of the chromium or the chromous and ferrous halides.

In stage 3 of the process the temperature of the furnace is raised to a temperature of at least 750° C. at which temperature chromising takes place and is held at this elevated temperature for as long a period as is required to alloy all the chromium in the initial coating with the ferrous metal and form an alloy coating of the desired thickness. For any given amount of chromium coated onto the substrate it is possible to obtain alloy coatings graduating from thin alloys of high chromium content to thick alloys of low chromium content. The thickness and composition of the alloy coating obtained from any given amount of chromium are controlled by the conditions, that is the time and temperature, under which chromising is achieved and the halogen content of the initial coating. In general the thickness of the alloy coating increases with an increase in these variables within the limits outlined herein. Thus, a corrosion resistant coating on mild steel having a thickness of 0.002 to 0.003 inch and containing approximately 30% chromium may be achieved by carrying out the chromising at 800° C. for a period of about 36 hours. Alternatively, coating containing 80 to 90% chromium and only 0.0005 inch thick may be obtained by carrying out the chromising at 750° C. for approximately 36 hours.

However, the interdependence of time, temperature and halogen content is complex and it is possible to obtain the same alloy coating by many permutations of the variables. It is not possible to specify which permutation would be the optimum for any one operation since the choice of the optimum is dependent upon factors, such as the cost of operating the plant used, which are peculiar to each operation. However, the optimum may be readily determined by simple trial and error tests. As a rough guide we have found that the use of chromising times of from 4 to 70 hours and of temperatures of from 800 to 1000° C. preferably 850° C. provides satisfactory results. Although we prefer to operate at temperatures below 1000° C. there is no set upper limit at which the chromising may be carried out, since in practice this limit is set by the nature of the substrate itself and, to a lesser extent, by the nature of the initial chromium coating applied to the substrate. The temperature employed should not be so high as to cause distortion of the substrate and/or coating or to cause any appreciable damage by overheating. In fact it is preferred to operate at as low a temperature as it possible having regard to the other variables. Having determined the optimum conditions where an initial coating containing a given amount of chromium is used, we have found that substantially these conditions may also be

employed with initial coatings containing other amounts of chromium to obtain coatings of the same thickness, provided the proportion of halogen to chromium in the initial coating is maintained. Where the proportion of halogen is altered it will usually be necessary to vary the time or temperature accordingly.

When the chromising has been completed to the desired extent, the residual halogen compounds in the furnace atmosphere may be removed from the furnace by purging with a non-oxidising gas before the furnace is cooled. Alternatively the furnace may be allowed to cool and the residual halides removed from the surface of the treated substrate by washing, for example with water. The treated substrate possesses a chromium/iron alloy surface whose depth and chromium content will vary with the chromising conditions employed. This coating is insoluble in boiling 50% nitric acid. Where surface coatings containing a high proportion of chromium have been obtained, such coatings have a bright appearance, particularly when the initial chromium coating of the substrate has been obtained by electro deposition.

The invention will now be illustrated by the following examples.

EXAMPLE 1

20 gauge 0.2% carbon steel sheet is degreased by immersion in an alkaline cleaner and is then treated anodically in 50% sulphuric acid for 30 seconds at a current density of 400 A./sq. ft. The sheet is transferred to a catalyzed chromic acid chromium plating bath and a current of 300 A./sq. ft. is passed until a layer of chromium 0.0003 in. thick has been deposited. The coated sheet is washed and dried and loaded into a suitable furnace. The furnace is purged with hydrogen and heated to 600° C. A quantity of chlorine equivalent to 60% of that theoretically required to react with the chromium in the coating is injected into the hydrogen purge, over a period of 6 hours. The flow of gases is then stopped and the furnace is heated to 800° C. and maintained at this temperature for 36 hours. After cooling, the sheet is removed from the furnace. The surfaces are silver-grey in colour and are resistant to corrosion by water, aqueous sodium chloride, aqueous nitric acid, etc., even after bending, etc. Removal of a portion of the coating by filing and treatment with 50% aqueous nitric acid to dissolve the steel core reveals a coating insoluble in nitric acid of 0.0009 in. thickness. Analysis of the coating after dissolution in hydrochloric acid shows an iron content of 71%.

EXAMPLE 2

0.2% carbon steel sheet is pickled and degreased as in Example 1 and plated with chromium 0.0012 in. thick. The sheet is then heat treated as in Example 1 for 36 hours. A chromised coating 0.0021 in. thick, containing 52% Fe is obtained.

EXAMPLE 3

20 gauge 0.2% carbon steel sheet is degreased and pickled as in Example 1 and plated with chromium 0.0004 in. thick. The sheet is then heat treated as in Example 1 except that the final stage of the heat treatment is one of 36 hours duration at 750° C. A chromised coating 0.0004 in. thick containing 12.7% iron is obtained.

EXAMPLE 4

20 gauge 0.2% carbon steel sheet is degreased, pickled and plated with 0.0003 in. chromium. Portions of the sheet are chromised, using 33% and 47% respectively of the theoretical quantity of hydrogen chloride required to react with the chromium. The final stage of the heat treatment is one of 36 hours duration at 800° C. Coatings of thickness of approximately 0.0003 in. containing 3.3% and 10% iron respectively are obtained.

EXAMPLE 5

20 gauge 0.2% carbon steel sheet is degreased electrolytically in an alkaline clearer and pickled in 10% v./v.

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nitric acid for 10 seconds chromium metal powder (200 BS mesh) is applied to the surface at the rate of 16.5 g./sq. foot and this is compacted onto the surface by passing the sheet between rolls. The strip is then chromised as in Example 1. On removing the sheet from the furnace it is found that a chromised coating 0.0034 in. thick containing 62% iron has been formed.

A similar sample of steel coated with 31.8 g./sq. ft. chromium powder which is subsequently compacted by rolling, and then the coated sheet chromised under identical conditions, gives a chromised coat 0.003 in. thick containing 16% iron.

EXAMPLE 6

20 gauge 0.2% carbon steel sheet is cleaned and pickled as in Example 5. A quantity of 200 mesh BS chromium powder is applied to the surface of the strip sufficient to give a coating after compacting by passing the strip between rolls of 0.00045 in. thickness. The steel sheet is then loaded into the furnace and after purging and heating to 600° C. a quantity of bromine equivalent to 80% of that required to react with all the chromium is injected with hydrogen into the furnace. The flow of gases is then stopped and heat treatment is carried out at 800° C. for 36 hours. A chromised coating 0.0008 in. thick containing 59% iron is obtained.

EXAMPLE 7

0.8% carbon steel sheet is degreased and pickled as in Example 1 and plated with chromium to a thickness of 0.00015 in. The sheet is then chromised as in Example 1. A chromised coating 0.00043 in. thick containing 61.2% iron is formed.

EXAMPLE 8

18/8 stainless steel sheet is degreased and pickled, plated with chromium to a thickness of 0.0003 in., and chromised as in Example 1. On removing the chromised stainless steel from the furnace it is found that enhanced resistance to high temperature oxidation has been obtained. On subjecting pieces of the original stainless steel, the chromium plated stainless steel and the chromised stainless steel to air at 800° C. for 7 hours, the samples showed weight gains of 0.38, 0.04 and 0.00 g. per sq. ft. of surface respectively.

We claim:

1. A process for the chromising of ferrous metal substrates which comprises:

- (1) applying a porous adherent chromium-containing coating to a ferrous metal substrate;
 - (2) heating the coated substrate in contact with a stream of hydrogen or at least one inert gas containing a hydrogen halide to a temperature such that the hydrogen halide reacts with the surface of the coated substrate, which temperature is below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation; and
 - (3) subsequently stopping the flow of gas and heating the coated substrate to a temperature of at least 750° C. for as long a period as is required to alloy all the chromium in the initial coating with the substrate and form an alloy coating of the desired thickness.
2. A process according to claim 1 wherein the coated substrate is heated in contact with a stream of hydrogen or argon containing a hydrogen halide to a temperature of from 400° to 700° C.
3. A process according to claim 2 wherein the temperature is of the order of 600° C.
4. A process according to claim 1 wherein the coated substrate is heated in contact with a stream of hydrogen or argon containing a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide.

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5. A process according to claim 4 wherein the hydrogen halide is produced in situ within the furnace.

6. A process according to claim 5 wherein the amount of hydrogen halide fed to the furnace is from 50% to 60% of the theoretical amount required to react with all the chromium in the coating on the substrate.

7. A process according to claim 1 wherein the amount of hydrogen halide fed to the furnace is from 30% to 60% of the theoretical amount required to react with all the chromium in the coating on the substrate.

8. A process for the chromising of ferrous metal substrates which comprises:

- (1) applying a porous adherent chromium-containing coating to the ferrous metal substrate;
- (2) heating the coated substrate in contact with a stream of at least one inert gas containing a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide to a temperature of from 400° to 700° C.; and
- (3) subsequently stopping the flow of gas and heating the coated substrate to a temperature of from 800° to 1000° C. for a period of from 4 to 70 hours.

9. A process for the chromising of ferrous metal substrates which comprises:

- (1) applying a porous adherent chromium-containing coating to the ferrous metal substrate by electrolysis, said chromium-containing coating being up to 0.001 inch thick;
- (2) heating the coated substrate in contact with a stream of hydrogen containing a hydrogen halide to a temperature such that the hydrogen halide reacts with the surface of the coated substrate, which temperature is below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation; and
- (3) subsequently stopping the flow of gas and heating the coated substrate to a temperature of at least 750° C. for as long a period as is required to alloy all the chromium in the initial coating with the substrate and form an alloy coating of the desired thickness.

10. A process for the chromising of ferrous metal substrates which comprises:

- (1) applying a porous adherent chromium-containing coating to the ferrous metal substrate by electrolysis, said chromium-containing coating being up to 0.001 inch thick;
- (2) heating the coated substrate in contact with a stream of hydrogen or argon containing a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide to a temperature of from 400° to 700° C.; and
- (3) subsequently stopping the flow of gas and heating the coated substrate to a temperature of from 800° to 1000° C. for a period of from 4 to 70 hours.

11. A process according to claim 10 wherein the chromium powder applied to the substrate has a particle size of 75 microns or less and the coating is up to 0.003 inch thick.

12. A process for the chromising of ferrous metal substrates which comprises:

- (1) providing a porous adherent chromium-containing coating on the ferrous metal substrate by applying a powder selected from a group consisting of chromium and chromium alloys having a particle size of up to 75 microns and subsequently compacting this powder upon the substrate by means of a rolling technique, said coating being up to 0.003 inch thick;
- (2) heating the coated substrate in contact with a stream of hydrogen containing a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide to a temperature of from 400° to 700° C.; and

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- (3) subsequently stopping the flow of gas and heating the coated substrate to a temperature of from 800° to 1000° C. for a period of from 4 to 70 hours.
13. A process for the chromising of ferrous metal substrates which comprises:
- (1) providing a porous adherent chromium-containing coating on the ferrous metal substrate by applying a powder selected from the group consisting of chromium and chromium alloys to the surface of the ferrous metal substrate and subsequently compacting this powder upon the substrate by means of a rolling technique;
 - (2) heating the coated substrate in contact with a stream of hydrogen or argon containing a hydrogen halide to a temperature such that the hydrogen halide reacts with the surface of the coated substrate, which temperature is below that at which any appreciable amounts of the resultant metal halides would be removed therefrom by evaporation; and
 - (3) subsequently stopping the flow of gas and heat-

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ing the coated substrate to a temperature of at least 750° C. for as long a period as is required to alloy all the chromium in the initial coating with the substrate and form an alloy coating of the desired thickness.

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