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G. A. SAMUEL ET AL

3,222,212

PROCESS FOR CHROMIZING

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Fig. 1.

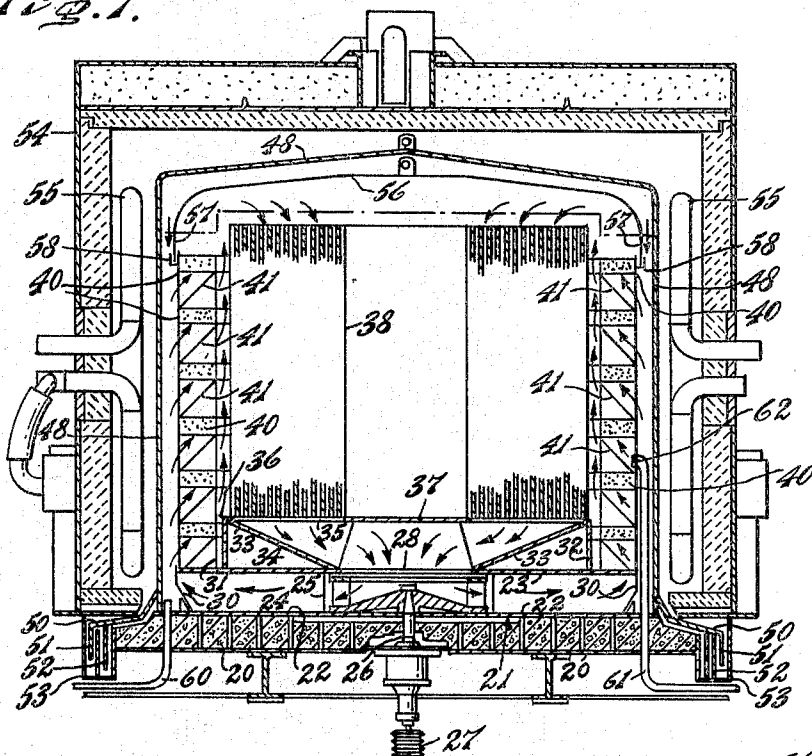
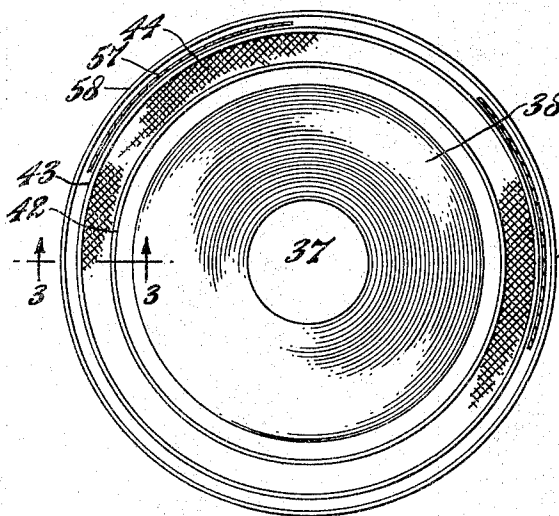


Fig. 2.

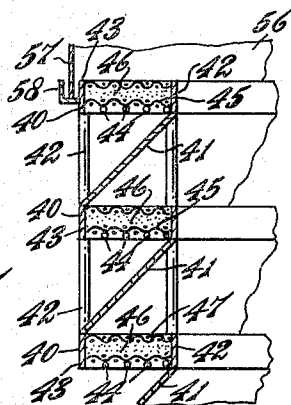


Fig. 3.

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1

3,222,212

PROCESS FOR CHROMIZING

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13 Claims. (Cl. 117—107.2)

The present application is a continuation-in-part of our copending application Serial No. 172,231, filed February 9, 1962, now abandoned for Process for Chromizing and Product, which is a continuation-in-part of our copending application Serial No. 160,764, filed December 20, 1961, now abandoned for Process for Chromizing and Product, which is in turn a continuation-in-part of our copending application Serial No. 119,085, filed June 23, 1961, now abandoned for Metal Diffusion. Subject matter relating to the Chromizing Product has been divided and appears in divisional application Serial No. 307,263, filed September 6, 1963, for Process of Chromizing and Product.

The present invention relates to the chromizing of ferrous metal parts, particularly low carbon steel and ingot iron, although permissibly including medium and high carbon steel.

A purpose of the invention is to circulate chromizing gases in a uni-directional manner in contact with the surface of ferrous metal work, which may suitably take the form of an open coil, but may be of some other character, and thus to obtain more rapid and more economical chromizing with lower expenditures of chromium and with greater throwing power.

A further purpose is to chromize more effectively at low temperature.

A further purpose is to circulate a gaseous atmosphere containing a halogen gas which essentially remains in the retort, endlessly through a source of chromium not in contact with the work, and then in contact with the work and then back to the source of chromium, the gaseous atmosphere always flowing continuously in the same direction.

A further purpose is to mount the work in the retort, the work suitably being an open coil, so that a stream of chromizing gases which has passed through a source of chromium not in contact with the work is directed under positive pressure so that it flows in contact with the work and then returns to the source of chromium without division or short-circuiting.

A further purpose is to circulate a carrier gas containing a halogen-containing gas through a source of chromium not in contact with the work in a chromizing retort, and to maintain the concentration of halogen in the halogen-containing gas at a sufficiently low level as to avoid priming the source of chromium or depositing a large excess of liquid or solid chromium halide on the source of chromium which would tend to react with moisture and interfere with chromizing in a later operation.

A further purpose, particularly when chromizing with hydrogen and hydrogen bromide (or bromine or chromous bromide), is to control the concentration of hydrogen bromide or the like so as to obtain more effective chromizing without accompanying disadvantages. This is particularly important where the source of chromium is porous and may become impregnated with liquid or solid chromium bromide which will be difficult to remove. In the preferred process of the invention, the partial pressure of hydrogen bromide or the like is kept at a value which will come close to saturating the vapor phase with chromium bromide, while at the same time not being high enough to impregnate the source of chromium with liquid or solid

2

chromous bromide and not high enough to deposit a great excess of liquid or solid chromous bromide, which when the retort is opened will react with oxygen in the air and moisture and cause difficulty on the next cycle of operation.

A further purpose is to utilize a combination of carrier gas and halogen-containing gas which has an inlet dew point of below -100°F. , and preferably below -110°F. , and is substantially free from oxygen.

A further purpose is to control the quantity of oxygen (as such or as oxides which can react) present in the retort so that the dew point of the exit gases will be below -40°F. or preferably be below -60°F. , and will in any case not be higher than $+5^{\circ}\text{F.}$

A further purpose is to protect the work during heating up to a temperature not exceeding 1100°F. by a non-explosive gas such as nitrogen and then to eliminate the presence of nitrogen and at higher temperatures avoid nitrogen and thereby avoid nitriding effects.

A further purpose is to chromize using ferrochrome or chromium or other source of chromium having a particle size range between 60 mesh and $\frac{1}{4}"$, the source of chromium being permissibly either porous chromium or dense chromium.

A further purpose is to agitate the particles forming the source of chromium during chromizing preferably by fluidizing the bed so that the particles are supported by the chromizing gas stream and thus surrounded by the chromizing gas.

A further purpose is to employ a surface area of the source of chromium to the area of the work which will be between 0.2 to 1 and 10 to 1 or higher, preferably between 0.8 to 1 and 10 to 1, and most desirably between 3 to 1 and 5 to 1.

A further purpose is to conduct the chromizing preferably at low temperatures in the range from 1600°F. to 1800°F. , particularly when using the system involving a source of chromium, hydrogen as a carrier gas, and hydrogen bromide (or bromine or chromous bromide) as a halogen-containing gas. Suitable times will be of the order of 5 to 10 hours or longer.

A further purpose is to use a coil space between adjoining laps of the order of 0.135 to 0.22 inch.

A further purpose is to employ the principles of the invention on steels or other ferrous metal products of low carbon content, having carbon contents below 0.03% and preferably below 0.003%.

A further purpose is to apply the principles of the invention to steels which have been stabilized for example by titanium, columbium, vanadium or tantalum, so that the carbon content uncombined with the alloying element is kept very low, below 0.03% and preferably 0.003%.

A further purpose is to render the steel more suitable for chromizing by decarburizing the steel, preferably in the same operation, as by introducing wet hydrogen, and in a temperature of the range of 1300°F. to 1400°F. and then thoroughly drying the retort before chromizing.

A further purpose is to obtain a chromized steel which will be non-aging, having an aging index of from 0 to 2%.

A further purpose is to redistribute any superficial skin which is abnormally high in chromium and which may tend to be brittle by diffusion of the chromium into the base metal by continuing the exposure to hydrogen at or about chromizing temperature while removing the halogen so that chromizing will cease.

Further purposes appear in the specification and in the claims.

In the drawings we have chosen to illustrate one of the numerous types of apparatus which may be used in carrying out the process of the invention.

FIGURE 1 is a vertical cross sectional view of one

form of apparatus for subjecting open coils of strip or sheet material to chromizing treatment.

FIGURE 2 is a horizontal cross sectional view taken substantially on the line 2—2 of FIGURE 1, and illustrating the form and arrangement of the trays for carrying the source of chromium.

FIGURE 3 is an enlarged vertical cross sectional view taken substantially on line 3—3 of FIGURE 2, of several of the upper trays carrying the source of chromium.

The particular furnace shown in respect to its constructional details forms no part of the present invention.

Describing in illustration but not in limitation and referring to the drawings:

Extensive use has been made in the prior art of chromizing processes in which a powder pack including a source of chromium such as ferrochrome and inert bodying material are placed in contact with the work and a compound such as ammonium chloride, ammonium bromide, ammonium bifluoride and ammonium iodide is caused to break down liberating halogen-containing gas to promote chromizing.

Efforts have also been made in the past to chromize by employing a halogen-containing gas such as hydrogen chloride, and a carrier gas such as hydrogen which were passed over a source of chromium to cause formation of chromous chloride and then to pass the chromous chloride over the work and out of the retort. Both of these processes have been subject to the limitation that they are relatively slow, cumbersome and expensive. They also are not always reliable, particularly because of infiltration of oxygen and in some cases because of the presence of moisture.

In the case where it is desired to produce chromized products from sheet or strip, there are two alternate possibilities. The practice usually used has been to produce the final components and then to chromize them after forming. This is subject, however, to the disadvantage that there is a very poor work load in the retort and the parts often suffer from heat distortion. Also, the effects of previous cold work are destroyed.

On the other hand, it has not been possible in the prior art to obtain effective chromizing of large areas in coil form.

In the case of the pack method, a serious limitation has been the very poor heat transfer. Another limitation in the pack method has been the poor throwing power which made it important to position the work in intimate contact with the pack. Poor finish on the work has also been a difficulty, as well as poor physical properties of the steel since treatment temperatures have been relatively high and also the treatments have been rather prolonged.

Where chromizing gas has been generated outside the retort and passed through the retort and then out of the retort, in the prior art, the waste in chemicals has been very serious. Furthermore, the directional character of the gas flow has produced shadowing effects in the deposition which limit the throwing power transverse to the direction of gas flow.

The previous systems have also been very uneconomical from the standpoint of chemical utilization. The present invention is concerned particularly with overcoming the difficulties noted and particularly obtaining a more economical, more efficient and more effective chromizing operation.

In accordance with the invention, the chromizing gases, which will preferably consist of a carrier gas plus a halogen-containing gas, are sequentially and repetitively passed through or over a source of chromium such as metallic chromium or ferrochrome, and then in contact with the work, and then back through or over the source of chromium to regenerate and again in contact with the work. This is accomplished under forced circulation as from a pump (or fan), so that the entire gaseous con-

tent of the retort can be recycled in a time as short as one second.

This process, therefore, permits very efficient charging of the retort, since it is no longer necessary to place in contact with, or interpose between the many layers of ferrous metal work, a powder pack as in the well known powder pack prior processes. The throwing power of the retort gaseous content is so great that it is possible to effectively chromize relatively tremendous areas of work as for example coiled sheet or strip in which the individual laps of the coils are opened sufficiently to allow gas circulation through the coil. The best prior art practice by the pack method in chromizing sheets has utilized a spacing of three sheets to the inch. By the technique of the present invention it is readily possible to chromize with laps of coil which are as close as 4 to 5 to the inch.

Since there is no longer any need for refractory materials such as alumina, the time of heating up the retort can be reduced to a minimum. Furthermore, the efficiency of charging the retort is greatly increased because no extra space must be occupied by the powder pack.

As compared with the prior process in which chromizing gases have been generated outside the retort, the present process uses the same gas content over and over, instead of discharging it from the retort when it has once come in contact with the work. As a consequence, it is only necessary to introduce or withdraw gas from the retort once the chromizing operation has started in sufficient quantity to maintain a superatmospheric pressure in the retort or to compensate for infiltration of air and to otherwise remove objectionable material such as water vapor which may have been present in the retort or may have been formed due to reduction of oxides present. Therefore, the chemical consumption is reduced to a minimum.

By reusing the gas, the waste of chromium and other metal halides, which would result from wasting the gas when it has once been used for chromizing is avoided, and also the halogen itself is conserved.

Use has been made in the prior art of static gaseous processes, in which the gaseous content which is to accomplish chromizing is essentially all contained within a sealed retort, in some cases with venting provided. These processes are extremely slow, and as compared with them, the throwing power of the present process is infinite since the gases can be made to follow any desired course within the retort which will bring them in contact with all parts of the work.

Efforts have been made in the past to chromize using a rotating retort containing gases and a powdered or granulated pack. In this case, however, the gas at any point is a haphazard mixture of regenerated and unregenerated gas unlike the gaseous content of the retort in the present invention.

The present invention lends itself particularly to the chromizing of very large charges, for example of open coil steel sheet, since there is no appreciable limitation of soaking time and no serious problem of heat transfer. Single coils as large as 20,000 pounds may be chromized in a single retort operation and in a time of the order of only 10 hours at chromizing temperature.

From the standpoint of the product, there have been serious difficulties in chromizing by prior art practices. When using the pack method, under certain circumstances it is likely that chromium from the source of chromium will sinter on the surface and produce roughness. There has also been difficulty through producing relatively abnormally light chromizing at certain places where gaseous diffusion or where pack material were not present.

The present invention lends itself particularly to the production of very high quality chromided steel products since chromizing is carried out in the absence of nitrogen and the chromizing operation can relieve from the presence of dissolved nitrogen. The absence of nitrogen is also

advantageous because it prevents nitriding the source of chromium which deteriorates the source of chromium and also tends to contaminate the steel.

The invention is particularly suitable for chromizing at low temperatures, which tends to minimize or avoid harm to the steel, either by grain growth or due to distortion.

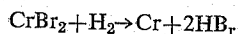
The chromized case which is obtained in the present invention is of very superior quality from the standpoint both of ductility and corrosion resistance because of the extremely low carbon content of the ferrous metal work, resulting in low chromium carbide content in the chromized layer. The carbon content of the case may be as low as 0.02% carbon when the case is formed on 20 gage steel which has been decarburized prior to chromizing.

Many prior art processes which have used a pack have depended upon priming of the pack so that it is impregnated with solid or liquid phase chromous chloride. It has been found that the priming of the source of chromium is likely to cause serious difficulties in subsequent processing. Certain processes require priming as a separate technique, which is time consuming and expensive, and use the priming material as the source of chromizing potential until it is so depleted that it must be replaced. For example, in some instances in the prior art extreme care must be exercised in protecting the primed source of chromium from moisture and oxidation, as otherwise this will lead to very high dew points in the chromizing gases, impairing the quality of the chromizing.

GASEOUS CONTENT

While the process of the present invention can operate effectively using any one of the halogens, as for example hydrogen chloride, chromous chloride, hydrogen fluoride, chromous fluoride, chlorine, hydrogen bromide, bromine, chromous bromide, hydrogen iodide, chromous iodide and various other metal halides having sufficiently high vapor pressure at chromizing temperature, such as aluminum chloride and aluminum bromide, there are great advantages in the process of the present invention in using hydrogen bromide, chromous bromide, or bromine, as later explained, and particularly when operating at temperatures of 1600° to 1800° F. These halogens are referred to herein as halogen acid gases.

There is also an important advantage in using hydrogen as a carrier gas when a bromine chromizing system is being employed, that is, hydrogen plus hydrogen bromide, or hydrogen plus bromine, or hydrogen plus chromous bromide. Hydrogen is readily available, can be obtained with very low oxygen contents and nitrogen contents and is not objectionable from the standpoint of effect on the steel. Hydrogen tends to promote the reduction type of chromizing reaction as follows:



Thus, the hydrogen carrier gas acts as a conveyor of the halogen-containing gas, and tends to reduce oxygen which may be present in the retort for example as oxide. Hydrogen procured with an oxygen content less than 2 ppm. and a dew point less than -110° F., and a nitrogen content less than 2 ppm. is obtainable at relatively low cost, and can be used in copious quantities to flush out the system and be added during chromizing in such quantities as are required to remove any oxygen introduced by leakage and also to remove water formed either by reaction with oxides which are present, or water driven off from the interior of the retort which was formerly absorbed or chemically combined. It will be understood that in many cases a porous source of chromium will be used which may give off moisture, oxygen or other objectionable materials under chromizing conditions. The source of chromium likely will contain some chromium oxide, and the hydrogen carrier gas will reduce this to metallic chromium when

supplied in sufficient quantities, and thus maintain low dew points in the exit gases as later explained.

It will of course be evident that adequate inspection techniques should be instituted to insure the purity of the hydrogen, as this is a critical feature of the process.

A convenient way to determine whether there is sufficient freedom from moisture vapor and oxide in the retort is to determine the dew point of exit gases. Dew points as high as +5° F. can be tolerated in the exit gases, although for best results, the dew points in the exit gases should be lower than -40° or preferably lower than -60° F.

In a retort having an internal free space of approximately 300 cubic feet, it was desirable to maintain a flow of hydrogen carrier gas of the order of 2000 cubic feet per hour during the drying period prior to mixing with the halogen-containing gas, and after chromizing started and halogen-containing gas was added, it was found that a flow rate of 300 cubic feet per hour was adequate (input of hydrogen at standard conditions). These gases are measured at 70° F. and one atmosphere.

In order to do effective chromizing with hydrogen bromide or a chemically equivalent amount of chromous bromide or bromine in a carrier gas of hydrogen, it is quite important that a minimum concentration of hydrogen bromide by volume of 2.00% be maintained in the temperature range from 1600° to 1800° F. where bromide chromizing is most effective. If the concentration of hydrogen bromide or equivalent is less than 2.00% by volume, satisfactory chromizing is not obtained.

In many cases, it is also important that a maximum percentage of hydrogen bromide or a chemically equivalent percentage of chromous bromide or bromine be maintained in the mixture with hydrogen carrier gas which is sufficiently low to prevent the deposition in the retort of solid or liquid chromous bromide in any substantial quantity. If solid or liquid chromous bromide deposits, difficulty is then likely to be encountered by absorption of oxygen and moisture when the retort is opened, and a great deal of delay and waste of hydrogen will occur in starting up the next heat before adequately low dew points can be obtained in the retort atmosphere and effective chromizing can start.

While the presence of deposited solid or liquid chromous bromide on the surface of the retort or on the surface of massive (dense) chromium or ferrochrome is objectionable, for the reasons stated and also because of the tendency to clog up gas passages, traps, and the like, the difficulty is much more serious when porous ferrochrome is used, for example ferrochrome produced by powder metallurgy techniques including vacuum sintering. In this case the solid, or more particularly liquid chromous bromide, tends to impregnate the porous ferrochrome and is particularly difficult to free from oxygen and moisture in subsequent cycles, acting as a continual drag on the chromizing potential of the retort.

It will, of course, be evident that if minor amounts of solid or liquid chromous bromide are deposited on the surface of the retort, they can be removed by washing or dissolving in water, but this procedure is not effective with porous ferrochrome.

In the preferred procedure, sufficient chromous bromide is formed to just saturate the gas phase inside the retort. From this standpoint the concentration of hydrogen bromide or the equivalent should be as close as convenient to but not substantially exceeding the upper limits set.

The following table shows maximum and minimum limits for hydrogen bromide in percentages by volume measured at 70° F. and one atmosphere for various temperatures in the range from 1600° to 1800° F. This applies only to mixtures of hydrogen bromide in hydrogen, although chemically equivalent percentages will likewise apply for mixtures of chromous bromide with hydrogen and of bromine with hydrogen.

7
Table I

Temperature (°F)	Percentage by volume of hydrogen bromide in hydrogen	
	Minimum	Maximum
1,600	2.00	2.67
1,650	2.00	3.65
1,675	2.00	4.29
1,700	2.00	5.13
1,750	2.00	7.01
1,800	2.00	9.45

It will be evident that the quantities of gases can be determined by weighing the gas cylinders from which the gases are supplied.

Where bromine is used instead of hydrogen bromide, with the hydrogen carrier gas, it is desirable to bubble the hydrogen through the bromine or pass the hydrogen through a chamber in which the bromine is being evaporated. However, this procedure is not recommended in case the process of the invention is used with chlorine because of the extreme hazard of an explosion when chlorine is introduced into hydrogen.

It will be evident that mixtures of halogen-containing gases which contain different halides may be employed in the process of the invention if desired, such as hydrogen bromide plus hydrogen chloride; hydrogen bromide plus hydrogen iodide; hydrogen iodide plus hydrogen chloride; hydrogen fluoride plus hydrogen bromide; hydrogen fluoride plus hydrogen chloride; hydrogen fluoride plus hydrogen iodide, etc.

SEQUENTIAL OPERATION

It is of great importance in some aspects of the process of the present invention to provide a positive means of circulating the gases in the retort, along with passages or chambers which will secure a sequential flow of substantially all the gases in the retort.

The positive circulation of the gases will conveniently be applied by any suitable pumping means, such as a fan or blower. Experience has indicated that for best results the pump should be capable of recirculating substantially all the gases of the retort at a high rate, conveniently once each second. In order to achieve this result, it has been found that in a retort having a free volume of the order of 300 cubic feet, a circulation flow of 13,600 cubic feet per minute (measured at 70° F. and one atmosphere pressure) is satisfactory.

It is quite important that the direction of gas flow will cause the gaseous atmosphere to pass through the source of chromium, so as to regenerate the gases and form new chromous bromide or other chromous halide, and then to pass the gases after regeneration over or around the work so as to accomplish chromizing. The gases should then be returned as promptly as possible to the intake of the pump or fan in order to come in contact again with the source of chromium. It is important for the success of the reaction that both the source of chromium and also the work be held at chromizing temperature and that the gases be at chromizing temperature, so that if the regeneration is accomplished by passing the gases through the source of chromium in an adjoining or separate retort chamber, such chamber should be adequately maintained at a temperature of approximately the chromizing temperature. It will be evident that once a chromizing cycle is completed, the source of chromium will be depleted in chromium content at the surface. It is very desirable prior to the next cycle or by the beginning of the next cycle to promote surface chromium restoration by diffusion from the interior of the individual particle to build up the chromium concentration at the surface of the source of chromium.

This is accomplished in the present invention by allow-

ing a period of several hours to elapse in the next chromizing cycle during which the source of chromium is held at an elevated temperature, preferably equal to or greater than the chromizing temperature, prior to the introduction of halogen and the inception of chromizing.

In the preferred apparatus, the source of chromium is located adjacent the heating means, and is therefore, at a slightly higher temperature than the work. This promotes more rapid chromium restoration in the initial stages of the new cycle prior to the introduction of halogen, and also allows the chromium source to supply chromium to the halogen-containing gases more rapidly during the chromizing cycle. All connecting passages must also be maintained at chromizing temperature to avoid condensation of the chromium halides.

The pump, of course, can be anywhere in the system.

SOURCE OF CHROMIUM

The source of chromium for use in the process of the invention can either be chromium or an alloy high in chromium such as ferrochrome. Where ferrochrome is used, it should be the low carbon and low nitrogen grade so as not to deposit nitrogen or carbon, and should preferably have a chromium content in excess of 65%, a typical analysis by weight being as follows:

Chromium	70% maximum.
Silicon	2% maximum.
Carbon	0.015% maximum.
Nitrogen	0.025% maximum.
Iron	Substantially balance.

The ferrochrome can be of the powder metallurgy porous type or of the dense solid type if desired. Chromium can be used. A typical analysis is:

Chromium	98.5% minimum.
Carbon	0.015% maximum.
Nitrogen	0.025% maximum.

It has been found that higher superficial chromium contents in the case may be obtained when chromium metal is used as source of chromium rather than ferrochrome. Thus, in a typical example, superficial chromium content in the case of 44% was obtained using chromium metal whereas when undepleted ferrochrome was used, the superficial chromium content of the case was 42%. In both instances a hydrogen bromide-hydrogen system was used at a temperature of 1650° F., and the chromizing was carried on at chromizing temperature.

While various sizes of chromium or ferrochrome particles can be used, in most cases it will be desirable to employ particles larger than 60 mesh (Tyler standard mesh per linear inch) and not in excess of 1/4 inch. A common nominal size is 1/16 inch or 1/32 inch. The size is chosen in order to strike a reasonable balance between the surface area of the source of chromium which should desirably be large and the ease with which the gases can penetrate the source of chromium.

Ferrochrome particles having the following sizes were studied in detail and actual counts of the particles per pound were made:

Table II

Size in inches	No. of granules per pound
-1/4, +1/8	16 (10 ²)
-1/8, +1/16	70 (10 ²)
-1/8, +1/32	57 (10 ³)
-1/16, +1/32	67 (10 ³)
-1/16, +1/64	19 (10 ⁴)
-1/32, +1/64	39 (10 ⁴)

The particles were generally cubical or rectangular. Accordingly, it was possible to calculate the surface area in square feet per pound of ferrochrome particles and the following data were obtained:

Table III

Size in inches	Surface area in square feet per pound
$\frac{1}{16}, +\frac{1}{32}$	2.3
$\frac{1}{8}, +\frac{1}{16}$	2.6
$\frac{3}{16}, +\frac{1}{8}$	4.4
$\frac{1}{4}, +\frac{3}{16}$	6.1
$\frac{5}{16}, +\frac{1}{4}$	7.1
$\frac{3}{8}, +\frac{1}{4}$	8.9

The surface area of the source of chromium should bear a relationship to the surface area of the work, which will be in the range of 0.2 to 1 to 10 to 1, and preferably 0.8 to 1 to 10 to 1, and most desirably between 3 to 1 and 5 to 1. For best results the ratio should be about 4 to 1. Larger proportions of surface area of the source of chromium may be employed, but are not necessary in common practice. Smaller area ratios decrease the chromium content of the case.

The area ratios have an effect on the superficial chromium percentage and the average chromium percentage in the case. Using treatments at 1650° F. for 10 hours at heat, with between 3.2 and 4.2% by volume of hydrogen bromide in hydrogen and a steel of AISI 1010 composition which was decarburized before chromizing to a carbon content of 0.002%, the values shown in the following table were obtained:

Table IV

Heat No.	Ratio area ferrochrome to area of work	Case in mills	Surface chromium, percent	Average chromium in case
896-----	0.83	1.0	28	21
897-----	0.44	0.80	28	19
898-----	0.40	0.77	21	18
902-----	0.20	0.72	18	16

TEMPERATURE

While chromizing using the broad principles of the present invention can be carried out at temperatures in the range between 1500 and 2300° F., the preferred temperature range should be between 1600° and 1800° F. and preferably between 1600° and 1750° F. where the hydrogen bromide-hydrogen system is employed. Chromous bromide, the effective chromizing agent, has an adequate partial vapor pressure within this temperature range.

Table V

VAPOR PRESSURE OF CHROMOUS BROMIDE
IN ATMOSPHERES

Temperature ° F.:	Atmospheres
1600 -----	0.041
1800 -----	0.19

It will be evident that if a lower rate of transportation of gases is employed, it may be desirable to use a system having higher vapor pressures such as the chromous iodide system in order to get as effective chromizing under the new conditions.

The preferred temperature range in using the hydrogen bromide-hydrogen system is 1675° to 1700° F. where open coils are being treated in the range of gages from 24 through 16 for thickness of the sheet. Using this temperature and a time not exceeding 10 hours chromized case depths of 0.0015 inch minimum can readily be obtained at 1700° F., and after 15 hours at 1660° F. case depths of 0.0011 inch can readily be obtained.

For low carbon steels having an uncombined carbon content not exceeding 0.03% where the effective chromizing agent is chromous bromide, it is preferred ordinarily not to go to temperatures above 1750° F. Where

the carbon content is greater than 0.08% temperatures no higher than 1900° F. are preferred, but in such cases chromous chloride or chromous fluoride will preferably be used as the effective chromizing agent.

STEEL COMPOSITION

The most important aspect of the composition of the steel or other ferrous metal is its carbon content. It is important in obtaining ductile cases on open coil strip and sheet to have carbon contents not exceeding 0.03% and preferably not exceeding 0.003%.

Steels and ingot irons of such low carbon contents are available commercially.

In many cases, however, it is preferable to obtain the low carbon content by starting with an initial moderately low carbon content such as AISI 1010 steel, and then further reducing the carbon content by decarburizing. The decarburizing can be carried out as a separate operation using any well recognized decarburizing technique.

It is, however, preferable to decarburize prior to the chromizing cycle but in the same heat. This can be accomplished rather readily by subjecting the open coil or other ferrous metal work to wet hydrogen at a temperature in the range of 1300° to 1400° F. An appreciable quantity of moisture is present in the hydrogen. An important aspect of the present invention is that the source of chromium is not primed and therefore it is not necessary to eliminate the effect of this moisture on primed chromium or ferrochrome prior to chromizing. After decarburization is complete, reducing the carbon content to a level below 0.003% and suitably of the order of 0.002%, it is merely necessary to pass dry hydrogen through the system during the heat up period to chromizing temperature in order to obtain adequately low dew points on the exit gases in order to start chromizing.

It will be understood that where decarburization is carried out in the presence of ferrochrome or chrome using wet hydrogen at say 1300 to 1400° F., the source of chromium itself is oxidized and to some extent carburized. However, after the steel has given up substantially all of its carbon in the form of effluent carbon monoxide gas and even after the carbon monoxide concentration of the effluent gases has reached a low value of 0.01% by volume, the use of wet hydrogen is continued for several hours in order to reduce the carbon content of the chromium source to its original value. Subsequent introduction of dry hydrogen incident to the elevation of temperature for chromizing, results in deoxidizing of the source of chromium, so that effective chromizing can be carried out at chromizing temperature.

It sometimes is desirable at the beginning of chromizing to introduce a richer halogen content than will subsequently be used. This accelerates the formation of the proper amount of chromous halide especially when very low flow rates of carrier gas are employed. Thus it may be advantageous in this case to use an initial content of halogen in the hydrogen stream of say ten to twelve percent of hydrogen bromide, and after a short time, say one hour, reduce the halogen content to the limits previously referred to.

In some cases the steel may be stabilized by the alloying of titanium, columbium, vanadium or tantalum in a quantity of the order of at least four times the carbon content. Such steels should not have an uncombined carbon content in excess of 0.03%, and preferably not in excess of 0.003%.

The invention is also applicable to silicon relay steels which often contain silicon in the range from 1 to 4½% with adequately low carbon contents as specified above.

The process of the invention can also be used to overcome the effect of chromium depletion at the surface, for example in straight chromium and chromium nickel steels of the stainless type, including the 200, 300, 400, and 500 series of stainless steel. Thus, annealing and other heat treating operations can be carried out without special

precautions against chromium depletion and those stainless steels which have been annealed in non-protective atmospheres can then be treated in the process described herein so as to bring about appropriate chromium restoration at the surface of the stainless steel.

There is evidence from immersion testing in corrosive media such as 5% aerated salt water solution at room temperature that for most favorable corrosion resistance the carbon content in the chromized case should be below 0.05%. Thus where a specimen with a carbon content in the chromized case of 0.32% failed after 43 hours, specimens with carbon contents in the chromized case of 0.061%, 0.094% and 0.051% withstood 120, 144 and 168 hours salt immersion respectively. Yet the chromium content at the surface of the failed specimen was 30% and the chromium contents at the surfaces of the good specimens were 33%, 28% and 33% respectively. Other data indicate that reasonably good salt spray resistance can be obtained if the carbon content is limited to 0.15% and for outstanding resistance to salt immersion or salt spray the carbon content in the chromized case should be kept below 0.05%.

HEATING AND COOLING

In actually carrying out the process of the invention, it may as a matter of economy or convenience be desirable to accomplish lower temperature heating and lower temperature cooling in an atmosphere other than an atmosphere of pure hydrogen. Thus, for example in heating up to a temperature of 1100° F. the atmosphere, if desired, may be nitrogen or nitrogen plus hydrogen in any desired proportions but generally less than 8% hydrogen by volume in order to avoid explosion problems. Similarly, at the end of the cycle the work may be cooled down from 1100° F. to room temperature in such an atmosphere of nitrogen or nitrogen plus hydrogen, without difficulty. The nitrogen at these low temperatures is not objectionable from the standpoint of reaction with the work to cause poor aging properties.

COIL SPACING

The spacing between adjoining surfaces of one lap and the next lap of the coil should be adequate to permit proper gas flow in the open coil. Good results have been obtained using such spacing in the order of 0.13 to 0.22 inch. This spacing may be maintained in a manner which has been previously practiced in the annealing art, by using spacers such as twist-over wires at the edges of the coil which have intruding loops at the edges of turns. Also, it will be evident that spacing can be obtained by corrugated strips or the like applied between laps at the top and bottom edges of the coil.

DIFFUSION

In some cases there is a tendency to deposit localized areas having superficial chromium skins which are brittle and lacking in corrosion resistance. In order to overcome this difficulty, it is in many cases desirable to remove the halogen gas and hold the work at or about chromizing temperature for an additional time to permit rediffusion of this skin. A time of 1 hour at chromizing temperature in dry hydrogen is sufficient. The flow of hydrogen during the rediffusion period need merely be sufficient to maintain a dew point of less than +5° F. and preferably less than -40° F., or most desirably less than -60° F. The hydrogen flow should be continued in adequate quantities to prevent the danger of building up an explosive mixture with air in the retort.

PROPERTIES OF THE CHROMIZED WORK

After treatment times of 10 hours at 1650° F. using the hydrogen bromide and hydrogen system, average case depths of 0.0010 inch have been obtained with an average chromium content of at least 20% and as high as 23%, and a surface chromium content of at least 31% and as high as 34%.

One of the important properties is that the case is quite ductile, so that the sheet is capable of undergoing an Olsen cupping test of 0.40 inch without failure of the core. The case started to orange peel at a value of 0.25 inch. The steel is free from aging and has an aging index of between 0 and 2%.

Thus, the steel of the invention has a number of exceptional properties which cooperate to provide good formability. An ASTM grain size of the core of the chromized steel not coarser than 3 is readily obtained. A carbon content in the core can readily be obtained which does not exceed 0.0015% and a nitrogen content in the core can readily be obtained which does not exceed 0.0005%. As already explained, the steel has an aging index between 0 and 2%. The steel can readily be obtained with an Olsen cupping value of the core of at least 0.40, and an Olsen cupping value of the case at which orange peel begins to appear of at least 0.25 inch.

One important aspect of the invention is that the carbon and nitrogen contents of the case will be related to the gage of the steel which has been chromized. Starting with a decarburized plain carbon steel which has a carbon content not in excess of 0.002%, and chromizing on both sides, the maximum carbon content in the chromized case will be as follows in relation to sheet thickness:

Table VI

Thickness (in.):	Maximum percent carbon in case on sheet chromized on both sides
.1406	0.15
.1250	0.14
.1094	0.12
.0937	0.096
.0781	0.082
.0703	0.072
.0625	0.065
.0562	0.058
.0500	0.052
.0437	0.046
.0375	0.040
.0344	0.036
.0312	0.033
.0281	0.030
.0250	0.027
.0219	0.024
.0187	0.021

Typical physical properties for the chromized plain carbon steel with a carbon content of less than 0.0015% is tensile strength 37,000 p.s.i.; yield strength 17,100 p.s.i.; elongation in 2 inches 45%. The ASTM grain size ranges from 3 to 4.

Using titanium stabilized steel (0.05% carbon, 0.25% titanium) and chromizing at 1650° F. for 15 hours at heat, it was found that exceptionally good mechanical properties accompanied with fine grain size were obtained. The chromizing was of normal high quality. The terminal grain size was ASTM No. 6-8, while the terminal grain size was ASTM No. 6-8, while the yield strength was 21,000 p.s.i. and the ultimate tensile strength was 46,000 p.s.i. and the elongation in 2 inches was 38%.

Table VII shows the results of chromizing according to the invention, but in several cases deliberately changing variables to illustrate the effect of various factors. In some cases where proper control has not been obtained, poorer chromizing has resulted.

In all cases the steel was a 20 gage coil of the weight and carbon content shown, the steel being plain carbon.

The weight of low carbon ferrochrome is indicated in the various examples. The size of the ferrochrome particles was in every case below 1/4 inch and larger than 1/64 inch.

The chromizing temperature in every case was 1650° F. to 1660° F. and the chromizing times are given.

Table VII

Heat Number	841	842	864	870	954	896	897	898	902	1004	1023	1080
Coil weight (lbs.)	3,000	2,700	2,900	3,000	2,200	3,100	3,100	3,100	3,100	1,800	3,600	2,940
Percent carbon content of steel prior to chromizing	0.002	0.002	0.001	0.001	0.001	0.002	0.002	0.002	0.002	.001	(*)	.002
Spacing between laps (in.)	0.20	0.20	0.20	0.18	0.18	0.18	0.18	0.18	0.18	0.20	0.15	.23
Weight of ferrochrome (lbs.)	3,600	3,590	3,542	3,442	3,480	3,600	1,800	1,655	815	4,380	3,860	2,160
Size of ferrochrome (in.)	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$	$-\frac{1}{4}+\frac{1}{8}$
Ratio of area of ferrochrome, area of steel	2.1	2.3	2.0	2.0	2.7	2.0	1.0	0.92	0.45	4.5	3.6	3.9
Exit dew point of hydrogen just prior to use of hydrogen halide (° F.)	-95	-72	-64	+3	-30	-62	-80	-65	-59	-42	-20	-41
Percent by volume of hydrogen halide used	1.45 HBr	3.64 HBr	7.05 HBr	7.82 HBr	3.68 HCl	4.01 HBr	3.95 HBr	3.75 HBr	3.16 HBr	11.4 HBr	9.0 HBr	4.4 HBr
Chromizing time (hrs.)	8.5	9.5	10.0	5.0	10.0	10.0	7.0	10.0	12.0	15	15	15
Case depth (mils)	<0.10	1.10	1.10	0.90	0.50	1.0	0.80	0.77	0.75	1.05	1.13	1.01
Average percent chromium in case	<12	20.0	22.9	22.5	<12	20.5	19.3	18.2	16.6	22	23	20
Percent chromium at the surface of the case	<12	26	31	25	12-18	28	28	23	18	32	29	27
Aging index (percent)	15	1.5	0	0-2.8	2.0-16.5	0	0	0	0	0	-----	0

*Coil decarburized in same heat, but as initial low temperature phase prior to chromizing phase.

During chromizing in each instance a hydrogen flow of 300 to 1000 cubic feet per hour measured at 70° F. and one atmosphere pressure was provided so as to exclude infiltration of oxygen and moisture, and permit measurement of exit dew point as indicated.

In Heat 841, with a concentration of hydrogen bromide in hydrogen of 1.45% by volume as measured at 70° F. and one atmosphere, poor chromizing was obtained, there being too little hydrogen bromide present.

When the concentration of hydrogen bromide as measured above was increased to 3.65% by volume as in Heat 842, good chromizing was produced. It will be noted that the steel has an aging index of 1.5%, whereas the aging index was 15% in Heat 841, this being the normal aging index for this steel unchromized.

In Heat 864 where the hydrogen bromide concentration as measured above was 7.05% by volume, it is shown that there is very slight improvement in the chromizing, although the aging index has been reduced to 0%. In this case there was a deposit of a great excess of chromous bromide. The porous ferrochrome used in this heat showed a chromous bromide content of 245 grams per 100 pounds. This indicates a substantial level of priming.

It is interesting to note that in Heat 842 where the hydrogen bromide concentration was 3.64% by volume, the porous ferrochrome was found to contain no chromous bromide.

In Heat 870, the results obtained are very similar to those of Heats 842 and 864, despite the fact that the exit gases now have a high dew point of +3° F. at the beginning of the chromizing cycle, and chromizing was accomplished in the relatively short time of five hours, although the concentration of hydrogen bromide was increased to 7.82% by volume, as measured above.

In order to compare the benefit obtained by chromous bromide with the chromizing where chloride was used at this low temperature of 1650° F., Heat 954 employs a concentration of hydrogen chloride of 3.68% by volume measured at 70° F. and one atmosphere, which is substantially comparable with the concentration of hydrogen bromide in Heat 842. However, in Heat 954 poor chromizing was obtained, as indicated by the low case depth of 0.54 mil, the low average chromium concentration in the case of less than 12%, the low surface concentration of chromium in the case of 12 to 18%, and the wide variation in aging index between the outside of the coil and the inside (2% to 16.5%). This is a clear indication of poor chromizing because the vapor pressure of chromous chloride is too low at the temperature of 1650° F. to provide an effective chromizing in the particular equipment at the circulation rate obtained. Notwithstanding the poor chromizing, there was actually priming

of the ferrochrome by chromous chloride to the extent of 216 grams per 100 pounds of ferrochrome.

Heats 896, 897, 898 and 902 employ conditions which are the same except that the ratio of the area of the source of chromium to the area of the steel progressively decreases from a maximum of 2.0 in the case of Heat 896 to a minimum of 0.45 in the case of Heat 902. Even in the case of Heat 896 the average chromium content in the case and the percentage of chromium at the surface of the case are not high enough to indicate optimum chromizing, although they were adequate from the standpoint of producing a low aging index in all cases, and the product is satisfactory for many applications. The important point to note, however, is that the average chromium content in the case decreases as the ratio of the area of the source of chromium to the area of the steel decreases, and the same is true of the percentage chromium at the surface of the case.

In Heat 1023 the 3600 pound AISI 1008 coil was decarburized at 1350° F. using inlet hydrogen at +100° F. dew point, and in the same cycle, but at a higher temperature after dry out with -110° F. dew point hydrogen it was chromized using more finely crushed ferrochromium in the $-\frac{1}{8}$ ", $+\frac{1}{32}$ " size range.

In Heat 1080 fine enough ferrochromium ($-\frac{1}{16}$ ", $+\frac{1}{4}$ ") was used so that the weight of the 20 gauge coil (2940 lbs.) now exceeds the weight of ferrochromium (2160 lbs.).

APPARATUS FOR CARRYING OUT THE PROCESS

While anyone of a wide variety of apparatus can be used to carry out the process, we illustrate in the drawing a very simple and convenient form which in itself is not part of the present invention. This apparatus was used in the above examples.

The apparatus may be in some way similar to that described by J. Arnold in Iron and Steel Engineer, August 1960, pages 91 to 111, which discusses open coil annealing, patent application Serial No. 155,585, filed November 29, 1961, now Patent No. 3,183,888, for Apparatus for Surface Coating of Strip Metal or the like.

Referring now to FIGURES 1, 2 and 3, the chromizing apparatus illustrated includes a base structure 20 in which is supported a change support and a diffuser 21 having a bottom wall 22, a top wall 23, and a plurality of radially extending diffusing vanes 24. A centrifugal type fan or blower 25 is supported in the central portion of diffuser 21 on a shaft 26 and is adapted to be driven from a suitable power source (not shown) through a drive pulley 27 or the like. The top wall 23 of diffuser 21 is provided with a central opening 28 forming the inlet to the blower 25 and the outer periphery of diffuser

21 is open at 30 forming an annular outlet passage for the atmosphere moved outwardly by the blower 25.

Supported on the upper wall portion 23 of the diffuser 21 is a plenum chamber structure 31 having an outer wall 32, and inclined annular baffle wall 33 and a plurality of radially extending support webs 34. Carried on these radial support webs 34 is a perforate coil supporting grid 35, and outer imperforate ring member 36 and an imperforate center closure plate 37.

When it is desired to chromize a coil of strip steel, the coil is first rewound into open form with the laps of the coil spaced apart preferably a distance equal to from one to ten times the thickness of the strip being treated. This may conveniently be effected by the procedure described in the application of Lee Wilson and Edwin A. Corns, Serial No. 639,939, now Patent No. 3,114,539 filed February 13, 1957. Such an open coil is indicated at 38 in FIGURE 1 and is carried by the grid 35 of the plenum chamber 31 after being placed thereon by an electromagnet or other suitable lifting means. As seen in FIGURE 1, the coil 38 is disposed with its axis vertical and with the outer lap just overlying the imperforate outer ring 36 of the plenum chamber 31 and with its inner lap just overlying the outer edge of the center closure plate 37.

Thus, it will be evident that the fan can suck the chromizing gases through the open coil in an axial direction without the possibility of short-circuiting to bring through the coil, gases which have not been regenerated as later described.

A series of superimposed annular material trays 40 for the source of chromium are arranged vertically spaced apart, in stacked or tiered relation, as best seen in FIGURE 3. These trays 40 are supported and held in position by inclined annular baffle spaces 41 and vertically extending circumferentially spaced apart spacer rods 42. Each tray 40 has an annular inner wall 42' and outer wall 43, is open at the top, and has a perforate bottom wall 44 which may conveniently be made of expanded metal or the like having sufficient strength and rigidity to serve its structural function while permitting the free flow of atmosphere therethrough. On top of the perforate bottom wall 44 is a layer of wire screening 45 of sufficiently fine mesh to prevent the passage of the source of chromium, indicated at 46 in the drawings, therethrough. Another annular ring or layer of screening 47 is placed on top of the source of chromium on the trays 40 to prevent it being picked up by the atmosphere moving through the trays and carried into the coil 38, particularly when the bed is fluidized.

As seen in FIGURE 1, the stack of trays 40 is supported on the upper wall portion 23 of the charge support and diffuser 21 just outside of the plenum chamber 31 and extends up in spaced relation to the outer periphery of the coil 38. To facilitate handling, it is preferably that the top tray 40 of the assembly be disposed slightly below the top of the coil 38 so that these trays will not have to be removed each time a new coil 38 is positioned for processing.

After the open coil 38 is placed on the grid 35 of plenum chamber 31 within the bank of trays 40 as seen in FIGURE 1, a removable housing in the form of an inner cover 48 having an open bottom bell shape is placed over the trays 40 and coil 38. This housing or inner cover 48 is supported at its lower edge on the base 20 and has an outwardly extending portion 50 having dependent flanges 51 and 52 which fit into a sealing channel 53 in the base structure 20. This channel 53 contains oil, sand or other suitable sealing material to form a gas-tight seal between the base 20 and the inner cover 48. If desired, a water cooled gasket can be used.

To provide the necessary heat to accomplish the chromizing action a bell-type furnace structure 54 is removably supported on the base structure 20 and carries a series of circumferentially arranged heating elements such as

the radiant combustion tubes 55 of well known type. The heat from the combustion tubes 55 is transferred through and by the wall of the inner cover 48 to the atmosphere circulating within the inner cover. It will be understood that although combustion tubes are illustrated as a source of heat, electrical heating elements or other suitable source of heat may be employed. It will also be understood that the base 20, diffuser 21, plenum chamber 31, trays 40, inner cover 48 and furnace 54 are preferably circular in horizontal cross-sectional form and that the furnace structure 54 is placed over the inner cover 48 preparatory to a chromizing operation and is removed after the heating operation is completed.

In order to direct the flow of atmosphere within the inner cover 48 in the desired path and to cause substantially all of the circulating atmosphere to pass repeatedly through the spaces between the laps of the coil without by-passing or channeling around the outside or through the inside of the coil, we provide a removable top baffle member 56 which has a downwardly depending outer flange portion 57 adapted to rest in an annular sealing trough or channel 58 disposed at the outer periphery of the uppermost tray 40. Suitable granular sealing material may be carried in the trough 58 to form a substantially gas-tight seal between the top tray 40 and the baffle member 56. This baffle member 56 is removably supported in the channel 58 and it will be understood that it is placed in position after the coil 38 is positioned on the top of the plenum 31 and before the inner cover 48 is dropped over the assembly. Other means may be provided for preventing the by-passing of atmosphere from the blower 25 past the trays 40, without getting through them, into the coil 38. For example, a baffle wall member could be carried by the inner cover 48 and extend across between the wall of the cover and the outer periphery of the top tray 40.

As it is necessary to purge the atmosphere within the inner cover 48 of the air at the start of a chromizing operation, an atmosphere outlet pipe 60 extends up through the base 20 up into the space within the inner cover 48 and it is provided with suitable valves and pressure regulating devices (not shown) to control the flow therethrough. One or more gas inlet pipes 61 also extend through the base 20 and, as seen in FIGURE 1, preferably have their upper outlet ends 62 disposed closely adjacent the source of chromium.

In the operation of the apparatus described below, assuming that the trays 40 are properly filled with a suitable source of chromium, the open coil 38 is placed in position on the grid 35 of the plenum chamber 31, the top baffle member 56 is put in place and the inner cover 48 is then lowered over the entire assembly. Next the bell-type heating furnace 54 is positioned over the inner cover 48 and the atmosphere within the inner cover 48 is purged of air by causing a suitable carrier gas, for example a mixture of approximately 95% nitrogen and 5% hydrogen to be charged into the inner cover 48 through the pipe 61 while permitting the escape of atmosphere through the outlet 60.

Before the purging operation, the blower 25 is started and then the furnace 54 is fired up to proper temperature. Because of the arrangement of the baffles and support members, the flow of the atmosphere circulated by the blower 25 is, as seen from the arrows of FIGURE 1, radially outwardly from the blower 25 past the diffuser vanes 24, out through the outlet passage 30 and upwardly along the wall of the inner cover 48 where it is heated from the cover 48. Due to the inclined baffle spacers 41 between the trays 40, and to the top baffle member 56, all of the atmosphere must necessarily pass upwardly through the perforated bottom 44 of the trays 40 and through the source of chromium 46 thereon. The screening 47 on top of the coating material 46 prevents the particles of chromium from being blown out of the trays. It then passes up along the outer surface of the open coil

38 and, as it cannot pass down through the center opening in coil 38 because of the closure plate 37, moves downwardly through the spaces between the laps of the coil 38 in intimate contact with all parts of the entire surface of the strip material making up the coil. After the atmosphere leaves the bottom of open coil 38, it passes through the supporting grid 35 and is directed by the inclined baffle wall 33 to the central opening 28 of the blower 25. This circulation is continued as long as the blower 25 operates.

By use of the apparatus described, the circulating atmosphere may be utilized first to heat the charge to the desired temperature without coating action and then, after admission of the activating agent, for conveying the metallic chromium from the granular material 46 to, and distributing it uniformly and evenly over, the entire surface of the strip metal making up the open coil 38

The construction material of the retort in many cases may be plain carbon steel or low alloy steel which will undergo chromizing in the furnaces. There may be advantages, however, in certain cases in employing heat resisting alloys such as high chromium and high chromium nickel alloys including stainless steel and Inconel (79.5% nickel; 13% chromium; 6.5% iron; 0.25% manganese; 0.25% silicon; 0.2% copper).

Because of the importance of avoiding oxygen and moisture within the retort, it is very desirable that any fire brick or other refractory used in construction of the retort be sheathed or covered with metal so that it will not be exposed to the gases within the retort.

MOTION OF THE SOURCE OF CHROMIUM

If desired, the bed formed of the source of chromium may be in motion or fluidized, by desirably blowing the gases of the retort through the bed at a suitable velocity and employing a particle size which is of fine enough and sufficient bed depth to provide levitation.

It will be understood that, of course, grain size control can be used so that some of the particles of the source of ferrochrome are of larger size which will not levitate and others are of smaller size which will levitate in the fluidized bed. Screen will suitably prevent the particles from becoming entrained in the gases.

In view of our invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art to obtain all or part of the benefits of our invention without copying the process or product shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

In view of our invention and disclosure, what we claim as new and desire to secure by Letters Patent is:

1. A process of chromizing ferrous metal work, which comprises providing a retort which is closed with respect to the atmosphere, placing in the retort ferrous metal work to be chromized and closing the retort, introducing into the retort a halogen acid gas, introducing into the retort a carrier gas free from nitrogen contamination, maintaining the retort and the work at a temperature of between 1500° and 2300° F., providing a source of chromium out of contact with the work, distributed in a series of layers through which the gas can flow sequentially, there being a ratio of the total surface area of the source of chromium to the total surface area of the work which is between 0.8 to 1 and 5 to 1, maintaining the source of chromium at a temperature between 1500° and 2300° F., providing a channel from the source of chromium to the work and providing a return channel from the work to the source of chromium, circulating the halogen gas and the carrier gas in admixture under positive pressure sequentially through the layers of the source of chromium and then in contact with the work to chromize the work and then back through the source of chromium to regenerate the gas, maintaining the chromizing potential high by withdrawing from the retort increments of carrier gas and

halogen gas and maintaining a sufficiently low dew point in the inlet gases, so that the dew point in the exit gas is not in excess of +5° F., and continuing the circulation of the gas and the chromizing for a time of at least 5 hours.

2. A process of claim 1, in which the carrier gas is oxygen-free hydrogen having a dew point when introduced into the retort of less than about -100° F.

3. A process of claim 1, in which the halogen gas is hydrogen bromide and in which the carrier gas comprises oxygen-free and nitrogen-free hydrogen.

4. A process of claim 3, in which the source of chromium is porous, which comprises maintaining a percentage of hydrogen bromide by volume at 70° F. and one atmosphere pressure in relation to the chromizing temperature which conforms with the following:

Temperature (° F.)	Minimum	Maximum
1,600.....	2.00	2.67
1,650.....	2.00	3.65
1,675.....	2.00	4.29
1,700.....	2.00	5.13
1,750.....	2.00	7.01
1,800.....	2.00	9.45

5. A process of claim 1, in which the work is stainless steel selected from the series 200, 300, 400 and 500, which has a depleted chromium content at the surface, the chromium content at the surface being replenished by the chromizing.

6. A process of claim 1, which comprises holding the source of chromium containing iron at a temperature higher than the temperature of the work prior to chromizing so as to diffuse chromium to the surface and diffuse iron to the interior of the source of chromium and thus replenish chromium at the surface.

7. A process of chromizing a coil of ferrous metal sheet having open spaces between laps, which comprises placing said coil in a chromizing retort with open spaces between the laps of the coil, maintaining in the retort a series of sequential layers of a source of chromium out of contact with the coil, establishing in the retort a circulating path for gas, which path brings the bulk of the gas within the retort into contact with the surface of the coil between the laps and then passes such gas sequentially through the layers of source of chromium, the ratio of the total surface area of the source of chromium to the total surface area of the sheet being between 0.8 to 1 and 5 to 1, introducing into the retort a halogen-acid gas, introducing into the retort a carrier gas free from nitrogen contamination, continuously circulating said halogen gas and said carrier gas through said path between the laps of the open coil and through the layers of source of chromium, maintaining the retort, the source of chromium, and the ferrous metal sheet at a temperature of between 1600° and 1800° F., withdrawing increments of gas from the retort, the dew point of the inlet gas and the rate of withdrawal being maintained so that the dew point of the exit gas is not in excess of +5° F., and continuing the chromizing operation for a time of at least 5 hours.

8. A process of claim 7, in which said halogen is bromine in the form of a material of the class consisting of hydrogen bromide, bromine and chromous bromide, and in which said carrier gas comprises hydrogen free from oxygen and free from nitrogen.

9. A process of claim 8, which comprises maintaining in the carrier gas a concentration of hydrogen bromide by volume measured at 70° F. and one atmosphere pressure shown by the following table, a chemically equiv-

alent concentration being employed where bromine or chromous bromide is used:

Temperature (° F.)	Minimum	Maximum
1,600	2.00	2.67
1,650	2.00	3.65
1,675	2.00	4.29
1,700	2.00	5.13
1,750	2.00	7.01
1,800	2.00	9.45

10. A process of claim 9, in which the ratio of surface areas is between 3 to 1 and 5 to 1.

11. A process of claim 7, in which the spacing between laps is in the range between 0.135" and 0.22".

12. A process of chromizing, which comprises placing an open coil of ferrous metal sheet within a retort, maintaining within the retort a body of protective gas which is predominantly nitrogen, heating the retort and the open coil and gas to a temperature of 1100° F., introducing a carrier gas of pure hydrogen and displacing the nitrogen from the retort, heating the retort and its contents to a temperature between 1600° and 1800° F., introducing a halogen into the gas, circulating all gas in the retort through a circulating path which includes the open coil work and a source of chromium separate from the work, and thereby chromizing the work, purging the retort of the halogen content by pure hydrogen and cooling the retort down to a temperature of 1100° F. and then introducing a gas predominantly containing nitrogen and displacing the hydrogen from the retort.

13. A process of claim 12, in which the halogen-containing gas is a gas selected from the group consisting of hydrogen bromide, bromine and chromous bromide.

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