

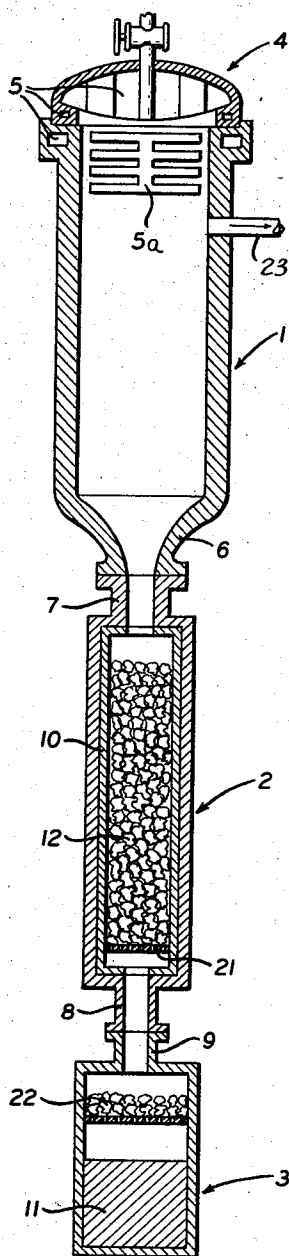
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PREPARATION OF DIFFUSION COATINGS ON METALS

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PREPARATION OF DIFFUSION COATINGS ON METALS

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10 Claims. (Cl. 117—107)

This invention relates to the preparation of diffusion coatings on iron and other metals and it has particular relation to the preparation of such coatings by reacting the metal to be coated with gaseous halogen compounds of suitable other metals.

It is an object of the present invention to provide a process and device for producing metallic diffusion coatings of high quality and uniform strength on articles consisting of iron, steel or other base metals, including articles having difficultly accessible parts.

It has been known that gaseous halogen compounds of suitable metals chemically react with solid iron and certain other base metals at elevated temperatures, forming gaseous halides of iron or said other metals and depositing the metallic element of the gaseous halogen compound or compounds used as starting material, in finest subdivision on the surface of iron or said other base metals. If the metallic element deposited or precipitated from the gaseous starting halogenide is capable of diffusion into the base metal at the temperature used, it will penetrate into the base metal, while atoms of the base metal will be brought from interior layers to the surface of the latter likewise by diffusion. The chemical reaction of the surface of iron, or said other base metals, can be carried on or continued by causing further amounts of the gaseous metal halide to come in contact with the iron or other base metal at diffusion temperature and removing the iron or other base metal halide formed in the reaction, from the iron or other base metal.

It has been found that in order to obtain high-grade, dense surface layers having the desired exact dimensions, on iron or other base metals, by the above mentioned chemical reaction between gaseous metal halides and solid iron or other base metals, it is essential that the gaseous metal halide or halides used as starting material be uniformly applied to all surface portions of the iron or other metal articles to be coated, i. e. at a uniform concentration of the gaseous halides in the reaction gas. Furthermore, the volume of metal deposited on iron or other base metal by said chemical reaction should be about equal to the volume of metallic iron, or other base metal, converted into and removed from the latter in the form of gaseous halide.

It has been found that said uniform application of the gaseous halide or halides requires the use of gaseous halides which do not contain admixtures, diluents or carriers. Owing to differences in specific gravity, the gaseous metal halides do not mix completely uniformly with carriers or diluents, e.g. inert gaseous carriers, and if the latter are used, uniformity of the surface coating is adversely affected. This also happens if a mixture containing gaseous and liquid and/or solid metallic halides is applied. If no other than gaseous metal halides are used, i.e. if the reaction gas consists of gaseous metal halides only, said lack of uniformity of the coating can be avoided even in the treatment of difficultly accessible surfaces of metallic articles, e.g. surfaces of long and narrow bores.

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However, the composition of the reaction gas consisting of gaseous metallic halides only, must be adjustable in order to adapt the reaction gas to the particular base metal on which the diffusion coating is supposed to be formed.

According to the present invention, the above requirements are met by placing the articles to be provided with a diffusion coating in a furnace which is connected during treatment with a second furnace and a third furnace interconnected to said second furnace, evacuating the three furnaces, producing the desired reaction gas to be used for coating said articles, in said second and third furnaces and regulating the composition of the reaction gas by the adjustment of the temperature in said second furnace and the temperature in the third furnace.

Thus, the main object of the present invention is to provide a process and a device and arrangement for providing metallic articles with a metallic diffusion coating of high quality by means of a reaction gas consisting of gaseous metallic halides, whereby the desired composition of the reaction gas is brought about by regulation of the temperature in said second furnace and of the temperature in said third furnace.

Other objects and the advantages of the invention will be apparent from the following specification and the appended claims and drawing, which disclose by way of example and without limitation some specific embodiments of and best ways for carrying out the invention.

In the embodiment shown in the drawing, articles consisting of the base metal, for example iron, are treated with a gaseous metal halide in a tubular furnace generally denoted by reference numeral 1. This furnace consists of highly heat-resistant steel and can be operated under ordinary atmospheric pressure, or excess pressure, or under vacuum. If it is desired to evacuate the furnace, a suction device or blower can be attached to pipe means 23 extending from the upper portion of the furnace. One end of furnace 1 is sealed by a cover 4, provided with cooling means 5, cooled, for example, by water, while its other end 6 is tightly connected with outlet 7 of a second tubular furnace generally denoted 2. Furnace 2 is tightly connected by its tubular extension 8 to tubular outlet 9 of a third furnace generally denoted 3. Thus, the three furnaces 1, 2, 3 are connected in series. They can be heated in any suitable manner, for example by immersion in heated salt solution, electric heating means, etc., not shown in the drawing. Furnace 2 is preferably provided with a ceramic lining 10, while furnace 3 can be made entirely of ceramic material, if desired. The three furnaces, 1, 2, and 3, are tightly connected with each other and their temperatures can be regulated by said heating means, separately and independently in each furnace. Furnace 3 may contain pieces 22 of a solid material arranged on a support. This solid material serves for preventing the entrance of liquid halide from furnace 3 into furnace 2, in the case of bumping of the boiling halide in furnace 3, and it consists for example of the metal present in furnace 2 or of some ceramic material. 5a denotes a ribbed insert, the temperature of which increases from that of cooled member 5 up to the temperature in the interior of furnace 1 and in the cooler ribs of which condensed halides, e.g. of iron are often deposited.

Example 1

If articles of iron should be provided with a diffusion coating of titanium, furnace 3 is charged with liquid titanium chloride (TiCl_4) as indicated at 11, while furnace 2 contains metallic titanium 12, in the form of pieces having a sufficiently large surface, e.g. pieces having an average size of 1 to 10 mm. The metallic titanium 12 rests on a perforated plate 21 arranged in

furnace 2, as shown in the drawing. In order to remove the air from the three furnaces, the system is first evacuated through a valve arranged preferably at the cover of furnace 1, the liquid titanium tetrachloride in furnace 3 being kept cold during this evacuation. After evacuation, there will be a pressure corresponding to the vapor tension of titanium chloride, in all three furnaces. As long as the titanium chloride is cold, this pressure is substantially below ordinary atmospheric pressure. Furnace 2 is now heated first to a temperature of for example about 400° C., at which the titanium tetrachloride vapors react with the metallic titanium 12, with the formation of titanium trichloride ($TiCl_3$) so that the gas entering furnace 1 consists of $TiCl_3$. Furthermore, furnace 1 which contains the iron articles to be treated (not shown in the drawing) is now heated to a temperature in the range of 700° to 1300° C., at which reaction of $TiCl_3$ with iron and diffusion of metallic titanium into the iron articles can take place, while furnace 3 is simultaneously heated to 100–150° C. in order to bring about the desired $TiCl_3$ vapor pressure which can be higher or lower than ordinary atmospheric pressure in the case of the present example. During this coating process, the temperature in furnace 2 is kept in the range of 400° to 700° C.

The gaseous titanium chloride ($TiCl_3$) reacts with the iron articles in furnace 1 with the formation of gaseous ferrous chloride ($FeCl_2$) which is condensed and collected on the cooled surfaces 5 and in the upper cooling ribs 5a of furnace 1. After sufficient titanium has been deposited in the treated iron articles, furnaces 1 and 3 are first permitted to become cool. By conducting the process for about 240 minutes, a titanium diffusion coating of 0.03–0.10 mm. thickness is obtained.

It is of particular advantage to operate furnace 1 at a high temperature at the beginning of the treatment and at a lower temperature at the end of the treatment. For example, the coating treatment is carried out for 240 minutes and the high temperature is applied for about 200 minutes and the low temperature for about 40 minutes. It has been found that by proceeding in this manner a particularly high concentration of the metal to be deposited in the base metal, can be attained in the top surface layer. In the treatment of iron and steel base metals in furnace 1, temperatures in the range of 1050° to 1300° C. can be used as high diffusion temperatures and the range of 700° to 1050° C. can be used for low diffusion temperatures. The same temperatures can be used in the treatment of hard metal alloys, e.g. metals having a tungsten carbide or titanium carbide-cobalt basis. These alloys can be treated also before being sintered. Thus the formation of diffusion coating and sintering can take place in the same step.

By maintaining the above described temperatures in furnaces 1, 2, and 3, respectively, the formation of a reaction gas consisting of $TiCl_3$ and the formation of very satisfactory titanium diffusion coatings on the iron articles is obtained.

Example 2

In order to obtain a uniform, dense and durable diffusion coating of chromium, the reaction gas must substantially consist of $CrCl_2$ vapor, because no uniform, satisfactory diffusion coatings are formed if there is substantial excess of Cl or Cr (in comparison with the formula of $CrCl_2$) in the reaction gas.

The articles to be coated—e.g. threaded pieces consisting of commercial soft iron—were placed in furnace 1 and the air was removed from the three connected furnaces by evacuation. Furnace 2 contained about 500 grams of chromium metal in small pieces and furnace 3 about 275 grams of $CrCl_2$. Furnace 1 was heated to about 1150° C., furnace 2 to about 1200° C., and the temperature in furnace 3 was kept at about 1000–1100° C. The pressure in the furnace system was about 30 Torr and the treatment was continued for about two

hours. At the end of this period, the pieces in furnace 1 were provided with a uniform, dense chromium coating of high quality.

Such satisfactory coating could not be obtained if—under otherwise equal conditions—furnace 2 was heated to 1100° C., whereby the proportion of Cr in the gaseous phase used in furnace 1 was reduced below the proportion corresponding to $CrCl_2$.

Example 3

In carrying out the present invention, diffusion coatings comprising several metals, such as coatings of titanium+chromium, or silicon+chromium, or vanadium+chromium, proved to be of particular interest. Such coatings can be, for example, prepared in a one step process by first depositing silicon or titanium at a relatively high pressure and subsequently depositing chromium at a relatively low pressure, i.e. below 100 mm. Hg, by cooling furnace 3 to the necessary extent. As a result of this treatment, a thick chromium diffusion layer of 0.35–0.5 mm. is formed in about four hours, while in the application of chromium alone, under otherwise equal conditions, a chromium diffusion layer of about 0.1 mm. only, is obtained.

In order to prepare a chromium-silicon diffusion coating on iron, a container placed in furnace 3 is charged with 1 part by weight of silicon tetrachloride ($SiCl_4$) and 3 parts by weight of chromous chloride ($CrCl_2$), to which 1 part by weight of chromium metal powder is added. Furnace 2 is charged with relatively coarse grained chromium metal, as mentioned in Example 2. The connected furnaces are evacuated as in the previous examples and the temperature is maintained at first in furnace 1 in the range of 900 to 1100° C.; in furnace 2 in the range of 300° to 500° C. and in furnace 3 in the range of 20° to 60° C. The treatment is continued for about 60 minutes. After this period the silicon tetrachloride is consumed, and there is a low pressure in the furnace. Then furnaces 1 to 3 are heated as mentioned for chromium diffusion coatings, i.e. furnace 1 to about 1150° C., furnace 2 to about 1200° C., and furnace 3 to about 1000–1100° C., whereby a diffusion coating of 0.2 to 0.5 mm. is obtained.

Example 4

In order to produce on iron a diffusion coating of chromium alloyed with vanadium, furnace 3 is charged with 300 grams of a mixture consisting of 3 parts by weight of $CrCl_2$ powder and 1 part by weight of metallic vanadium powder and furnace 2 is charged with a mixture of 3 parts by weight of metallic chromium (grained) powder and 1 part by weight of metallic vanadium (grained), while into furnace 1, in which the parts to be coated are placed, 1 part by weight of freshly prepared $CrCl_2$ is introduced. The connected furnaces are evacuated as in the previous examples and the temperature is maintained in furnace 1 in the range of 1050° to 1150° C.; in furnace 2 in the range of 1100° to 1200° C. and in furnace 3 in the range of 1000° to 1100° C. The treatment is continued for about 240 minutes under a pressure of 30 Torr, whereby a diffusion coating of about 0.15 mm. is obtained.

Example 5

In order to prepare a titanium diffusion coating on iron, furnace 3 is charged with 1 part by weight of $TiCl_4$ and furnace 2 is charged with 2 parts by weight of titanium metal. The connected furnaces are evacuated as in the previous examples and the temperature is maintained in furnace 1 in the range of 700° to 1300° C.; in furnace 2 in the range of 400° to 700° C. and in furnace 3 in the range of 100° to 150° C. The treatment is continued for about 240 minutes under a pressure of 500–1500 Torr, whereby a diffusion coating of 0.03–0.8 mm. is obtained.

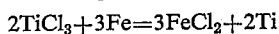
The pressure to be used in the above described process and device depends on the circumstances of each indi-

vidual case, and may be ordinary atmospheric, or sub-atmospheric, or superatmospheric pressure. In general, a pressure in the range of 300–1000 mm. Hg is desirable. Under higher pressure the reaction velocity is higher than under lower pressure, other conditions being equal. If a deep penetration of the metal to be deposited at low concentration is desired, a relatively low pressure can be of advantage. The pressure used in carrying out the present invention is in practice often limited by the vapor pressure of the halides used and also by the material of the furnaces. If the furnaces are operated under high thermal strain, the use of high pressure or high vacuum is preferably avoided. Thus, the optimum pressure to be used is determined, on the one hand, by the fundamental desirability of high pressure and, on the other hand, by the specific conditions of the individual case.

The specific halide of the metal to be used in coating iron or other base metal, should be selected to comply with the requirement of depositing by chemical reaction of the halide with the base metal, a volume of the coating metal which is substantially equal, or nearly equal, to the volume of the base metal converted into halide by said chemical reaction. Thereby, instead of one halide, a mixture of two or several halides of the coating metal or metals can be used.

As an example of carrying the above described principle into effect, the preparation of a titanium diffusion coating on iron is mentioned.

The molecular volume of titanium is about 10.8, while the molecular volume of iron is about 7.1. All chlorides of titanium—the tetrachloride $TiCl_4$, as well as the lower chlorides—form ferrous chloride ($FeCl_2$) in the reaction with iron. Therefore, an optimum effect will be obtained by depositing 2 molecular volumes of titanium, while removing 3 molecular volumes of iron from the iron base metal according to the equation:



Instead of $2TiCl_3$, a mixture of $TiCl_2$ and $TiCl_4$, containing substantially the same amount of Ti as $TiCl_3$ can be used. Furthermore, instead of using a single metal, a mixture of halides of more than one metal, for example a mixture of $TiCl_3$ and $ZrCl_4$ can be used. But in this case too, the sum of volumes of the metals deposited, i.e. Ti and Zr, should be substantially, or nearly, equal to the volume of Fe removed in the form of $FeCl_2$ from the base metal. Instead of chlorides, other halides, e.g. fluorides, or mixtures of various halides can be used.

The invention can be used in the preparation of diffusion coatings on articles consisting of various metals or of mixtures or alloys of two or more metals. The invention is particularly suitable for the preparation on steel and iron of diffusion coatings consisting of metals or other elements which are capable of diffusion in iron and form easily volatile halides, particularly chlorides, such as, for example, silicon, titanium, zirconium, uranium, vanadium, niobium, boron, aluminum, arsenic, beryllium, germanium, copper, nickel, phosphorus, rhenium, sulfur, selenium, tantalum, tellurium, thorium, thallium, etc. chlorides, the boiling and/or sublimation temperatures of which are lower than those of ferrous chloride ($FeCl_2$). However, instead of these chlorides, or in mixture with them, other chlorides having boiling and/or sublimation temperatures which are higher than those of $FeCl_2$, such as for example $CrCl_3$, can also be used. In using the latter, or other metal halides having such higher boiling and/or sublimation temperatures, the present process should be carried out under relatively low pressures, if necessary under the continuous action of a pump connected with the system of furnaces 1, 2 and 3. Furthermore, in such cases part of the chlorides can be introduced directly into furnace 1.

The present invention can be applied with particular advantage to sintered and hard metals, the pores of which become filled with the deposited metal to the desired

extent and the density of which is increased by the process of the invention. Articles of sintered iron and of sintered hard metals can be provided with diffusion coatings in this manner. In many cases, sintering and production of diffusion coatings on the articles, can take place in the same step in furnace 1.

If articles of steel are treated according to the present process with metals having high affinity to carbon, diffusion of said metals into steel is facilitated if in the articles to be treated the carbon of the steel has been previously combined with elements which easily form carbides, such as titanium, vanadium, zirconium, molybdenum, tungsten, or excess chromium or manganese.

The $CrCl_2$ powder used in carrying out the invention is preferably prepared by the reduction of chromium chloride with hydrogen. It is highly hygroscopic and should be very carefully protected from moisture. It can be also prepared by the action of chlorine and of hydrogen chloride on metallic chromium, or by the action of mixtures of chlorine and hydrogen chloride on metallic chromium, directly in liquid state at about 850–900° C.

The average duration of the present process amounts to 2–4 hours when the system is heated to the necessary temperature, i.e. this period does not include the time necessary for heating the furnaces to the reaction temperature and for cooling.

The term "base metal" is used in the present specification and claims to include metals or alloys which are subjected to the process of the present invention by reacting them with halides of metals to be deposited on the base metals. The term "diffusion coating" is used to denote surface layers obtained by subjecting base metals to the process of this invention in order to deposit other metals on the base metals at temperatures, at which the deposited metals penetrate into the base metals by diffusion, and "diffusion temperature" denotes a temperature at which such diffusion occurs.

It will be understood that this invention is not limited to the specific steps, materials, construction and other specific details described above and can be carried out with various modifications. For example, base metals other than those described above can be used and as examples of such other base metals tungsten, nickel and sintered hard metals, i.e. metals having a tungsten carbide-, or titanium carbide-cobalt-basis are mentioned. Hard metals can be provided, for example, with a diffusion coating of chromium or titanium in a manner substantially similar to that described above in connection with base metals or iron or steel. Corrosion resistant surface coatings on hard metals can be thus obtained. Furnace 1 can be charged with articles, the sintering of which has not been completed yet. The depth of penetration is relatively high in this procedure. Sintering can be carried out simultaneously with formation of the coating or subsequently.

Reference is made to my co-pending patent application filed under Serial Number 236,678 on July 13, 1951, and now abandoned, of which this is a continuation-in-part.

What is claimed is:

1. In a process for diffusion coating a base metal with a coating metal by halide substitution, the steps comprising positioning said base metal in a first furnace, positioning said coating metal in a second furnace communicating with said first furnace, positioning a halide of said coating metal in a third furnace communicating with said second furnace, evacuating said three furnaces, applying heat to said third furnace to vaporize said halide, applying heat to said second furnace to react said halide with said coating metal to produce a halide reaction product, and applying heat to said first furnace to react said reaction product with said base metal.

2. A process as defined in claim 1 wherein the heat applied to said second furnace is varied to control the chemical composition of said reaction product.

3. A process as defined in claim 1, wherein the heat applied to said third furnace is varied to control the chemical composition of said reaction product.

4. A process as defined in claim 1, wherein the heat applied to said second and third furnaces is independently varied to control the chemical composition of said reaction product.

5. A process as defined in claim 1, wherein the temperature of said first furnace is substantially reduced prior to completion of said diffusion coating.

6. A process as defined in claim 1, wherein the chemical composition of said reaction product is varied by controlling the heat applied to said second and third furnaces to produce a volume of deposited coating metal substantially equal to the volume of base metal removed.

7. A process as defined in claim 1, wherein no chemical element is present in any of said three furnaces except said base metal, said coating metal and the selected halogen forming a part of said coating metal halide compound.

8. A process as defined in claim 1, wherein the amount of heat applied to said second furnace is sufficient to

cause said second furnace to reach the reaction temperature of said coating metal and said coating metal halide.

9. In a process for diffusion coating a base metal with a coating metal by substitution reaction of a vapor phase halide of said coating metal with said base metal to deposit said coating metal on said base metal and remove the halide of said base metal, the step comprising varying the ratio of coating metal to halogen in said vapor phase coating metal halide composition, whereby the volume of coating metal deposited is substantially equal to the volume of base metal removed.

10. A process as defined in claim 9, wherein the ratio is varied by reacting said coating metal halide with said coating metal and simultaneously controlling the temperature at which said reaction takes place.

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