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METHOD OF UNITING METALS AND COMPOUND METAL ARTICLE

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This invention has to do with compound metal bodies and method of making the same, and it relates particularly to bodies composed of ferrous metal and copper. A compound metal body produced in accordance with the invention may take the form of a body composed largely of ferrous metal having a coating of copper over all or some of its surfaces.

The invention is directed particularly toward the provision of a copper coating for a body of ferrous metal, wherein the coating is of an impervious nature, so that it forms a protective covering for the ferrous metal resisting corrosion, and wherein the metals are strongly united one with the other to the end that the copper coating is substantially non-peelable, or in other words, will not strip off the ferrous metal, with the compound body comprising substantially an integral mass. While the invention contemplates particularly a compound metal body comprising ferrous metal with a copper coating, wherein the coating may be relatively thin, the copper element may have appreciable thickness. The compound metal bodies may comprise sheets, strips or wire with a copper coating; or plates, billets or the like with a copper element of a thickness such as to constitute more than a coating. The sheets or strips, for example, may be suitably shaped and worked into finished articles, and the plates or billets may be worked or drawn as desired. Also shaped articles such as machine elements, shafts, and divers articles of manufacture may be copper coated by the method.

The ferrous metal employed may be iron with little or no carbon content, or different grades of steel with varying carbon content, or alloy steels among which may be nickel steel, manganese steel, vanadium steel, and others. Likewise, the copper constituent may comprise an alloy when and if desired; such alloys may be brass, bronze, copper-nickel alloy and others. However, in the following detailed description of the invention and in the claims, the terms iron and copper are employed for the purpose of simplifying the description, and it is to be understood that these terms are used in a broad sense so as to include iron, steel and alloy steels, copper in its commercially pure form, or copper alloys.

The method of this invention comprises, principally, bringing iron and copper into intimate contact, and while in such relation subjecting the same to heat under such conditions and for such length of time as to effect a desired diffusion of the metals and a desired condition in the copper constituent. In carrying out the heating step the same may be governed or controlled in such wise, particularly as regards the temperature and time period, to control the diffusion of the metals into each other and to also control the back precipitation phenomena incident to the subsequent cooling of the metals.

An advantageous manner of bringing the metals into intimate contact is that of electro-depositing the copper constituent upon a body of iron. The copper constituent may be in the form of a relatively thin copper plating. Electro-deposited copper plate, however, is of a porous nature and capable of being peeled or stripped off the iron. The electro-deposited copper, accordingly, does not provide an efficient corrosion-resisting covering, as corrosion of the iron may start in the pin holes afforded by the porous nature of the copper. Actual salt spray tests have shown this fact to be true. However, the body of iron with its electro-deposited plating is subjected to a heating, or what may be termed an annealing step in the process, to strongly unite the metals and to render the electro-deposited copper substantially impervious. This is preferably done by placing the same in a furnace and, during the heating step preferably maintaining the same under conditions precluding oxidation. For this purpose a neutral or reducing atmosphere may be employed. Various gases are available for such purpose, as for example, ordinary city illuminating gas, hydrogen, and carbon monoxide.

As regards the controlling of the heating step to obtain the desired diffusion, and to control back precipitation, it is advantageous here to refer to the transformation of the iron from alpha to gamma, and the upper critical temperature of the ferrous metal commonly called ac3. In the case of iron with no carbon content the transformation from alpha iron to gamma occurs at 900° C. With carbon steels transformation from alpha to gamma occurs over a range; the lower critical temperature, that is the lower temperature defining the range, is 725° C.; as the carbon content increases the upper critical temperature, that is the temperature at which the transformation is complete, decreases from 900° C., until the carbon content in the steel is about 0.9%, where the upper critical temperature and lower critical temperature meet at 725° C. At this point the alpha iron changes to gamma iron at constant temperature.

It is believed that, in this heating step the metals diffuse one into the other and form a solid solution, and in this manner the iron and copper

elements are tenaciously united. In this regard the solubility of copper into iron is to be considered. At ordinary room temperature the possible solubility of copper into iron is relatively low, and according to the available information at present, is less than 0.2%. That is to say, iron is saturated with copper at ordinary room temperature when it contains this percentage of copper. As the temperature is increased the solubility of copper into iron increases very slowly up to about 500° C. As the temperature further increases the solubility of copper in iron rapidly increases. At about 600° C. the solubility is about 0.45%, and at 700° C. the solubility is about 1%. Whereas the transformation temperature for pure iron from alpha iron to gamma iron is 900° C., the presence of the copper lowers this critical temperature. The temperature at which the gamma-alpha transformation of the iron takes place is gradually lowered by increasing the amount of copper in solution in the gamma iron, this temperature decreasing from 900° C. for pure gamma iron to 810° C. for 5.5% copper in solution in gamma. At this temperature the solubility of copper in alpha iron reaches 3.4%, and by the absorption of further heat at this temperature of 810° C., which absorption does not increase the temperature during transformation, the solubility of copper into iron suddenly jumps to 5.5% in gamma iron. As a matter of fact, the transformation occurs at constant temperature with 3.4% of copper in alpha iron at 810° C. with absorption of heat. This jump in the solubility of copper in iron occurs as the alpha transforms to gamma. Upon still further increase of temperature the solubility of copper in gamma iron rapidly increases and at about 1100° C. is about 8%. It is apparent, therefore, that the solubility of copper in gamma iron is materially greater than the solubility of copper in alpha iron as a sudden increase occurs upon the transformation of alpha iron to gamma iron with a continued increase as the temperature raises beyond the transformation. An explanation of this may be that the structure of gamma iron crystals and copper crystals are similar, and the attraction between copper atoms and gamma iron atoms is higher than the attraction between copper atoms and alpha iron atoms.

Now considering the solubility of iron in copper. From ordinary room temperature up to about 810° C. the solubility of iron and copper is, generally speaking, about 0.2% and is fairly constant. At 810° C., as the saturated alpha iron changes into gamma iron, the solubility of iron in copper begins to increase more rapidly and is about 4% at 1100° C. The above figures of solubility of copper in iron and iron in copper are given for iron without carbon content. It is believed that these solubility figures do not change to a great extent in steel of very low carbon content.

I have found that it is preferable to so regulate and control the heating of the metals, to control the diffusion so that the diffusion of copper into the iron does not exceed, at any point, 3.4% at which percentage alpha iron is saturated with copper at 810° C. By this same token a control is effected for minimizing the diffusion of iron into the copper with the result that the copper coating is not contaminated with an undesirable amount of iron. For example, let us take a strip of sheet steel, say of 0.1% carbon, with an electro-deposited covering of copper thereon and place this in a furnace in neutral or reducing environment.

The temperature is now increased; and it may be maintained below the upper critical point which, in the case of 0.1% carbon steel is about 880° C., in the absence of copper, and about 810° C. with 3.4% copper in solution in the alpha iron. Suppose, for example, that the temperature is raised to 750° C. At this point the solubility of copper in alpha iron reaches about 2%. The copper atoms become diffused in the ferrous metal forming a solid solution therewith, uniting the copper constituent and the ferrous metal constituent. At this temperature the solubility of iron in copper has not increased materially with the result that there is more diffusion of copper atoms in the ferrous metal than iron atoms into the copper. This may be a satisfactory condition in some instances as the copper coating becomes united with the iron while at the same time the copper coating is not contaminated or rendered impure by the presence therein of an undesirable amount of iron. I have merely picked out the point of 750° C. to express this example, but it is to be understood that other temperatures may be employed. The higher the temperature the more rapid the diffusion and the less time required in the heating process, whereas the lower the temperature the longer the time required to obtain the desired diffusion.

Satisfactory results have been obtained by maintaining the compound metals in a furnace for a period of ten hours with a temperature of 760° C., and the iron in this case was low carbon steel of about 0.1% carbon. It will be appreciated that by using a lower temperature the time period may be extended, and by using a higher temperature the time period may be shortened. Both however may be varied to produce desired results. Although the time period is lengthened the percentage of copper diffusing into the iron will never exceed the saturation point for a given temperature, but, the depth of the diffusion into the iron increases with time. For example, if the union between the metal constituents is desired to be stronger, the temperature may be raised and the time period extended; on the other hand, only one of these factors may be varied. If the union need not be so efficient in the resultant compound metal, depending upon the desires of the one practicing the method or upon the desired nature of the finished product, either the temperature may be lowered or the time period shortened, or both temperature and time period lowered and shortened, respectively.

It has been found that when the copper coating has thus been applied to ferrous metal that it becomes strongly bonded to the ferrous metal and is of dense impervious nature. Actual salt spray tests have clearly indicated that the pin holes in an electro-plated layer of copper resulting from its porosity, are efficiently closed when thus subjected to the heat treatment.

It may be pointed out that if the temperature is raised to a point above transformation temperature with the alpha iron transformed to gamma iron, and the time period be sufficiently long to result in more than 3.4% copper going into solid solution with the iron, the resultant copper coating appears inferior to the copper coating obtained where 3.4% or less of copper diffuses into the iron. It is thought that as the gamma changes to alpha upon cooling, the copper in the gamma iron in excess of the saturation point in alpha is precipitated back and that

this copper is precipitated back in a eutectoid form. This back precipitation apparently favors corrosion. If the temperature is raised above the transformation point the solubility of iron into copper increases, resulting in a high iron content in the copper coating, if the time period is sufficiently long, which is undesirable and aids corrosion.

Accordingly, a point of prime importance is that of controlling the heating step so that the copper which enters into solution with the iron does not exceed at any point 3.4%. Where the temperature of the heat treatment is maintained below the upper critical temperature this condition is assured. However, the effecting of the diffusion of the metals, one into the other while in a solid state, is not a rapid process. Accordingly, the heat treatment may be carried out with temperatures higher than the upper critical temperature of the ferrous metal involved. In such a case the diffusion of the copper into the gamma iron takes place more rapidly than the diffusion of copper into alpha iron, but as the metals are yet in a solid condition, the diffusion on the whole is not rapid. Therefore, temperatures above the alpha-gamma transformation may be employed, but the time element may be controlled to the end that copper in excess of 3.4% does not enter into solution with the gamma iron. In short, this means that the time element may be shortened. Of course, when the temperature exceeds the alpha-gamma transformation it is possible that the gamma iron will take into solution copper in excess of 3.4% when sufficient time is allowed, but in accordance with this invention the time period is controlled to prevent this. Likewise the control of the time period is such as to prevent an undesirable amount of iron entering into solid solution with the copper. Accordingly, in the subsequent cooling step, even though the alpha-gamma transformation temperature has been exceeded, the alpha iron can hold in solution all the copper which has been diffused as the time element has been controlled to prevent diffusion of more than 3.4% at any point, and accordingly in this cooling step there is no excess copper precipitated back in eutectoid form upon the gamma-alpha transformation.

Accordingly, the invention lends itself to relatively rapid treatment as time may be saved by utilizing temperatures higher than the alpha-gamma transformation. In this regard the invention contemplates a method wherein a strip of metal may be run through a furnace with a continuous movement, and the utilization of a higher temperature and shorter time facilitates such a process.

It will be appreciated that when the two metals disposed in intimate contact are thus heat treated to effect diffusion of the metals, that there is a resulting zone where the copper penetrates the iron, but the copper content diminishes with zone depth. For example, there may be 3.4% of copper diffused immediately adjacent the surface of the iron, but this percentage diminishes with zone depth into the iron, and it is preferable that no place in the zone has a copper content exceeding 3.4%. Likewise, there is a zone where the iron penetrates the copper, and the iron content diminishes with zone depth into the copper. Where the copper element has material thickness there is little or no opportunity for diffusion of iron through the copper to its exposed surface, but theoretically this is possible with a long time period. It is accordingly preferred when securing a thin copper coating to a ferrous metal base that the control of the method, particularly the temperature and time period be such that the iron does not penetrate through the copper layer, thus leaving the outer regions of the copper coating substantially free of iron content so that it is not contaminated and, as a result, may effectively resist corrosion.

If, as set forth above, the amount of copper diffused in the iron exceeds at no place 3.4% there will be no back precipitation of copper in eutectoid form upon gamma-alpha transformation. However, as the metals cool from a temperature, for example, just below the gamma-alpha transformation, there is a tendency for the alpha iron to precipitate copper due to the decreasing solubility caused by decreasing temperature. It is preferred that this cooling of the metals, speaking now of the cooling which takes place below the transformation, be relatively rapid so that such copper as may be precipitated back is very finely dispersed and with the particles of copper substantially sub-microscopic. If the cooling is unduly long, the sub-microscopic particles coalesce and grow in size and thus may become visible under a microscope. As mentioned above, it is preferable to prevent this by effecting a relatively rapid cooling. This cooling rate may, however, be such as to obtain the desired annealing of the ferrous metal, and it may be pointed out that the desired results relative to the diffused metals and back precipitation, may be obtained while at the same time obtaining the desired annealing of the ferrous metal.

In the production of compound metals of copper coated ferrous bodies in accordance with the method it may be desirable to first subject the metals to a rolling process, as such would serve to initially densify and compact the copper. This is applicable to ferrous metal stock having an electro-deposited layer of copper thereon, as such rolling initially compacts and densifies the electro-deposited copper. Then in the subsequent heating step imperviousness of the copper is obtained to a high degree.

A finished article, accordingly, may have a body formed primarily of ferrous metal provided with a coating of copper. This copper coating when applied in accordance with the method is substantially impervious thus offering an efficient resistance to corrosion. Moreover, between the copper coating and the body of ferrous metal there is a zone in which the metals are diffused in solid solution. Accordingly, there is a zone of copper-bearing iron underlying the copper coating which in itself affords resistance to corrosion so that not only is an efficient corrosion-resistance coating provided, but underlying the coating is the corrosion-resisting copper-bearing iron which performs the further function of tenaciously uniting the iron and copper.

I claim:

1. A compound metal article comprising a body of ferrous metal and a body of copper brought into intimate contact by electro-deposition and united by a zone in which copper is in solid solution with the ferrous metal with the total amount of copper in said zone not exceeding the possible solubility of copper in alpha iron.

2. A compound metal article comprising a body of ferrous metal and a body of copper brought into intimate contact by electro-deposition and united by a zone in which copper is in solid

solution with the ferrous metal with the total amount of copper in said zone not exceeding the possible solubility of copper in alpha iron, said compound metal article being substantially free of back precipitated copper.

3. A compound metal body comprising a body of ferrous metal and a body of copper brought into intimate contact by electro-deposition and united by a zone in which the metals are diffused in solid solution effected by the application of heat with the metals in solid state and with the ferrous metal in alpha form.

4. The method of uniting a ferrous metal body and a copper body which comprises bringing the metals into intimate contact, subjecting the same to a heat treatment at a temperature higher than the alpha-gamma transformation of the ferrous metal, and controlling the time period of the heat treatment to obtain a diffusion of copper into the iron to an extent not exceeding the maximum possible saturation of alpha iron with copper.

5. The method of uniting a ferrous metal body and a copper body which comprises bringing the metals into intimate contact, subjecting the same to a heat treatment at a temperature higher than the alpha-gamma transformation of the ferrous metal, limiting the time period of the heat treatment to obtain a diffusion of copper into the iron to an extent not exceeding the solubility of copper in alpha iron at the eutectoid temperature, whereby in the subsequent cooling through the gamma-alpha transformation precipitation of copper in eutectoid form is prevented, and then cooling the metals relatively rapidly from a point below the gamma-alpha transformation to prevent substantial precipitation of copper by the cooling alpha iron.

6. The method of copper coating a ferrous metal body which comprises electro-depositing a copper coating upon the ferrous body, subjecting the same to heat to cause the metals to diffuse one into the other in solid solution, employing a temperature in the heat treatment above the alpha-gamma transformation of the ferrous metal, and controlling the time period of the heat treatment to obtain a diffusion of copper into the iron to an extent so that the total amount of copper diffused does not exceed the possible solubility of copper in alpha iron.

7. The method of copper coating a ferrous metal body which comprises electro-depositing a copper coating on a ferrous body, subjecting the same to heat to cause the metals to diffuse one into the other in solid solution to form uniting alloy zones, employing a temperature in the heat treatment above the alpha-gamma transformation of the ferrous metal, and limiting the time period of the heat treatment to limit the amount of copper diffusing into the iron, whereby in the subsequent cooling through the gamma-alpha transformation, back precipitation of copper in eutectoid form is prevented.

8. In the method of fixing a copper coating to a ferrous metal body wherein the copper coating is electro-deposited upon the ferrous body and wherein the copper coated ferrous body is subjected to heat, the steps of selecting a temperature below the alpha-gamma transformation temperature of the ferrous metal at which temperature the maximum possible solubility of copper in alpha iron does not exceed the desired solubility of copper in iron in a finished product, maintaining the heat treatment at such selected temperature for diffusion of the copper in solid solution with the alpha iron, terminating the heat treatment at a definite time to obtain a definite depth of diffusion of the copper into the ferrous metal, and then cooling the metals relatively rapidly to substantially prevent back precipitation of copper in solid solution with the iron.

9. A compound metal article comprising a base of ferrous metal, a continuous body of copper positioned over at least some of the surfaces of the ferrous metal and constituting a coating, said bodies being united by a heat effected alloy zone in which the copper is in solid solution with the iron and in which ferrous metal is in solid solution with the copper, said metal article being substantially free of back precipitated copper and the zone in which the iron is in solid solution with the copper having a depth less than that of the thickness of the continuous copper body constituting the coating whereby the exposed surface is substantially pure copper.

10. The method of copper coating a ferrous metal body which comprises disposing a continuous body of copper over at least some of the surfaces of a ferrous metal body which continuous copper body is to constitute a coating, subjecting the metals to a heat treatment the temperature of which is below the melting point of either metal involved and above the transformation range of the ferrous metal involved to cause the metals to diffuse in solid solution, and limiting the time period of the heat treatment to obtain a diffusion of the copper into the ferrous metal which does not exceed substantially 3.4%.

11. The method of copper coating a ferrous metal body which comprises, electro-depositing a coating of copper upon the ferrous body, subjecting the same to a heat treatment the temperature of which is below the alpha-gamma transformation range of the ferrous metal involved to diffuse the metals one into the other in solid solution to form zones of the metal in solution uniting the ferrous metal and copper, and discontinuing the heat treatment when the metals have penetrated one into the other to a substantially predetermined depth.

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