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TREATMENT OF STEEL

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This invention relates to the metallurgy of steel and has for an object the provision of an improved method of forming copper steel products. More particularly, the invention contemplates the provision of a process for preventing surface checking of copper steel during mechanical shaping operations such, for example, as forging, rolling and drawing operations. The invention further contemplates the production of copper steel products having improved shaping properties.

This application is a continuation in part of our application Serial Number 636,577, filed October 6, 1932.

Copper steels have long had the reputation of being "red short" and "cold short", the reason being that copper magnified the ill effects of oxygen and sulphur present in the steel. Copper steels in which the sulphur and oxygen contents have been reduced sufficiently low may be forged or rolled easily, but, after forging or rolling under usual conditions, the finished shapes have had very poor surfaces due to surface checks or cracks. Also, due to penetration of scale into these checks or cracks, the scale is very adherent, cannot be removed readily, and may be rolled into the steel.

While the scaling of steel is modified in type by the presence of copper in the steel, it should be understood that the present invention deals with the prevention of checking. The check, being a crack, usually of microscopic dimensions, merely modifies scaling by permitting scaling to start in or at the check. While one aspect of this invention involves control of scale type or scale formation in order to control or modify checking, the object in view is always the restraint of checking.

The severity of surface checking of copper steels varies with the copper content, the higher the copper content the worse the checking. A copper content of about 2% or more, in steel, will cause severe surface checking when the steel is forged or rolled under usual conditions of heating and working. A copper content of 1.5% causes only a moderate amount of surface checking, and a copper content of less than 1% causes only very slight surface checking. A copper-free steel scales easily but under comparable conditions shows little or no checking.

The surface checks on copper steels have the effect of reducing the apparent strength of the steels in that they act as "nicks" or "notches" and cause premature failure or rupture when the steel is strained beyond its elastic limit, either hot or cold. This is especially serious in steel that must be bent to shape, after being forged or rolled under usual conditions, since the checks are the beginnings of tears in the metal and result in serious weakening or complete failure at the bend.

We have demonstrated that the surface checks on copper steels are not the result of "red shortness" or "cold shortness" by grinding or machining off the surface of a forged copper steel bar, below the depth of penetration of the checks, and then testing the bar. A bar so treated will bend hot or cold as well as a bar of copper-free steel of equal hardness, thus showing that the surface checks are not the result of "red shortness" or "cold shortness".

Our researches indicate that surface checking of copper steel probably can be attributed to the existence of a film of liquid copper on the surface of the steel, resulting from selective oxidation of iron. When a copper steel is heated in the presence of a gas that will oxidize iron, the iron is selectively oxidized to iron oxide which forms scale and the copper is concentrated on the steel surface, the degree of concentration depending on the temperature and amount of scaling. The maximum concentration seems to take place at a temperature near the melting point of copper.

The following is an example of scaling tests made to determine the effect of temperature on the concentration of copper on a steel surface during scaling. Pieces of copper steel containing 2% copper were heated in an electric muffle furnace, with fairly free access of air, for times and temperatures indicated below. The pieces were cooled in air, and the scale was cracked off and analyzed for iron and copper:

Temperature	Time	Percent Fe	Percent Cu
°C.	Hours		
950	1	73.0	0.80
1000	1	74.4	0.51
1050	1	73.1	0.25
1086	1	74.0	0.15
1100	½	73.2	0.40
1150	½	72.2	0.25

The above figures appear to indicate that a very considerable concentration of copper on the steel surface takes place during scale formation while the steel is being heated to forging temperatures. Once the copper film is formed on the surface of the steel, further scale formation apparently takes place by transfer of iron through the cop-

per plate. The copper tends to alloy with the iron and the iron is oxidized away from the outer copper surface. We probably have the following conditions when copper steel is being treated in an oxidizing atmosphere: starting with the body of the iron and proceeding to the exterior, we have—Fe; Cu-rich Fe; Fe-rich Cu grading into Fe lean-O_2 rich Cu; and finally Fe oxide scale. Under these conditions, and especially above the melting point of copper, the copper becomes an active corrosion agent dissolving iron and expediting its oxidation. The attack of the iron by the copper proceeds relatively uniformly over the iron surfaces, that is, without apparent relation to the Fe grain boundaries. Likewise, the liquid copper appears capable of readily wetting the iron surface, when the temperature is above the melting point of copper.

The above described precipitation of copper on the surface of copper steel, together with the attack of the iron by the combination of oxygen and copper does not in itself effect surface checking, a surface plating of copper being the result. However, if the steel is worked at a temperature at which the copper film is liquid, serious surface checking will result. This probably is due to the penetration of the copper between the iron grains or its capillary penetration into minute crevices opened up by the working.

We have discovered that objectionable surface checking of copper steel may be avoided through control of the character of the surface of the steel at the commencement of the shaping operation. Thus, for example, we have discovered that objectionable surface checking may be avoided by so preparing the steel for forging or rolling as to preclude the existence of surface films of liquid copper.

In accordance with our invention, copper steel may be prepared for shaping, as by drawing, forging or rolling, as follows:

(1) By alloying the steel with one or more elements which will increase the resistance of the steel surface to scaling with consequent segregation of copper.

(2) By alloying the steel with one or more elements which will raise the melting point of such copper as does segregate.

(3) By alloying the steel with one or more elements which will inhibit or prevent the spreading of liquid copper over the steel surface.

(4) By alloying the steel with one or more elements capable of increasing the solubility of copper in iron.

In carrying out our improved method for the production of improved copper steel products in accordance with the invention, the alloying elements may be incorporated in the steel in any suitable manner. Thus, for example, the alloying elements may be added to and dispersed in the steel, in the solid or molten state, while the steel is molten to produce a substantially homogeneous steel product; or the steel articles to be shaped may be subjected to the action of the alloying elements, in elemental form or in the form of suitable compounds thereof, at elevated temperatures to incorporate the alloying elements in the surface portions only of the articles; or the steel while molten may be cast in molds having their surfaces coated with the alloying elements or suitable compounds thereof in finely divided forms to incorporate the alloying elements in the surface portions only of articles to be shaped.

The alloying elements may be employed in elemental forms or as compounds, and, when two or more alloying elements are employed, any suitable number or all may be in elemental form and any suitable number or all may be in chemical combination. Also, when two or more alloying elements are employed they may be employed separately or as alloys or mixtures of those elements.

The invention contemplates the production of improved copper steel products by the incorporation of alloying elements in steel containing copper as well as by the incorporation of copper and suitable alloying elements in copper-free steel. The invention also contemplates the production of improved copper steel products by the incorporation of copper in steel containing one or more alloying elements. In the production of copper steel from copper-free steel, the copper and the alloying elements may be employed separately or in any suitable combination or aggregation with each other.

Throughout the specification and claims of this application the expression "alloying element" is used to designate an element which influences the behavior of copper and does not refer to the copper or iron of the copper steel.

We have employed the following elements successfully for the restraint of surface checking during the shaping of copper steel by adding those elements, as ferro alloys, to molten copper steel: manganese, chromium, silicon, aluminum, zirconium, nickel, molybdenum, vanadium, and titanium.

In employing manganese, chromium, silicon, aluminum, titanium, and zirconium, we added those elements, each to a separate batch of copper steel while molten, for the combined purpose of deoxidizing or scavenging the steel and establishing in the steel, in each case, an excess of the element sufficient to influence the behavior of the copper to a desired extent. Favorable results were obtained in all cases, but the more desirable results were obtained when aluminum, titanium, and zirconium were employed, amounts of these latter elements equal to and less than one percent of the weight of the resulting steel causing marked improvement in resistance to surface checking.

Aluminum (and manganese and silicon through limited composition ranges) lowers the melting point of copper, whereas titanium, zirconium and chromium raise the melting point of copper. The improvement in resistance toward surface checking obtained through the use of titanium, zirconium and chromium might be attributed to the raising of the melting point of the copper in the steel. The improvement resulting from the use of aluminum, which lowers the melting point of copper, might be explained by the capacity of aluminum for protecting iron surfaces from oxidation through the formation of a very firmly adherent and impervious film of aluminum oxide. Aluminum is also known to increase the solubility of copper in liquid or solid iron.

Nickel, molybdenum and vanadium also raise the melting point of copper. We have used these elements successfully to improve the resistance of copper steel to surface checking by adding them separately to different batches of molten copper steel, in such proportions as to form with the copper of the steel, copper-nickel, copper-molybdenum and copper-vanadium alloys having melting points higher than the melting point of copper.

Molybdenum and vanadium are not regarded as of much value by steel makers for preventing

scale formation and any effect they produce is probably attributable to the raising of the melting point of the copper. Nickel not only tends to alloy with copper and raise its melting point but also increases the solubility of copper in iron and adds some resistance to scaling so that it probably functions in several ways. Iron itself alloys with copper and thereby raises its melting point, but apparently it does not do so with sufficient rapidity to prevent complete spreading of a film of copper during rapid oxidation and scaling at the high temperatures, as is shown by quenching a piece of copper steel from a temperature above the melting point of copper, after heating and scaling in air. Breaking off the scale shows a plating of copper beneath.

The spreading of liquid copper on iron is a well recognized phenomenon and it has even been used for "soldering" at high temperatures. Some elements if alloyed with the iron render its surface less easily wetted by liquid copper. Thus, chromizing the surface of iron with chromium or its ferro alloys leaves a surface on which liquid copper does not spread. Chromium may also impart scaling resistance to iron so it is evident that the various elements mentioned above probably all function in several ways although each may give its most marked effect in one of the four ways outlined above.

Among the alloying elements which increase the solubility of copper in iron are nickel, silicon, aluminum, cobalt and manganese. Of these elements, nickel and manganese are the most effective. Nickel is about twice as effective as silicon and about 25% more effective than aluminum. Copper tends to segregate under scale in all cases, but if the metal beneath the scale is a better solvent than iron for copper the copper tends to go into the metal more rapidly, thus decreasing the severity of segregation and, hence, the tendency to check.

Steel products in which the copper and alloying element are substantially uniformly distributed throughout may be formed in any suitable manner. Thus, for example, the alloying element, in any suitable physical or chemical condition, may be added to a molten bath of iron or steel containing copper or to which copper must also be added; or the alloying element or copper or the alloying element and copper may be mixed with iron and the mixture melted; or the copper or alloying element, or the copper and alloying element may be incorporated in the iron or steel product by introduction into the process for the recovery of the iron from its ore; or an ore containing the alloying element may be so treated as to produce a metallic iron product in which the alloying element is present in suitable proportion. In the latter case, copper may also be present in the ore, and the metallic iron product formed may contain copper and the alloying agent in suitable proportions. When the alloying element or copper or the alloying element and copper is present in the ore, additional quantities of either or both may be incorporated in the metallic iron product in any suitable manner.

Alloying elements may be incorporated in the surface portions of a copper steel article to be shaped in any suitable manner. For example, a copper steel article such as an ingot may be electroplated with the alloying element; it may be dipped hot or cold into a molten bath of alloying element or alloy, or even into a molten bath of a metal such as iron; it may be dipped into a bath of molten compound of a metal reducible by iron and containing also a flux to remove scale; the ingot may be cast into a mold lined with powdered metal or ferro alloy; the ingot may be cast in a can or casing of mild steel or alloyed steel or of the alloying element under conditions leading to welding together of the can or casing and of the cast metal; the coating metal may be applied as an atomized spray or as a powder at an intermediate temperature such as that used in calorizing with aluminum powder or chromizing with chromium powder; fluxes may be used in any of these methods where necessary. The ingot mold wash method of applying alloying elements is relatively inexpensive and easy to operate. By this method nickel and aluminum have given good coats and good spreading over the surface of the ingot. In general, ferro alloys are slower to be absorbed from mold washes than are pure metals. They seem to also require more care in fluxing, suggesting that oxidation products on the grain surfaces are preventing perfect absorption. Those alloying elements like chromium, manganese, aluminum and silicon, which have a greater affinity for oxygen than iron, seem to burn off the ingot surface under usual conditions of heating for shaping, leaving only small amounts of the protective metals in the steel surface beneath the scale and this may explain why they are less effective than an element like nickel.

Use of an element like nickel in a coating or in the surface portions instead of alloying the whole bulk of the metal offers considerable economy. The tendency to concentrate in a film under the iron oxide scale permits of reaching a desirable ratio of nickel to copper with the use of only a small fraction of the metal required for forming a homogeneous alloy. For instance, in the treatment of ingots weighing 150 pounds and containing 1.5% copper, ⅓ to ½ of a pound or less of nickel incorporated in the surface portion only of an ingot will produce results comparable to those obtained through the use of 1.12 pounds of nickel dispersed throughout the metal of an ingot.

Continuous application of a powdered alloying element like nickel can take place in a number of ways during an operation like rolling. An atomizing pistol might spray new nickel onto the extended surface produced by working. Also the water used to cool the surfaces of rolls might carry powdered nickel, a part of which would stick to the steel.

In applying alloying elements to mold surfaces for the purpose of incorporating the alloying elements in copper steel we have obtained satisfactory results by applying the alloying elements in amounts equal to about 25 to 50 grams per square foot of mold surface.

Copper steel products formed in accordance with the method of our invention may be shaped in any suitable manner at any suitable temperatures. According to our preferred practices, copper steel products in which alloying elements have been incorporated may be further prepared for shaping in accordance with any of the following procedures as indicated in our aforementioned copending application:

(*a*) By heating to suitable shaping temperatures under such conditions as to prevent scale formation;

(*b*) By maintaining or establishing non-liquid surfaces through temperature regulation; and

(c) By eliminating scale and copper films formed during oxidizing heat treatments.

By preventing or minimizing the formation of scale, selective oxidation of the iron in the surface portions of the steel is avoided and concentration of metallic copper on the surface of the steel is prevented. Scale formation at temperatures higher than those at which the added alloying agents provide protection against scaling may be prevented by heating in an atmosphere non-oxidizing with respect to iron or in a reducing atmosphere. Copper steel heated with no scale formation, alloyed or unalloyed, at temperatures considerably higher than the melting point of copper, may be forged or rolled into finished shapes with access of air without serious surface checking resulting. Bars forged by us from such scale free steel were bent through 180° without any apparent rupturing or tearing resulting, while bars forged from the steel heated under scaling conditions were torn on the outside of the bend when bent at an angle of about 90°.

Regulation of the temperatures of steel products to maintain or establish non-liquid surfaces may be accomplished by heating, prior to forging or rolling, to temperatures below the temperatures at which copper in the surface portions of the products will exist in liquid condition or by heating to high temperatures and cooling, prior to forging or rolling, to temperatures below the temperatures at which the copper in the surface portions of the products will exist in liquid condition.

Elimination of scale and copper films may be accomplished by shaving, grinding, or machining or by heating the steel in a strongly reducing atmosphere to reduce the iron oxide of the scale. The metallic iron produced by reduction of the iron oxide forms an alloy with the metallic copper and any alloying element present which has a higher melting point than the copper and which freezes and forms a solid metallic surface on the steel. Elimination of the scale and copper films mechanically or through the use of reducing agents permits the production of shapes substantially free from surface checks from steel at temperatures as high as may be required for forging, provided, of course that the time required for the shaping operation is not so great as to permit excessive scale formation before its completion.

We have found that a copper steel containing no alloying element can be successfully shaped with access of air by starting the shaping operation at a temperature above the melting point of copper and carrying out the operation rapidly. When forging, it is necessary to hammer sufficiently rapidly that scale formed between blows is not permitted to accumulate for any considerable length of time. It appears that under such conditions, the scale formed when the oxygen of the air contacts fresh steel surface will contain both copper and iron oxides in proportions equivalent to the proportions of copper and iron in the steel. Copper steel containing an alloying element or having no alloying element present therein may be shaped, without serious surface checking resulting, in an oxidizing atmosphere at a temperature above the melting point of copper or above the melting point of an alloy consisting of copper and the alloying element in the proportions in which the copper and alloying element are present in the surface portions of the steel if the shaping operation is carried out sufficiently rapidly to prevent or inhibit selective oxidation of the iron with consequent segregation of the copper or the copper and the alloying agent.

In shaping copper steel in accordance with our invention, it is advisable to avoid the existence of a film of liquid copper on the steel at the commencement of the shaping operation and to avoid the production of liquid copper during the shaping operation. Thus, products having scale formed thereon preferably should be shaped at temperatures at which the copper contained in the surface portions can not exist in liquid condition. If such products have been heated to temperatures at which copper in the surface portions may exist in liquid form, they may be cooled by standing in the atmosphere or by means of a water spray, steam or air blast to a suitable temperature at which the copper in the surface portions can not exist in liquid form. If the shaping of copper steel having scale and a film of copper thereon is to be conducted at temperatures at which the copper in the surface portions can exist in liquid form, it is advisable to remove the scale and film of copper prior to the commencement of the shaping operation mechanically, as by scraping, machining or planing, or chemically, as by heating in a reducing atmosphere to reduce the iron oxide of the scale.

Shaping operations for converting scale-free copper steel products into finished shapes should not be conducted at unnecessarily high temperatures. The initial temperature selected in each case should be such that the steel will not remain above the melting point of the copper in the surface portions for a period of time which will permit sufficient oxidation to cause checking. This precaution should be observed particularly in the forging or rolling of large ingots when relatively long periods of working are required. In general, any initial shaping temperature that is suitable to the particular steel may be employed in the shaping of scale-free steel.

When a copper steel product is to be reduced to a finished shape in two or more stages, any suitable heat treatment may be employed for establishing any suitable shaping temperature for all stages except the final stage. The temperature or manner of heating or the temperature and manner of heating for the final stage should be such as to preclude the existence of liquid copper when working is commenced or the production of liquid copper during working, or scale and film of copper appearing on the steel at the end of the stage preceding the final stage should be removed chemically or mechanically before the final working stage is commenced. Thus, for example, a preliminary mechanical reduction of steel having scale thereon at a temperature above that at which copper in the surface portions will remain in non-liquid condition may be followed by chemical reduction of the iron oxide of the scale or by lowering of the temperature to a point below that at which copper in the surface portions may exist in liquid condition, or the scale and copper film may be removed by shaving, grinding or machining, before the commencement of the final mechanical reducing operation.

Throughout the course of our investigation of copper steel products, we have been aware of the fact that certain classes of copper steel products are not amenable to working at the relatively low temperatures specified in our aforementioned copending application, and it was with this fact in mind that our study of the effects of alloying elements was undertaken. For instance, a copper bearing steel containing under 0.1% carbon and also steels alloyed with chromium or man-

ganese, do not forge well at lower temperatures, due to tearing, and we have found that in such cases the addition of an element like nickel in proper amounts is sufficient to restrain checking when a suitably high temperature for working is used. As an example, a steel which analyzed as follows: 1.9% Cu, 0.96% Cr, 1.14% Ni, 0.27% C, was forged very successfully at a temperature estimated between 1250° C. and 1300° C.

In accordance with our invention one or more alloying elements may be incorporated in copper steel in any amounts which will aid in achieving the result sought. The amounts of alloying elements employed preferably will be correlated with the amounts of copper in the steel or to be added to or incorporated in the steel. The types and quantities of alloying elements to be employed in various cases may be determined readily by testing various samples of the steel to be treated in which varying types, quantities and combinations of alloying elements have been incorporated, and, in many instances the results which may be obtained through the use of various types, quantities and combinations of alloying elements may be predicted from a consideration of scientific data such, for example, as temperature-equilibrium diagrams, which are available or which may be obtained readily by means of relatively simple laboratory investigations. For example, a very good temperature-equilibrium diagram for nickel-copper alloys is available in the International Critical Tables (Vol. II, p. 433). This shows that for a forging or rolling temperature of 1200° C., assuming that all the copper and nickel can alloy with each other in the presence of iron, a minimum ratio of 38 parts nickel to 62 parts of copper is demanded to give Cu-Ni alloy which will not melt at that temperature. Tests involving the use of increasing amounts of nickel from zero to approximately this proportion indicate that the diagram may be used as a satisfactory guide for the determination of nickel requirements for any given copper content and working temperature.

Our investigations indicate that resistance to checking is increased appreciably by the presence in copper steel containing 1.5% copper of as little as 0.25% nickel, but optimum results are obtained when such a product contains about 0.75% nickel. Copper steel containing 2.0% copper to which 0.2% molybdenum was added showed a marked increase in its resistance to surface checking.

Steel containing copper and nickel, throughout its entire mass or in its surface portions alone, in the ratio of about two parts of copper to one part of nickel (by weight) may be shaped under the conditions usually encountered in normal shaping operations without serious surface checking resulting.

While it is generally possible to shape copper steel containing copper and one or more alloying elements capable of raising the melting point of copper in proportions different than those which might be employed for producing the highest melting point alloy of the copper and the one or more alloying elements without producing surface checking, it may in some instances be advisable to employ the alloying elements in such amounts, relatively to the amounts of copper present, as may be required for producing the highest melting point alloy. It is to be understood, therefore, that our invention contemplates the use of such elements in all amounts and proportions capable of producing alloys with copper which have melting points higher than the melting point of copper.

As hereinbefore pointed out suitable proportions of copper and alloying elements may be established in a steel product in any suitable manner, as, for example, by incorporating the alloying elements in steel containing copper; or by incorporating the alloying agents in steel to which copper also is added; or by incorporating copper in steel containing one or more alloying agents; or by treating a metallurgical charge containing iron and copper with or without one or more alloying elements to produce a metallic iron product.

According to one limited aspect of our invention, we propose to treat ore containing sulphides of iron and copper to produce copper steel and treat the resulting copper steel to form copper steel products suitable for shaping at elevated temperatures, or shaped copper steel products of improved quality, in accordance with the procedures outlined herein and in accordance with the procedures outlined in our copending application.

In treating sulphide ores containing copper to produce metallic iron products (in accordance with the process outlined in the patent to Charles R. Kuzell No. 1,976,735, dated October 16, 1934, for example) it is possible readily to produce metallic iron containing copper and substantially free of sulphur. The metallic iron produced may contain copper in amounts varying from about 0.1% to about 2.5% or more depending upon the procedure followed, the copper content of the original ore and precautions employed to effect the separation of the copper and iron.

The copper produces a beneficial effect on the iron products and, in small amounts, causes no difficulties in shaping operations conducted at elevated temperatures. When the copper is present in relatively large amounts, serious surface checking is encountered in shaping at elevated temperatures. Restriction of the amount of copper in the metallic iron product can be accomplished, but the measures required may be inconvenient or costly to apply. Our inventions (described herein and in our aforementioned copending application) permit the utilization of such metallic iron products to produce improved copper steel products even when the metallic iron products contain amounts of copper which would cause serious surface checking in shaping operations of the heretofore customary type conducted at elevated temperatures. This specific aspect of our invention, therefore, permits the production of desirable copper steel products from sulphide ores containing copper without necessitating the use of costly and inconvenient procedures for restricting the copper content of the copper steel.

A preferred complete process of our invention involves oxidation of a sulphide ore containing copper to produce a substantially sulphur-free iron oxide product containing copper, reduction of the resulting iron oxide product to form a metallic iron product containing copper, and treatment of the resulting metallic iron product to control the character of its surface and produce shaped copper steel products in accordance with the procedures described in our aforementioned copending application, or in accordance with the procedures described herein. Any suitable method may be employed for recovering a metallic iron product containing copper from sul-

phide ores containing copper and iron, but we prefer to employ the method described in the aforementioned patent to Charles R. Kuzell No. 1,976,735.

When iron sulphide ores containing copper also contain an alloying element such as nickel, we prefer to so control the processes for the recovery of the metallic iron products as to produce products containing copper and nickel in suitable proportions to permit shaping without serious surface checking resulting. If the resulting metallic iron products are deficient in either nickel or copper, or in both, suitable amounts of these elements may be added or incorporated in accordance with any of the procedures hereinbefore suggested.

According to another limited aspect of our invention, we treat ores containing one or more alloying elements but substantially free of copper to produce metallic iron products containing the alloying elements. Copper may be incorporated in the resulting products in any suitable manner to produce copper steel products suitable for shaping. Instead of incorporating copper in the metallic iron products after they have been produced, we may incorporate copper in elemental form, or in chemical combination, in the original ore charges or in the charges undergoing treatment at any suitable stages of the iron recovery processes. If the ores are deficient in alloying elements, suitable amounts of alloying elements may be added to the ore or to the charge undergoing treatment or to the metallic iron product.

As hereinbefore pointed out, copper steel products formed in accordance with our invention may be shaped in any suitable manner at any suitable temperatures. The steel products of our invention may be shaped immediately after their production or stored and shaped later at or near their points of production or at points remote from their points of production. In some cases as, for example, when alloying agents are applied to or incorporated in the surface portions only of the steel products, the temperatures of the products may be sufficiently high that shaping may be carried out with slight additional heating or with no additional heating.

Shaping immediately after treatment of the copper steel with an alloying element may be carried out advantageously by subjecting the steel to the action of the alloying element while heated to a suitable shaping temperature. Treatment of the steel with the alloying element may be carried out immediately before shaping is commenced or during the course of the shaping operation, or treatment with the alloying element may be carried out both before and after commencement of the shaping operation.

When the alloying elements are applied to the steel products at elevated temperatures, we have found it to be advantageous to employ fluxing agents. According to our preferred method of carrying out this phase of our invention, a mixture of fluxing agent and alloying element is applied to the surface of the steel while the steel is heated to a suitable shaping temperature and immediately before the shaping operation is commenced. If scale accumulates on the steel during the course of the heat treatment, we prefer to employ a fluxing agent for aiding in removing the scale from the surface prior to the application thereto of the alloying element or mixture of alloying element and fluxing agent.

We have produced excellent shaped products by applying to the surfaces of copper steel products to be shaped, after heating to suitable shaping temperatures, a mixture of borax and nickel oxide.

In carrying out a preferred method in accordance with this phase of our invention, a copper steel product to be shaped, such as an ingot, is heated to the proper shaping temperature or to a temperature slightly above the desired shaping temperature. If scale is formed on the ingot, borax glass is applied to the surface to loosen the scale, and the loosened scale is removed in any suitable manner. A mixture of borax glass and nickel oxide is then applied to the clean surface of the heated ingot. The mixture fuses and spreads, and a coating of nickel is formed substantially immediately. The ingot is then ready for shaping.

Any suitable fluxing agent may be employed and any suitable alloying element may be employed. The fluxing agent and alloying element may be employed in any suitable proportions. We have employed borax glass in which nickel oxide has been dissolved to the extent to 2 to 5 percent with the production of satisfactory results. The fluxing agent and the mixture of fluxing agent and alloying element may be applied in any suitable manner and in either the liquid or solid state. When employed in the solid state, they may be sprinkled on the steel surfaces in finely divided form, and, when employed in the liquid or molten state they may form baths into which the steel products to be shaped may be dipped.

We claim:

1. The method of shaping copper steel which comprises incorporating nickel in the surface portions only of the steel in such amount that the surface portions of the resulting product contain copper and nickel in proportions suitable for forming a copper-nickel alloy having a melting point substantially higher than the melting point of copper, and subjecting the resulting product to a shaping operation at a temperature higher than the melting point of copper.

2. The method of shaping copper steel which comprises incorporating in the surface portions only of the steel nickel in such amount that the surface portions of the resulting product contain copper and nickel in the proportions of about two parts of copper to one part of nickel, and subjecting the resulting product to a shaping operation at a temperature higher than the melting point of copper.

3. The method of shaping copper steel which comprises heating the steel to a suitable shaping temperature, applying a mixture of fluxing material and nickel oxide to the surface of the steel, and subjecting the resulting steel product to a mechanical shaping operation at a temperature above the melting point of copper.

4. The method of shaping copper steel which comprises heating the steel to a suitable shaping temperature, applying a mixture of borax glass and nickel oxide to the surface of the steel, and subjecting the resulting steel product to a mechanical shaping operation at a temperature above the melting point of copper.

5. The method of shaping copper steel which comprises heating the steel to a suitable shaping temperature, subjecting the heated steel to the action of a fluxing agent to remove scale formed thereon, applying to the cleaned surface of the steel a fluxing agent and nickel oxide, and subjecting the resulting steel product to a shaping

operation at a temperature above the melting point of copper.

6. The method of shaping copper steel which comprises heating the steel to a suitable shaping temperature, subjecting the heated steel to the action of borax glass to remove scale formed thereon, applying to the cleaned surface of the steel borax glass and nickel oxide, and subjecting the resulting steel product to a shaping operation at a temperature above the melting point of copper.

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