

J. F. MONNOT.
ART OF HOT WORKING METALS.
APPLICATION FILED MAR. 2, 1906.

972,559.

Patented Oct. 11, 1910.

Fig. 1.

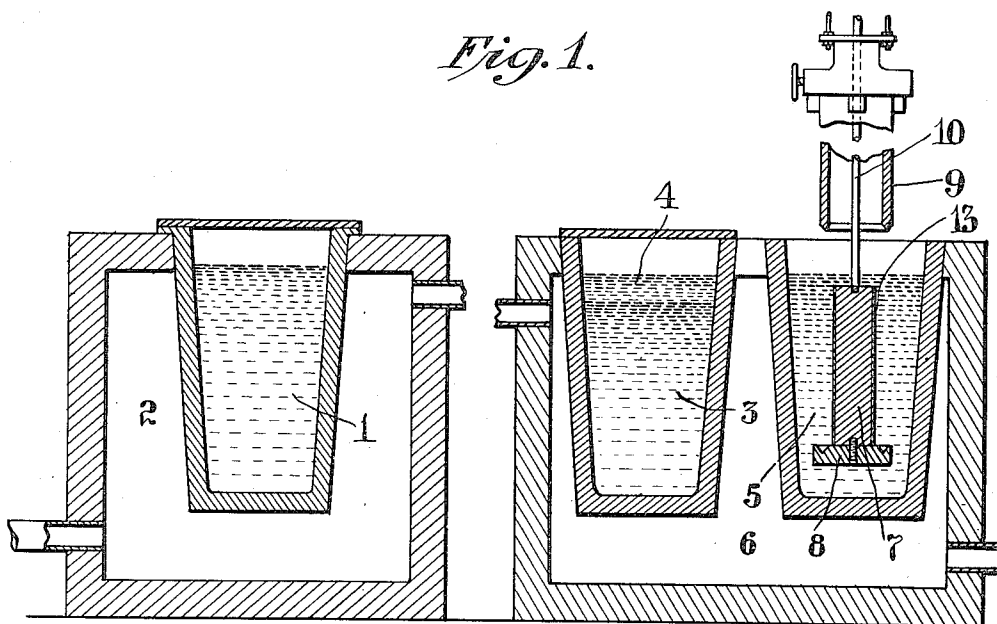
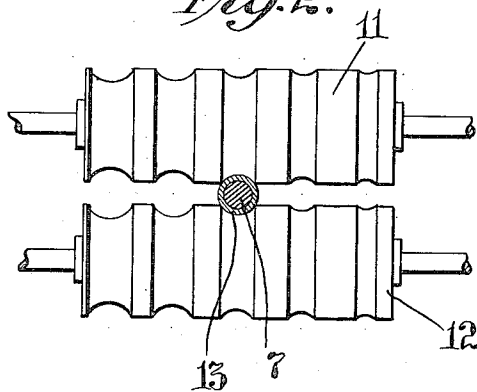


Fig. 2.



Attest:
E. Mitchell
A. M. Houghton

by

Inventor:
J. F. Monnot
Marble & Mitchell
Attys

UNITED STATES PATENT OFFICE.

JOHN FERREOL MONNOT, OF NEW YORK, N. Y., ASSIGNOR TO DUPLEX METALS COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

ART OF HOT-WORKING METALS.

972,559.

Specification of Letters Patent.

Patented Oct. 11, 1910.

Application filed March 2, 1906. Serial No. 303,917.

To all whom it may concern:

Be it known that I, JOHN FERREOL MONNOT, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented certain new and useful Improvements in the Art of Hot-Working Metals; and I do hereby declare the following to be a full, clear, and exact description of the same, such as it will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to improvements in the art of working metals, and particularly in working metals which are subject to excessive oxidation or other deterioration when worked hot in the presence of air, products of combustion or other contaminating substance, such for example as sulfur in fuel or in products of combustion. Such metals I will term generically "sensitive metals". A familiar example is nickel, which is so subject to deterioration when exposed to the air at or about a red heat that in practice it is at present usually worked in a neutral or indifferent atmosphere, or in an atmosphere of producer gas. Operating in a neutral or indifferent atmosphere, or in an atmosphere of producer gas, is both disadvantageous and exceedingly expensive and is not free from danger to the workmen; furthermore nickel is quite sensitive, under certain conditions, to the action of carbon monoxid, present in large quantities in producer gas, and is even sensitive to nitrogen; so that the so-called "neutral" atmospheres are, in many cases at least, not neutral at all, but merely less objectionable than air. I avoid the necessity of employing such an atmosphere in the working of "sensitive metals", by incasing the ingots, bars or slabs of such metals with a relatively thin dense impervious hermetically sealing coating of a less sensitive ductile or malleable metal, such coating being thoroughly welded at all points to the ingot, bar or slab of sensitive metal, and covering the entire surface thereof, or at least substantially the entire exposed lateral surface thereof so that the coating may be extended down with the said body of sensitive metal, which I will speak of hereafter as the "core" or "base", without rupture. In this way the said core or base is thoroughly sealed against the entrance of air or other contaminating sub-

stance and may be worked hot between rolls, in a press, or under the hammer, with the same freedom from injury as if worked in a neutral atmosphere but without the excessive difficulties attending working in a neutral atmosphere. At the conclusion of the operation the coating or envelop of less sensitive metal which is generally a mere film may be removed by the action of chemicals or in any other suitable manner.

My invention consists in coating all exposed lateral surfaces of a base or core of sensitive metal, such as above referred to, with an impervious envelop of less sensitive metal firmly weld-united thereto, and in working or "ccextending" both core and coating jointly, finally removing the coating if such be necessary or desirable. Specifically, my invention consists in coating nickel or allied metal, (such for example as cobalt), with copper or other less sensitive metal and working the compound ingot thus produced, finally removing the coating.

In the accompanying drawings I illustrate one method of carrying out my process, also, diagrammatically, apparatus such as may be used in carrying out the process.

In said drawings, Figure 1 shows, diagrammatically and in vertical section, apparatus for covering the sensitive metal with a welded-on coating of less sensitive metal; and Fig. 2 shows, diagrammatically, a pair of rolls, indicating the working of the coated object with the protective coating thereon.

I will describe my invention with particular reference to the working of nickel and nickel alloys, but it will be understood that practically the same description applies to cobalt, which for metallurgical purposes possesses the same properties and acts in the same way as nickel and may be considered for the purpose of this specification as the equivalent of nickel. Much of the commercial metallic "nickel" contains large amounts of metallic cobalt, as I am advised. Likewise the process may be carried out with other metals as the core or base—for example high carbon steel, such as tool steel, which at present is usually worked at the lowest possible temperatures, hardly rising above low red heat, in order to avoid burning.

Nickel is peculiarly sensitive to the action of many metalloids and gases when in a

heated condition and particularly at temperatures above a red heat, and for that reason is unduly expensive and difficult to manipulate. If worked in the air at or
5 above a red heat it seems to crumble and becomes practically worthless; this being due doubtless to oxidation. For this reason it is the practice to work nickel in an indifferent atmosphere, or one less active than
10 air, as already mentioned. But as stated heretofore, both nitrogen and carbon monoxid, usually present in considerable quantities in any atmosphere employed, are not inactive with respect to nickel. For carbon
15 monoxid metallic nickel has a strong and peculiar affinity manifesting itself at varying temperatures in varying reactions. At one range of temperatures, it combines directly forming a volatile compound, the so-
20 called nickel carbonyl, which breaks up in another higher range, depositing its contained metal as dust or films, while at still another and higher range, the gas dissolves in the metal, making it spongy. By reason
25 of these reactions, working nickel in ordinary reducing flames is more or less impractical. Nickel is even sensitive to the action of nitrogen. Carbon and silicon it takes up readily in reducing atmospheres and loses
30 again almost as readily, so that the composition of a worked article is always uncertain as regards these two important substances. As a result of these reactions, pure nickel articles are almost unknown in the arts;
35 and such as are made are usually produced by the relatively difficult and costly processes of cold working. Nickel working today is therefore to be ranked among the difficult and expensive arts; and the metal
40 is not used for many purposes to which its beauty and its resistance to atmospheric influences at common temperatures and to chemicals would well adapt it. Neither is it used as a covering for other and cheaper
45 metals as generally as its properties would indicate, and for much the same reason. It is often applied as an electrocoating, but such coatings suffer from the same defect as other electroplatings, viz., that of being
50 relatively expensive and porous; and also from a defect peculiar to this metal, that of being thrown down by the current in a condition of peculiar tension, often described as one of "surface tension," which
55 causes the metal to have more adherence to itself, so to speak, than to the base metal, and to be in a condition of internal stresses and strains. This fact limits the thickness of nickel electroplatings to a certain limited
60 amount; attempts at producing greater thicknesses causing the metal to curl up and away from the base metal. And when the base metal, as in the case of iron, oxidizes by penetration of moisture through the in-
65 evitable pores of the electroplating, the

nickel tends to detach and roll up in the familiar curly pellicles.

Many attempts have been made to plate hot, or to anneal the electroplatings, to obtain coatings free of this condition of strain
70 and of this porosity, but they have not been particularly successful. The stated sensitiveness of nickel in mass of course also obtains with nickel films and in a greater degree. Plating from nickel carbonyl atmos-
75 pheres gives good coating in small experiments where the conditions can be carefully controlled, but on the practical scale it does not work so well. The operation is expensive and uncertain, and moreover gives porous coatings. I have however, discovered
80 that by the use of certain expedients I can work pure nickel into all sorts of articles at any temperature and with any tools without fear of contamination; manipulating it very
85 much as mild steel is worked, and with equal ease, certainty and cheapness, while using no more than ordinary tools and avoiding the use of the expensive and uncertain non-oxidizing atmospheres mentioned. Further,
90 by this method the nickel in the original bloom, billet or ingot can be rolled and stamped down to the thinnest articles or implements, preserving exactly its original
95 properties and composition. If the original ingot contained a certain per cent. of carbon or of silicon, the finished article will show the same analysis. This is done by placing
100 on all exposed surfaces, or at least on substantially the entire exposed lateral surface, of the original ingot or bloom a sealing coating of a malleable, less sensitive metal, hermetically separating the nickel from the action of air, gases, carbon, silica, etc., and
105 accompanying it throughout its working. As particularly suitable for this purpose, I have found copper, bronze and aluminum bronze.

I prefer to apply the coating in certain
manners described in my co-pending applications Ser. Nos. 265,508 (Patent No. 110
851,684, dated April 30, 1907), 281,680, and 333,570, (Patent No. 853,716, dated May 14, 1907), although I do not limit myself to these methods. The process therein described depends upon the fact observed by
115 me that while nickel and other ironlike metals have no special affinity or disposition to unite with unlike metals of the type of copper or silver at common casting temperatures of such unlike metals, yet if the copper, etc., be raised far above its melting point and be in what may be called a supermolten condition, a union with the ironlike metal may be instantly effected by contacting the
120 latter in a clean condition therewith, producing a welded-on film of metal derived from the molten bath. To this film may then be welded any desired amount of said unlike metal at a more convenient casting temperature, producing an autogeneous, permanent
130

union of the ironlike and the unlike metal, in the nature of a weld, and one which resists tools and heat. To utilize this discovery in coating nickel, etc., for the purposes stated, any of a number of methods may be used. One which is convenient, is to thoroughly clean the surfaces of the ingot, as by sandblasting; heat it under circumstances precluding oxidation, for which purpose a plunge bath of a non-alloying metal, such as molten lead, or a molten flux like borax, fluorspar, cuprous chlorid, sodium silicate, etc., may be used; remove it from this bath when sufficiently heated and momentarily plunge it into a bath of melted copper heated far above its melting point or in the "supermolten" condition. Upon withdrawal from this bath, it will be found coated on all exposed surfaces with a layer of copper cohering, as distinguished from adhering, to the base and resisting stripping therefrom by the action of cutting tools or violent changes of temperature. To this copper layer, more copper may be attached in amount sufficient to give the thickness desired by casting on at a more convenient temperature, such as the ordinary casting temperature of copper. The coated billet may then be worked with tools to compact the copper, if necessary. A portion of molten flux may be conveniently kept floating on the metal in the supermolten bath to protect it from the air. In removing from the flux bath, a portion of the flux will adhere to or glaze the surface, protecting it in transit through the air to the supermolten dip. A portion of flux is also conveniently kept floating on the metal in the supermolten dip.

Fig. 1 illustrates the method just described of welding a coating of protective metal to the sensitive metal to be worked, 1 designating the preliminary heating bath, of molten lead, flux or the like, located within a suitable furnace 2 by which heat may be imparted to said bath without contact of the article to be heated with the furnace gases. 3 designates a bath of "supermolten" protective metal, 4 a layer of flux on the surface thereof, and 5 a bath of protective metal from which the main portion of the protective coating is to be formed; both of these baths 3 and 5 being located within a suitable furnace 6. 7 designates a body of sensitive metal, supposedly one which has just received a film coating in the supermolten bath 3; 8 designates a suitable bottom plate secured to said metal body 7, and 9 designates a casing adapted to be dropped over said body 7, into engagement with the bottom plate 8, so as to inclose against the sides of the film-coated object 7 a layer of the molten metal of bath 5. 10 designates a suitable porter bar by means of which the billet 7 may be

handled. After a layer of molten protective metal has been inclosed, around the billet 7, by the dropping of casing 9, the billet, casing and all are raised, out of the molten metal, and the molten metal within the casing is permitted to solidify, and when solid it hermetically seals substantially the entire lateral surface of the billet against the action of air or other gases. The coated billet may then be removed from the casing, and worked hot between rolls (as for instance the rolls 11 and 12, of Fig. 2) or in any other suitable manner; the sensitive metal being protected, throughout this working, by the welded-on envelop of less sensitive metal. In Fig. 2, 7 designates the sensitive metal, and 13 the protective envelop of less sensitive metal. In Figs. 1 and 2, the thickness of the coatings is exaggerated.

When the ingot is of small size and is not to be extended or worked to any great extent, the supermolten dip alone is often sufficient without casting on more copper, but if the ingot is to be much reduced in size to form the finished articles, the cast-on coating should also be applied. In either case, the copper will be found to accompany the nickel through its subsequent manipulation, co-extending therewith and forming a protective coating shielding it absolutely from air, carbon monoxid, sulfur, silicon, carbon, etc. If the original coating be 3 per cent. of the thickness of the ingot, that in the finished article will also be 3 per cent.

Another and very convenient method, also more fully described in one of the acknowledged co-pending applications, is to cast the whole amount of copper desired in a supermolten condition around the ingot centered in a mold, after preferably first heating in the manner described. The first contacting layer of the supermolten copper will form the weld film and as the rest of the copper cools and shrinks on, the nickel and coating will be found to be permanently and indissolubly united, so far as heat or the action of tools is concerned. With an ingot of nickel so protected, all the ordinary operations of hot metal working, such as rolling, drawing and stamping may be performed without fear of contamination and at the operator's leisure; re-heating and annealing being done as often as desired and in any heating apparatus desired.

The nickel of the compound billet being hermetically sealed-in by the cohering poreless copper coating and being firmly welded to such coating, the compound billet may be safely handled like a simple copper billet and in much the same way.

After the finished article has been made, the copper may be simply dissolved off, as by the action of a nitric acid strong enough to make the nickel passive; by electric solution in any of the numerous baths, like cya-

nid, etc. For example in making a dish of pure nickel for use in the laboratory or the household, the nickel ingot may be brought to heat by plunging in a bath of fused cryolite; momentarily dipped in a bath of supermolten copper protected from oxidation by a surmounting covering of cryolite; removed and either with or without casting on more copper according to the size of the ingot, heated and rolled down into a plate, and finally stamped into shape. This will produce a nickel dish with a thin adhering coating of copper which may be removed by plunging into nitric acid solution, or other suitable solvent, leaving the surface of the nickel bare, ready for polishing. Pure nickel wire may be produced the same way by substituting wire drawing mechanism for the rolls and stamps.

Nickel plated ware of any size, shape or kind may be cheaply and economically produced by substituting for the pure nickel ingot a compound ingot with iron or steel core, and the core may be tubular, the nickel coating being applied both inside and outside. The compound film-protected ingot is drawn, rolled, spun, stamped or otherwise treated exactly as in the case of the pure ingot, producing wire, plates, articles, tubing, etc., consisting of steel or iron with a coating of nickel as thin or as thick as may be desired, perfectly adherent, perfectly nonporous and free from any condition of internal stress or strain. Bicycle and boiler tubing may be very conveniently produced this way.

Besides nickel and steel-cored nickel, there are many other industrial metals which may be treated in the same way with advantage. Among them is cobalt which in nearly every respect behaves as does nickel and is equally advantageous for laboratory ware and for plating, and which, since new sources of cobalt have been discovered, is likely to become industrially important in such metallic forms. Much of the commercial "nickel" now contains greater or less amounts of cobalt. Such metals as chromium, manganese, tantalum and tungsten, whose inordinate reactivity with metalloids has hitherto precluded their industrial use, in the pure state and, to a large extent, in that of definite alloys, may also be so worked when protected in the manner described.

Nickel steels and other steels offer a very important field for my invention. As is well known, after attaining a steel of a definite composition and therefore definite properties, it is very hard to maintain it of definite composition and definite properties throughout the extensive manipulation necessary to form a chisel or a watch spring therefrom. The high carbon steels lose more or less carbon and silicon, the metalloid burning out in superficial layers and equalizing to sup-

ply the loss in underlying layers. In a thin article like wire or a chisel, this is serious. Similarly, chromium, manganese, tungsten, vanadium, and similar alloying, readily oxidizable metals, also tend to burn out. This is a very serious matter in making and tempering tools of the modern special steels. By, however, covering the bloom or billet of steel with copper or other suitable material in the manner described, the original composition of the bloom can be maintained throughout all the operations necessary to form a finished article. This renders it possible to make tools of very exact properties and it also much facilitates working. For instance, in ordinary tool making the copper coated steel can be worked at much higher temperatures than the comparatively low temperature it is now thought necessary to use, with resultant ease and economy of working.

In the case of tools and similar articles where the appearance of the shielded metals is not a consideration, as it is in the case of nickel articles, it is unnecessary to remove the coating of copper in most cases, although this of course may be done. The coating of copper on a chisel for instance, and especially when merely the alloy-film described is applied, does it no harm whatever, but on the other hand is even desirable as protecting it from rusting and enhancing its appearance. The copper coated steel works well under the blacksmith's hammer, the copper following the steel through its extension. Copper is made possible for use as a protecting envelop in the process herein described, by the fact that it is not particularly sensitive to the action of metalloids at high temperatures and is indefinitely ductile and malleable, enabling it to follow the base metal throughout its working.

To recapitulate, my method consists in covering the entire surface of, or at least substantially the entire lateral surface of, bodies of metals sensitive to contamination or outside influence at high temperatures, with a sealing coating of a less sensitive metal, before using ordinary hot manipulations; in employing such hot working and finally, where desired, removing the coating.

I employ the term "ferrous metals" in the following claims as a term generic to iron, the various steels, including nickel steel, cobalt steel, manganese steel, chrome steel, tungsten steel, etc., and also to the metals nickel, cobalt, manganese, chromium, tungsten, vanadium, titanium, etc., all of which metals are somewhat allied to iron chemically. I employ the term "nickelous metals" as a term generic to nickel, cobalt, and others of the metals mentioned which are closely allied to nickel, as is cobalt for example.

I employ the term "sensitive metals" as

a term generic to metals which are extremely subject to contamination or deterioration at high temperatures, such for example as nickel, cobalt, tool steel, etc., and as distinguishing from metals which may be worked readily at high temperatures, and without material contamination or deterioration, as for example, mild steel, copper, etc.

What I claim is:—

1. The process of hot-working sensitive metals susceptible to oxidation or other contamination or deterioration at high temperatures which consists in enveloping substantially the entire exposed lateral surface of a body of such a sensitive metal with a hermetically sealing, cast-on coating of a less sensitive metal, before such surface has been exposed materially to the action of a hot contaminating gas, and then heating the coated object and working the base and coating jointly while hot.

2. The process of hot-working metals susceptible to oxidation or other contamination or deterioration at high temperatures, which consists in enveloping bodies of such metals with a hermetically sealing cast-on coating of a less sensitive metal, and then heating the coated object and working both base and coating jointly while hot, and finally removing the coating.

3. The process of hot-working sensitive ferrous metals susceptible to oxidation or other contamination or deterioration at high temperatures which consists in producing a clean metallic surface on a body of such a sensitive metal, enveloping substantially the entire exposed lateral surface of such body after such a metallic surface has been produced with a hermetically sealing, cast-on coating of an unlike and less sensitive metal before such surface has been exposed materially to the action of a hot contaminating gas, and then heating the coated body and working both base and coating jointly while hot.

4. The process of hot-working sensitive ferrous metals susceptible to oxidation or other contamination or deterioration at high temperatures, which consists in enveloping substantially the entire exposed lateral surface of a body of such sensitive metal with a hermetically sealing, cast-on coating of copper before such surface has been exposed materially to the action of a hot contaminating gas, and then heating the coated object and working both base and coating jointly while hot.

5. The process of hot-working sensitive ferrous metals susceptible to oxidation or other contamination or deterioration at high temperatures, which consists in enveloping bodies of such sensitive metals with a hermetically sealing cast-on coating of copper, and then heating the coated object and working both base and coating jointly while

hot, and finally removing the coating with a solvent.

6. The process of hot-working nickelous metals which consists in enveloping substantially the entire exposed lateral surface of a body of nickelous metal with a hermetically sealing, cast-on coating of a less sensitive metal before such surface has been exposed materially to the action of a hot contaminating gas, and heating and working such nickelous base and the coating jointly and finally removing the coating.

7. The process of hot-working nickelous metals which consists in covering a body of such metal with a welded-on, hermetically sealing coating of a less sensitive metal, heating and working such nickelous base and the coating jointly, and finally removing the coating.

8. The process of hot-working nickelous metals which consists in covering a body of such metal with a hermetically sealing cast-on coating of a less sensitive metal, heating and working such nickelous base and the coating jointly, and finally removing the coating by the action of a solvent.

9. The process of hot-working sensitive metals susceptible to oxidation or other contamination or deterioration at high temperatures which consists in welding to substantially the entire lateral surface of a body of such sensitive metal, before such surface has been exposed materially to the action of a hot contaminating gas, a completely enveloping, impervious, cohering, hermetically sealing coating of a less sensitive metal, and then heating and working such base and its coating together.

10. The process of hot-working nickelous metals which consists in welding to substantially the entire lateral surface of a body of such metal, before such surface has been exposed materially to the action of a hot contaminating gas, a completely enveloping, impervious, cohering, hermetically sealing coating of a less sensitive metal and working such body and its coating together.

11. The process of hot-working nickelous metals which consists in producing a clean metallic surface on a body of such a metal, forming an impervious, cohering coating of copper completely enveloping and hermetically sealing substantially the whole of such surface by contacting such surface with molten copper at a temperature much above the melting point of copper, before material contact of such surface with hot contaminating gas, and then working the body and the coating jointly while hot.

In testimony whereof I affix my signature in the presence of two witnesses.

JOHN FERREOL MONNOT.

Witnesses:

J. B. HANNUM, Jr.,
W. I. SCHAFER.