UNITED STATES PATENT OFFICE.

AUGUSTE J. ROSSI AND WILLIAM F. MEREDITH, OF NIAGARA FALLS, NEW YORK, ASSIGNORS TO THE TITANIUM ALLOY MANUFACTURING COMPANY, OF NEW YORK, N. Y., A CORPORATION OF MAINE.

METHOD OF TREATING METALS.

1,056,125. Specification of Letters Patent. Patented Mar. 18, 1913.

No Drawing. Application filed April 17, 1912. Serial No. 691,514.

To all whom it may concern:

Be it known that we, AUGUSTE J. ROSSI and WILLIAM F. MEREDITH, both citizens of the United States, and residing at Niagara Falls, in the county of Niagara and State of New York, have jointly invented a certain new and useful Method of Treating Metals, of which the following is a specification.

Our present invention relates to methods of cleansing, or improving, metals whether by adding thereto, while molten, agents qualified to combine chemically with undesired impurities, these including oxygen, or nitrogen, and their compounds, also slags, etc., or furthermore by doing this and retaining also in the product some of such agent, whereby desirable characteristics are imparted to the metals so treated.

The objects of our invention comprise the accomplishment of such improvements of the metal better, and more economically, than heretofore, with, if desired, smaller than previously aggregate additions of the purifying agent suitably prepared for the purpose more rapidly and economically than hitherto.

We attain these objects by the procedures hereinafter described.

It is now established, as evidenced by the magnitude of actual industrial operations, that free titanium in its elemental, *i. e.* metallic form is exceptionally efficacious to purify and improve metals as aforesaid, titanium when thus free possessing remarkable avidity for the said impurities with which it combines chemically in the molten metal treated to form compounds including slags which promptly rise to the surface of the bath whereby the underlying molten metal is efficiently cleansed and the final product rendered pure and free from blow holes and other causes of weakness, or furthermore improved by retention therein also of some titanium. The numerous United States Letters Patent heretofore granted to Auguste J. Rossi also disclose such efficacy of titanium for the purposes mentioned. It has however been hitherto, naturally, supposed as evidenced by said patents, that such purification by titanium could be successfully accomplished only by additions to the metals treated while molten of an alloy or compound containing titanium in its said elemental or metallic state. The present industrial practice of such purification on extended scales has apparently proceeded exclusively on this theory, the methods practised in producing such alloys, for instance those of iron and titanium as evidenced for example by said Rossi's Patent No. 609,466, dated August 23, 1898 involving procedures carefully guarded to secure final products devoid, as far as possible of chemical compounds of titanium with other elements, and, particularly, it has not, prior to our present invention, been known or suggested, so far as we are aware, that compounds of titanium with carbon, *i. e.* carbid of titanium could, as additions to molten metal, operate successfully, or at all, to accomplish its desired purification. We are now however satisfied that this is an error, and that, on the contrary, carbid of titanium, provided it be, as per our method, very intimately mixed and homogeneously conglomerated in very minute sub-divisions with other metal, is, if the compound so constituted be added for purification to molten metal, ultimately as efficacious, or more so, than metallic titanium and at considerably less cost to the manufacturer. This novel compound, so containing the carbid of titanium, as substitute for metallic titanium, possesses, we have found, characteristics rendering it superior, for industrial uses and purposes, to said alloys of elemental titanium with other metals, as for instance the ferro-titanium product of the aforesaid Letters Patent, such superiorities comprising its comparatively economical production as per the method hereinafter described, and also its comparative stability and capacity to delay momentarily liberation of the metallic titanium, thus enabling less of latter to produce more complete purification owing to its more complete permeation and distribution throughout the bath by disintegration of the carbid therein before actual purification by liberated metallic titanium begins.

It will be understood that, prior to our present invention, the practised methods of producing alloys of titanium by carbon reduction, as for example per the process described in said Letters Patent No. 609,466, involved application of temperature, *i. e.* energy, to the charge, sufficiently great to

insure presence, in the final product, of the most possible of metallic titanium; also the addition of substantially no more carbon than calculated to be sufficient to reduce the oxids of said charge, and leave in the final product not to exceed a comparatively small percentage of uncombined carbon, *i. e.* carbon in graphitic state, thereby insuring the acquisition and retention in the alloy of the greatest amount of metallic titanium derivable from the charge. To this end, in producing said alloys, the additions of carbon were regulated accordingly, and, the temperature of the bath raised and maintained, at corresponding expense of energy, to insure not only the reduction of the oxids but also the prevention of carbids in the final product. This procedure has resulted in two considerable items of expense, which our method saves to the manufacturer, viz: the expense of maintaining the temperature sufficiently high and long to attain the desired metallic titanium result, and also the expensive drafts meanwhile made upon the constituents of the carbon electrodes employed and also upon the graphitic walls of the furnace because of the stinting of carbon added to insure the aforesaid hitherto required constitution of the purifying alloy.

Our carbid-containing compounds required for practise of our present invention may be produced as follows:—In a furnace capable of developing and maintaining the required temperatures, as for example preferably an electric furnace of ordinary type and construction, such for instance as shown and described in U. S. Letters Patent to Auguste J. Rossi, No. 802,941, dated October 24, 1905, or No. 822,305, dated June 5, 1906, is charged, in such proportions as may be desired, metal, for example iron, also titanium oxid and also carbon, the latter preferably in such proportions as not only to satisfy the affinity therefor of the oxygen of said oxid, but also enough to satisfy the affinity therefor of the therefrom liberated titanium, and also enough carbon besides to impart to the resulting product such uncombined carbon content as may be desired, and this with as little expense as possible to the carbon of the electrodes, and the graphite linings of the hearth or crucible.

It will be understood that instead of the metal, or iron, mentioned, oxids thereof might be charged, care being, in that case, taken to regulate the proportion of carbon so as to insure their reduction also. The temperature of the charge is then raised, as by turning on the current, no higher than sufficient to insure reduction of the oxid of titanium. It will be understood that the application of such temperature will result in the formation of a bath of the molten metal other than titanium, and this whether introduced in elemental or in oxid form, provided in the later case sufficient carbon be added. The said temperature is then maintained only sufficiently long and high to insure, as thoroughly as possible, not only the said reduction of oxids, but also formation, throughout the bath, of the most possible of carbid of titanium. When this stage has been reached, the temperature must be lowered as rapidly as is enconomically possible, lest continuation, or even slow diminution, thereof result in robbing the carbid of its carbon, as by latter's passing into the graphitic state, or making new combinations as with oxids present. The required lowering of the temperature thus speedily may be accomplished by tapping the charge promptly as soon as it has reached the stage mentioned, and casting the molten product sufficiently distributed in graphite, or other heat conductive, receptacles.

It will be understood that our compounds of titanium carbid with other metals than iron are producible by the method above specifically described, the procedure in each case being substantially the same except that such other desired metal or its oxid is substituted for the iron. Thus compounds of carbid of titanium with copper, tin, lead, zinc, manganese, antimony, etc., may be produced for use in the purification of such metals, or also their other improvement as aforesaid. Our novel, unitary, compounds thus attained, consist essentially of metal having therewith intimately mixed and homogeneously conglomerated, therewith mutually cohesive, very minute particles of carbid of titanium, and are then ready for use as purifiers of other metal, etc.

Distinguishing beneficial characteristics of our said compounds are, we believe, due to their production by carbon reduction of oxid of titanium in the metal while molten, the which imparts to the therein resulting carbid, for our purposes, properties otherwise unattainable, including unprecedented minuteness of sub-division, and intimacy, homogeneousness, and cohesiveness, of mixture with the metal, whereby such carbid of titanium has been, for the first time in our experience, rendered available for use in successfully purifying other metals;—mechanical or other unions of metal with therefrom separately produced carbids being, as we believe, industrially useless for such purposes.

To carry out our present invention we add to a bath of to-be-purified molten metal one of our said compounds consisting of titanium carbid mixed with, preferably, such metal. Taking for example purification of steel, we add thereto, preferably while in the teeming ladle, a proportion of the said compound consisting principally of iron having therewith intermixed as aforesaid carbid of titanium. This compound is

preferably, preliminarily, more or less comminuted, and is preferably added while the metal to be purified is being poured into the ladle, or it may be introduced while the metal is in the converter, hearth, or crucible, or even in the molds. After such addition an interval should be accorded sufficient to enable the compound to dissolve in, and thus thoroughly permeate, the bath, to enable the carbon of the carbid to quit its titanium and to enable the thus liberated metallic titanium to accomplish its reactions with undesired elements and compounds, and the resulting new compounds to rise to the surface as slags, etc. Such interval amounts usually to not less than three minutes, though the time required will, of course, vary somewhat in each case according to its special conditions, and can readily be determined by those skilled in the art by usual observations and tests. We find that, in usual practice, the best results are attained most economically by additions of said compound, the titanium carbid content of which is from 10 per cent. to 20 per cent. by weight of the mass, but such compounds containing as low as 3 per cent. of said carbid may be profitably employed, and also as high as 80 per cent. It will be understood that a low content of the carbid may prove undesirable owing to the proportionally greater bulk of the compound required for purifying. On the other hand it seems inadvisable to exceed 80 per cent. of carbid in the compound because of inversely proportional influence of the therewith associated constituent metal of the compound when the latter is added as aforesaid to a bath of molten metal. It will be understood that if purification only is desired, the amount of our said compound added will be proportioned according to its titanium content, so as to supply the metal treated only about so much metallic titanium as is required to satisfy the chemical affinities therefor of all the undesired elements and compounds, including slags, present, and produce a final purified product containing substantially no, or traces only of, titanium. Those skilled in the art will readily understand how to thus proportion the compound to the charge as by preliminary analysis of the compound and of the metal to be purified and therefrom calculating the amount of compound to be added, or by analysis of the final products and varying the amount of compound added to the next charge so as to more nearly attain thereby the desired final result. In some instances, in which it is desired to not only thus purify the metal treated but also to impart thereto desired qualities by retention of substantial amounts of titanium in the final product, the amount of our new compound added to the bath will be increased correspondingly, and thus if desired even alloys with titanium of the metal treated produced.

Our novel method of treating metals by our said production, and thereafter addition thereto while molten, of compounds consisting essentially of metal containing therewith intimately commingled and homogeneously conglomerated carbid of titanium appears more useful than the previously practised production of alloys of titanium with metal and addition of such alloys to molten metal treated, in that our said novel compound is easier and cheaper to produce, and insures at less expenditure of titanium the required amount in the bath, whether for purifying or other purposes, all of which is particularly important in view of the present magnitude of metal purifying operations being practised by aid of metallic titanium.

We are satisfied that additions of isolated carbid of titanium to baths of molten metal must prove ineffective to purify them, owing not only to the magnitude of the sub-divisions of such carbid, however finely pulverized by any economically practicable mechanical means, but also to the comparative indissolubility, in the bath, of carbid thus added by itself alone. We have found, however, that the carbid, if added in association with other metal, and in that condition of much smaller sub-division and homogeneous conglomeration with such metal resulting from our method of production, not only dissolves freely, rapidly, and homogeneously, throughout the bath of metal treated, thus permeating it thoroughly, but also that its content of combined carbon soon thereafter, owing to the temperature and other conditions, separates from its content of titanium, thus releasing within the metal treated, and when and where most needed, a multitude of comparatively homogeneously distributed very minute particles of free metallic titanium, which then combine with the undesired elements and componds present to form new compounds which, as is now well understood, accomplishes the desired purification.

It will be observed that the addition of the titanic purifier in the form of its carbid thus serves, in a measure, as it were, to postpone the action of the titanium as a purifier until better opportunity accorded for its extended and intimate co-mixture with the ingredients of the bath, as compared to the hitherto additions of the titanium in metallic state when it immediately commences its reactions at the points where introduced and without similar opportunity accorded for preliminary, more uniform, distribution. It may be that this increases momentarily the time of treatment required, *i. e.* the interval in the operation after addition of the purifying agent, but this, requir-

ing only a few minutes, we regard as more than counterbalanced by the greater opportunity for more evenly distributed action and purification accorded by the carbid character in which the purifier is introduced as above explained, the result including a saving in the total amount of metallic titanium otherwise required to produce the desired final result.

When metals other than steel or iron are to be purified, or treated, by adding our said carbid-containing compounds, such additions are made, in the manner above described, to the molten baths of such other metals. It will be observed however that if a final product is desired containing no other than the treated metal and titanium, or traces of latter, the compound added should comprise as its elementary metal constituent metal of the same kind as that treated. Thus for example should it be desired to purify, or treat, molten copper, our compound added thereto should consist essentially of copper and therewith intermixed as aforesaid particles of titanium carbid.

Having now described our invention, what we claim as new and desire to secure by Letters Patent is the following, viz:—

1. The method of purifying metal which comprises adding thereto while molten a compound comprising metal and therewith mutually cohesive, and conglomerated, particles of carbid of titanium.

2. The method of purifying metal which comprises adding thereto while molten a compound comprising similar metal therewith mutually cohesive, and conglomerated, particles of carbid of titanium.

3. The method of purifying steel which comprises adding thereto while molten a compound comprising iron and therewith mutually cohesive, and conglomerated, particles of carbid of titanium.

4. The method of cleansing metal from undesired elements and compounds including slags which comprises adding to such metal while molten a compound consisting predominantly of metal having therewith mutually cohesive, and conglomerated, carbid of titanium.

5. The method of cleansing steel from undesired elements and compounds including slags which comprises adding to said steel while molten a compound consisting predominantly of iron having therewith mutually cohesive, and conglomerated, carbid of titanium.

6. The method of cleansing metal from undesired elements and compounds including slags, which comprises adding to such metal, while molten, carbid of titanium cohesively conglomerated with metal, and then allowing the resulting bath to stand until therein contained compounds of titanium have risen to the surface thereof.

7. The method of cleansing steel from undesired elements and compounds including slags, which comprises adding to said steel while molten, carbid of titanium cohesively conglomerated with iron, and then allowing the resulting bath to stand until therein contained compounds of titanium have risen to the surface thereof.

8. The method of purifying metal which comprises adding thereto while molten metal containing therewith intimately mixed not less than 5 per cent. and not more than 80 per cent. of carbid of titanium.

9. The method of purifying steel which comprises adding thereto while molten iron containing therewith intimately mixed not less than 5 per cent. and not more than 80 per cent. of carbid of titanium.

10. The method of treating metal which comprises adding thereto while molten metal containing therewith intimately mixed particles of carbid of titanium produced by carbon reduction of oxid of titanium while in contact with a molten bath of said last mentioned metal.

11. The method of treating ferro metal which comprises adding thereto while molten a ferro metal containing therewith intimately mixed particles of carbid of titanium produced by carbon reduction of oxid of titanium while in contact with a molten bath of said last mentioned ferro metal.

12. The method of treating metal which comprises adding thereto while molten metal containing therewith intimately mixed carbid of titanium in form and quantity adequate to supply to said first mentioned metal enough metallic titanium to chemically combine with therein undesired elements and compounds including slags, and allowing the resulting bath to stand until therein contained compounds of titanium have riven to the surface thereof.

13. The method of treating ferro metal which comprises adding thereto while molten a ferro metal containing therewith intimately mixed carbid of titanium in form and quantity adequate to supply to said first mentioned ferro metal enough metallic titanium to chemically combine with therein undesired elements and compounds including slags, and allowing the resulting bath to stand until the therein contained compounds of titanium have risen to the surface thereof.

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Witnesses:
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