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TITANIUM ADDITIONS TO STAINLESS STEELS

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This invention pertains to improved iron and steel, and more particularly, to the production of alloy and stainless steels having titanium additions.

My investigations into the utilization of titanium additions have disclosed that they are advantageous from certain standpoints and disadvantageous from others. Titanium has very strong degasifying and deoxidizing properties and may be used for cleaning a molten metal bath. However, titanium in larger quantities has a tendency to precipitate ferrites and to form nonmetallic inclusions; it also has a tendency to decrease ductility and normal corrosion resistance of the metal as indicated, for example, by a nitric acid test. On the other hand, in suitable quantities it has the property of combining with carbon to form titanium carbide and to increase the fluidity of the slag. When utilized with silicon, for example, it fluxes the silicates and other slag particles; its own dioxide has relatively low refractory properties. In proper amounts, it also decreases intergranular corrosion.

Heretofore, those skilled in the art have endeavored to make use of the desired properties of titanium and to minimize its undesirable properties by either proportioning the titanium to the ferric oxide content of the slag or from the standpoint of the stoichiometrical amount necessary to combine with the carbon. In this connection, although the stoichiometrical amount is approximately four times the amount of carbon, those skilled in the art have found it necessary to use around six to eight times as much titanium on the basis that the carbon is in a diluted form. It has been somewhat generally thought that the titanium when added for the purpose of improving the quality of steel should be held for a very short period of time (a maximum of about three to five minutes), preferably a matter of seconds; this period has not been sufficient to provide full diffusion of the titanium through the molten metal. It will also be appreciated that titanium is a relatively expensive metal and greater quantities thereof increase the cost of the steel involved.

I have discovered that titanium if properly added directly to the molten metal, can be utilized in much less quantity than heretofore thought necessary to obtain desired results, for example, improved workability and machineability, and that such additions may be well below the so-called stoichiometrical amounts, so that substantially free carbon may be present in the resultant alloy. Consideration of the ferric oxide

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slag content can also be avoided by properly introducing and utilizing the titanium. I find that in accordance with my process, the time element is an important factor, and, contrary to the teaching of the prior art, should be for a sufficient above normal minimum period such that the titanium is fully diffused through the molten alloy and titanium carbide is formed. The optimum minimum period of holding is about one half to one hour. That is, I have found that the full utilization of the desired features of the titanium can be effected and the undesired features can be minimized to such appreciable extent that a highly improved form of steel having hot working properties and suitable cleanness can be provided and at less expense. That is, in accordance with my process, I have been able to minimize the requirements of titanium and in this way obtain desired results, while at the same time, insuring against undesired results which normally occur.

The improvement effected from a standpoint of workability, rollability, etc., is particularly valuable from the standpoint of steels having about 12% or less of nickel. That is, the lower percentages of nickel in an alloy tend to increase the problems of workability. I have been able to produce a steel that can be broken or rolled down from an ingot without cracking and that is more free of slag inclusions.

This is a continuation-in-part of my now abandoned application Serial No. 718,259 filed December 24, 1946, and entitled "Titanium Additions to Stainless Steels."

It thus has been an object of my invention to provide iron or steel of improved workability, particularly, under hot conditions.

Another object of my invention has been to provide a new and improved and less expensive procedure for utilizing titanium additions in the manufacture of iron and steel.

Another object has been to widen the field of utilization of stainless iron and steels and/or to increase the yield thereof.

A further object has been to devise new and improved procedure for utilizing titanium additions.

These and many other objects of my invention will appear to those skilled in the art from the exemplary embodiments chosen for the purpose of illustration, the general specification, and the claims.

Although my invention is of particular importance in connection with austenitic stainless steels, it will be appreciated by those skilled in the art that it has application to iron and steel

generally, and particularly to their alloys where the problem of overcoming disadvantageous features of titanium is presented. The process has particular application to the production of low carbon stainless steel or iron.

As previously intimated, I have been able to take full advantage of desirable features of titanium by utilizing appreciable lower quantities or amounts thereof in such a way that the ultimate tensile strength of the metal will be increased, while its workability will be greatly increased. The formation of undesired ferrites is prevented by reason of the small quantity of titanium involved. Intergranular corrosion resistance will be improved; and, ductility and corrosion resistance (acid test), will be substantially the same as if titanium had not been added to the melt.

In accordance with my invention, I add titanium to the melt near the end of the final operation with or without final alloying additions such as ferrosilicon. If the necessary silicon content, for example, is present, I add only titanium which may be in the form of ferrotitanium to the molten metal bath after first removing at least a portion of the slag so that the titanium can be introduced directly to the molten metal. Lime, fluorspar, etc., may be added to reslag or to cover up the opening. In any event, the bath is held with the titanium additions under a slag to insure desired results, such slag may be formed of the usual ingredients to give it a neutral, mildly oxidizing, or a reducing character (acid, neutral or basic). I find that the maximum utilization of minimum amounts of titanium can thus be effected and that it is not lost in the slag, but combines with slag inclusions in the molten metal and with carbon to form titanium carbide to increase workability. The full stoichiometrical amount of titanium with reference to the carbon is not necessary nor desired.

If silicon is added before or with the titanium, for example, in the form of ferrosilicon, I find that the titanium aids in fluxing the silicates. In any event, whether the titanium is added with the final silicon additions or not, the cleanness of the steel is improved and the workability markedly improved without any danger of formation of ferrite. Corrosion resistance and ductility of stainless steels is maintained.

I hold the melt underlying a supernatant slag, and preferably, for a minimum period of one hour. The holding under a slag is important in that it permits the full diffusion of the titanium through the molten metal beneath the slag and the full utilization of its desirable properties without its loss. By this method, the amount of titanium, as an average, may be about $1\frac{11}{16}$ (one and eleven sixteenths) times the amount of carbon in the steel and preferably below four times the carbon or in other words below the stoichiometrical amounts. It will be appreciated that the lower the amount of titanium, the less expensive the operation and the less danger of titanium forming ferrites and the less tendency of a decrease of ductility or normal corrosion resistance.

In general, although any suitable non-carbonaceous reducing agent or agents employed may be utilized, such as manganese, aluminum, and silicon, I prefer to make such additions to the original bath before the addition of the titanium. If a non-carbonaceous reducing agent, such as silicon, is used, it may be added immediately prior

to the addition of titanium, although I prefer to limit such latter additions to those necessary to bring the alloy up to the desired content. The process has been successfully employed with a neutral, mildly oxidizing, or reducing slag.

As an exemplification, I have finished the heat except, for example, any necessary silicon additions, ready to tap under the type of slag most suited for the grade involved. I then deslag sufficiently to produce a bare spot on the metal surface of sufficient size to directly incorporate the necessary amount of titanium, and if an element such as silicon is to be added, the necessary amount of silicon, for example, in the form of ferrosilicon. I cover the additions over with an amount of neutral, slightly oxidizing, or reducing slag, and maintain the slag in this shape with 75% silicon fines for a minimum period of about one hour. Lime, fluorspar, etc., (with or without non-carbonaceous reducing agents) may be added to form such a slag.

As an example of utilization of my invention in connection with austenitic stainless steels, I set forth the following table:

Table I

Carbon	.048 to .25% maximum (.12% maximum generally preferred).
Chromium	12 to 30%.
Nickel	0 to 40%.
Manganese	0.20 to 2.50%.
Molybdenum	0 to 4%.
Silicon	0.20 to 5% (3.50% maximum generally preferred).
Copper	0 to 1.5%.
Phosphorus and Sulphur.	.03% maximum usual (.35% maximum free machining grades).
Titanium	.03 to .42% (may be in the form of a ferrotitanium to the alloy additions) (.20% maximum in final melt preferred, generally under .10%.)
Remainder iron or substantially iron	

In the alloy of Table I, an optimum resultant range of titanium will be about .035 to .20% (titanium carbide being produced).

Of course, it will be appreciated that normal impurities may be present and that suitable amounts of other alloy additions, such as copper, can be employed in connection with the examples exemplifying applications of my invention.

A further exemplification is a stainless steel containing .08% maximum carbon, 1.50 to 2% manganese, 18 to 18.50% chromium, 12 to 13% nickel, 3 to 3.50% molybdenum, .30 to .60% silicon, and .025% maximum phosphorus and sulphur. The final additions were made and melted, the slag was removed, ferrotitanium and ferrosilicon were added, slag was added and held for substantially one hour, twenty minutes. Then the slag was removed and the metal tapped. In this particular example, 125 pounds of ferrosilicon containing 75% silicon, and 225 pounds of ferrotitanium containing 25% titanium were added to the bare metal after the preliminary deslagging. The resultant alloy not only had all the original desired characteristics of an austenitic stainless steel alloy of the type involved without the addition of titanium, but also had exceptional workability and weldability. Ferrotitanium containing 20 to 40% titanium has been used.

The following table of austenitic steel alloys is representative of groups that have been successfully utilized in accordance with my invention. It will be understood that they do not limit the application of the invention, but are merely

exemplary of stainless steels having improved properties, such as workability, that have been produced employing additions of about .03 to .42% titanium.

Table II

	A	B	C	D	E	F	G
C	.08-.20%	.20% max.	.08% max.	.25% max.	.10% max.	.10% max.	.08%.
Cr	17-20%	24-26%	22-23%	24-26%	16-18%	18-20%	18-18.50%.
Ni	8-10%	12-14%	14-15%	19-21%	10-14%	10-14%	12-13%.
Mn	2% max.	1.25% max.	1.50-2%	1.25-1.75%	2% max.	2% max.	1.50-2%.
Mo					2-3%	3-4%	3-3.50%.
Si	2-3%	.75% max.	1.75-2.25%	.75% max.	.75%	.75%	.30-.60%.
P&S	.03% max.	.03% max.	.03% max.	.03% max.	.03 max.	.03% max.	.03% max.

Remainder iron (except for Ti content)

In Table II and elsewhere in the specification where I mention "remainder iron," I also include "or substantially iron."

Table III

C ..... .06-.12%
Cr 12-30%
Ni 0-1.00%
Mn 20-1.00%
Mo 0-1.50%
Si 20-1.00%
Cu 0-1.50%
P&S, Ti, and iron as set forth in Table I

Table IV

C ..... .048-.25% max. (.12% max. generally preferred)
Cr 16-26%
Ni 8-24%
Mn 30-2.50%
Mo 0-4%
Si ..... .30-5% (3.50% max. generally preferred)
P&S, Ti, and iron as set forth in Table I

Table V

Cr 14-30%
Ni 6-40%
C, Mn, Mo, Si, P&S, Ti, and iron as set forth in Table I

Briefly summarized, my process involves the selection of a steel or iron alloy on the basis of elements and element range that will normally, in themselves, produce an alloy of desired characteristics except for the properties to be imparted by titanium. Such ingredients are melted down in a suitable furnace, such as an electric furnace, a slag is formed, titanium is added directly to the molten metal, the melt is held under a slag for a period sufficient to substantially thoroughly diffuse the titanium through the metal, and the metal is tapped in the usual manner. In the claims, when speaking of "remainder substantially iron," I have reference to iron with incidental impurities which do not materially change the desired characteristics of the alloy.

Although for the purpose of illustrating my invention I have referred to specific applications thereof, it will be apparent to those skilled in the art that various modifications, substitutions, revisions, additions and subtractions may be made without departing from the spirit and scope thereof as indicated by the appended claims. When I mention "steel" or "steels" in the claims, I refer to iron or steel, unless the ingredients or their proportions as set forth are such as to preclude the terminology, iron.

In accordance with my invention, the titanium

is introduced directly to the melt, near the end of the final melting down of the previously introduced alloying ingredients, and in a proportioned amount to the carbon content of the melt that is substantially below the stoichiometric amount to combine with such carbon. The titanium is then held in the metal of the molten alloy bath under a supernatant slag blanket for a period that is considerably longer than the normal holding period for a titanium addition and that is maintained until the titanium is fully diffused through the molten metal and titanium carbide formed.

What I claim is:

1. A process for making chromium-containing alloy steel having a titanium content in the form of titanium carbide and having highly improved hot working properties which comprises, providing a molten ferrous metal bath, melting down alloying ingredients in the molten ferrous metal bath under a slag blanket to provide a molten alloy bath, making any further additions to the molten metal alloy bath, directly introducing titanium to the metal of the molten alloy bath, holding the titanium-containing alloy bath under a supernatant slag blanket for a minimum period of about one hour and until the titanium has fully diffused through the molten metal and formed titanium carbide, and tapping the metal of the bath.

2. A process as defined in claim 1, wherein the titanium is introduced in an amount substantially below the empirical amount required to combine with the carbon content of the molten alloy metal of the bath.

3. A process as defined in claim 1, wherein silicon is introduced directly to the metal of the molten alloy bath before the titanium is introduced thereto.

4. A method as defined in claim 1, wherein an opening is provided in the slag blanket of the molten alloy bath through which the titanium is directly introduced to the metal thereof, and such opening is covered over by additional slag after the titanium has been introduced into the molten alloy bath.

5. A method as defined in claim 1, wherein the titanium is added in an amount of about .03% to .42% of the content of the molten alloy metal of the bath.

6. A method as defined in claim 1, wherein the resultant alloy contains about .048% to .25% maximum carbon, about 12% to 30% chromium, up to about 40% nickel, about .20% to 2.50% manganese, up to about 4% molybdenum, about .20% to 5% silicon, up to about 1.5% copper, about .35% maximum of phosphorus and sulphur, up to about .20% titanium in the form of titanium carbide, and the remainder substantially iron.

7. A process for, without the formation of undesirable ferrites, making an inexpensive titanium and chromium-containing ferrous alloy steel having its titanium content in the form of

titanium carbide and having highly improved hot working properties which comprises: melting down alloying ingredients in a molten ferrous metal bath to provide a molten alloy bath; near the end of the final melting down operation, directly introducing titanium into the metal of the molten metal bath in a proportioned amount to the actual carbon content of the metal of the molten alloy bath that is substantially below the stoichiometric amount to combine with such carbon content; holding the titanium in the metal of the molten alloy bath under a supernatant slag blanket for a period substantially longer than a maximum holding period for a titanium addition and as an optimum, for a minimum period of about one hour, while thoroughly diffusing the titanium through the metal of the molten metal bath and forming it into titanium carbide.

8. A process as defined in claim 7 wherein, non-carbonaceous reducing agents are added to the molten bath before the titanium is introduced.

9. A process for, without the formation of undesirable ferrites, making an inexpensive titanium and chromium-containing ferrous alloy steel having a greatly improved hot workability and better ductility which comprises: melting down its alloying ingredients in a molten ferrous metal bath; near the end of the final melting down operation, directly introducing titanium into the metal of the molten metal bath in a proportioned amount to the actual carbon content thereof that is substantially below the stoichiometric amount to combine with such carbon content; holding the titanium in the metal of the molten alloy bath under a supernatant slag blanket for a period substantially longer than a normal maximum holding period for a titanium addition and until the titanium is fully diffused through the metal of the molten metal bath and titanium carbide is formed, the holding period being a minimum of about one-half to one hour; and tapping the metal of the bath.

10. A process as defined in claim 9 wherein, the resultant alloy contains about .035 to .20% titanium.

11. A process as defined in claim 9 wherein, the resultant product contains about .048 to .25% maximum carbon, about 12 to 30% chromium, up to about 40% nickel, about .20 to 2.50% manganese, up to about 4% molybdenum, about .20 to 5% silicon and up to about 1.5% copper, and the titanium is directly introduced into the metal of the molten metal bath in an amount of about .03 to .42%.

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REFERENCES CITED

The following references are of record in the file of this patent:

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