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MOLYBDENUM-TITANIUM FERRO-ALLOYS

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My invention relates generally to ferrous alloys, and more particularly to molybdenum-titanium ferro-alloys for treating ferro-metals, such as a new and improved combined alloy of this character for treating iron and steel to remove therefrom gaseous and other impurities that have injurious effects, and also to modify the properties of such ferro-metals by incorporating therewith proper amounts of molybdenum and titanium that combine advantageously with the molten ferro-metals in forming the finished product which, from an industrial and commercial viewpoint, is both economical and satisfactory.

The advantages of small additions of molybdenum, generally under 1%, to cast iron are well-recognized, whereby an increase in strength, a slight increase in ductility and resistance to shock, a reduction in the size of the graphite flakes, and a slight increase in hardness and chilling tendency are beneficially effected.

The usual commercial varieties of ferro-molybdenum as used in steel are not well suited for additions to cast iron, since their melting point is too high, and their solution in the iron at ordinary foundry temperatures is too slow. Thus ferromolybdenum intended for use in cast iron is made with a very low carbon content and with considerable silicon so as to lower its melting point to meet the industrial conditions.

The advantages of small additions of titanium to cast iron were discovered many years ago, and this use of titanium has attracted considerable attention recently with the development of a ferro-titanium alloy that is low in carbon and high in silicon, so as to have a low melting point and rapid solubility in cast iron, such alloy being described in U. S. Letters Patent No. 1,946,670 issued to me February 13, 1934.

The effects of titanium comprise a marked decrease in size of the graphite flakes, an increase in graphitization, a slight increase in strength, and a retardation of the chilling tendency. The addition of titanium is therefore very useful in connection with a hardening element, such as molybdenum or chromium, since such titanium counteracts the chilling tendency of the latter elements, and supplements the increase in strength by a much more marked refinement of the graphite flakes.

The use of titanium and molybdenum together in cast iron, while desirable for the reasons mentioned above, is rather difficult in ordinary foundry practice, especially when the iron is melted in a cupola, and also when other alloys, such as chromium or nickel, must be added simultaneously after the iron is tapped from the furnace.

This difficulty is due to the fact that the addition of too much cold material to the iron at that time may decrease its fluidity so that it will not flow well into the molds. It may be impossible to superheat the iron sufficiently in the cupola to take care of this difficulty, and preheating the alloy additions not only makes handling them inconvenient, but also in case a highly reactive alloy is used, such as ferro-titanium, it may impair the value of the alloy by oxidizing the surface.

The objects of this invention are, among other things, to combine the titanium and molybdenum which it may be desired to add to cast iron into a single alloy so that the advantages of both elements may be obtained in the iron, without adding more cold material than would be involved by the addition of a single alloy.

For example, if it should be desired to add 0.6% molybdenum and 0.2% titanium to a cast iron, the addition of about 1.3% of a ferro-molybdenum-titanium alloy such as I have produced and will hereinafter describe containing approximately 15% titanium and 45% molybdenum, would be sufficient, and would require only 13 pounds of cold alloy to be melted by and dissolved in 1000 pounds of cupola iron. On the other hand, if the same addition were made by means of the previously known ferro-alloys containing respectively about 60% molybdenum and 20% titanium, the incorporation of 20 pounds of cold alloy to the 1000 pounds of the molten iron would be necessary, or more than 50% in excess of that involved with the use of my new combined molybdenum-titanium ferro-alloy. Furthermore the melting point of the latter would naturally be lower than that of the more pure ferromolybdenum previously available for alloying additions.

The combined molybdenum-titanium ferro-alloys hereinafter described are of course useful for incorporating such alloys in steel as well as in cast iron. Owing to the well-recognized deoxidizing and cleaning effects of titanium in steel, a cleaner and more sound molybdenum alloy steel may be produced by using this improved combined alloy as a source of molybdenum instead of the ordinary ferro-molybdenum, and the advantages of deoxidation and purification by titanium are likewise obtained in that way without the necessity for making any further additions of solid alloys to the finished molten steel.

My improved molybdenum-titanium ferro-alloy herein described may be produced in a number of ways, and my invention is not confined to

any one method of manufacture, nor to any one composition of alloy product.

As an example of one method which has been used to form the desired combined alloy product, the following procedure is given:

A mixture of 251 grams of rutile, containing 78% TiO_2, 2% silica and 20% iron oxide;

179 grams of roasted molybdenite containing 81% MoO_3, 12% silica, 4% iron oxide, about 1% sulphur, and 2% other miscellaneous impurities;

144 grams of finely divided aluminum metal; and

36 grams of cryolite (sodium-aluminum fluoride, of commercial purity) as a flux (totaling 610 grams) were milled together in a ball mill for 15 hours, and the resulting powder was then placed in a graphite crucible. Such mixture was then ignited by an electric arc resulting in a vigorous alumino-thermic reaction the duration of which was about 45 seconds.

The contents of the crucible were taken out when cold, and a metal button of the following analysis was easily separated from the slag:—

	Per cent
Molybdenum	47.52
Titanium	15.06
Iron	29.40
Aluminum	2.81
Silicon (by difference)	5.21
	100.00

Production on a larger scale would result in an alloy of lower residual aluminum content, and the relative amounts of the various constituents may be controlled by changing the mix used for the charge. A somewhat higher silicon content may often be desired for promoting easy fusibility and rapid solution of the alloy when used.

The proportions of ingredients in the mixture used for the alumino-thermic reaction may be varied within wide limits, depending on the composition of metallic product desired. For example a similar reaction was started with the following proportions of the same ingredients as described in the above example:

	Per cent
Rutile	25.7
Roasted molybdenite	44.8
Aluminum	24.4
Cryolite	5.1
	100.0

This gave a clean metallic product containing

	Per cent
Molybdenum	66.66
Titanium	8.04
Aluminum	2.91
Silicon	5.86
Iron (by difference)	16.53
	100.00

Alloys of similar character may be made in the electric furnace, by smelting ores of molybdenum and titanium in the same operation. Since the production of ferromolybdenum in the electric furnace requires a limeslag for best results, and since titanium cannot be reduced readily into a ferro-alloy out of a lime slag, it is advisable for making the combined alloy in an electric furnace either to reduce the molybdenum first, pour off the lime slag, and then reduce the titanium from another slag; or to make the ferromolybdenum separately and then add it, in place of scrap iron, to the bath from which titanium is reduced.

As examples of these two methods the following procedures were followed:

Example 3.—In a single-phase two-electrode furnace lined with magnesite, a charge consisting of:

	Per cent
Roasted molybdenite (93% MoO_3)	53.2
Petroleum coke	13.4
Hydrated lime	14.7
Iron ore (52.8% Fe)	13.4
Rutile (78% TiO_2)	2.0
Ferro-titanium (20.5% Ti)	3.3
	100.0

was smelted for about 2 hours, using 2000 to 2500 amperes at 60 volts.

The slag was then poured off, leaving the alloy in the furnace, and a new charge composed of

	Per cent
Aluminum	25
Titanium oxide (TiO_2)	62.5
Steel scrap	9.4
Cryolite	3.1
	100.0

was added, the aluminum being melted first, and the scrap last. This charge was smelted for about 2 hours, using 2500 to 3000 amperes at 60 volts, and finally both slag and alloy were poured out of the furnace. The alloy produced was found to contain

	Per cent
Titanium	13.10
Molybdenum	43.10
Silicon	1.67
Aluminum	3.57
Carbon	0.09
Iron plus impurities	38.47
	100.00

Example 4.—The other electric-furnace method may be illustrated by the following:—The same furnace as above described was used, and a charge consisting of

	Per cent
Aluminum	21.6
Ferromolybdenum (64% molybdenum)	21.6
Rutile (97% TiO_2)	54
Cryolite	2.8
	100.0

was added, the aluminum being melted first and followed by the ferromolybdenum. The charge was smelted for 1½ hours, using about 3000 amperes and 60 volts, and the alloy produced contained

	Per cent
Titanium	19.09
Molybdenum	51.38
Silicon	2.20
Aluminum	3.37
Carbon	0.09
Iron plus impurities	23.87
	100.00

In the production of these improved molybdenum-titanium ferro-alloys, it is advantageous if the contents of silicon and aluminum are fairly high, for instance up to 10 or 15%, as the presence of these elements lowers the melting points of the

alloys and increases their fluidity, so that they separate more completely from the slag formed when the alloys are made.

However, in the use of these alloys for additions to molten steel or cast iron, the presence of aluminum is not desirable because it may result in the formation of alumina in the steel or cast iron so treated with the alloy. Alumina in steel or iron is very apt to cause dirtiness from the presence of non-metallic inclusions, or may form a tough skin on the surface of the molten metal so as to interfere with the smooth flow of the metal into the molds in which it is cast. Probably the effect of about 3 to 4% of aluminum in the molybdenum-titanium ferro-alloys would not be noticeably objectionable, but larger amounts of aluminum should be avoided, for it is desirable to keep the aluminum content as low as possible. Hence aluminum should not be used to lower the melting point and increase the fluidity of these alloys.

Silicon, on the other hand, may be incorporated in my improved alloys to advantage as it improves production in the same way as aluminum does, and does not have the same detrimental effect as aluminum on steel or iron in which the alloys may be used. The presence of silicon to the extent of about 5 to 10% of the alloy is not only permissible, but definitely advantageous, especially in the alumino-thermic method of production, where it increases the yield by making the alloy more fluid and more easily separated from the slag in a clean form; and silicon is likewise advantageous in the use of the alloys in cast iron, where the lower melting point due to silicon is helpful in promoting the solution of the alloy, and the rapid diffusion in the iron of the more difficultly fusible elements, such as titanium and molybdenum.

As a suitable source of silicon in these improved molybdenum-titanium ferro-alloys made by the alumino-thermic method, I have found that calcium silicide as an addition to the mix offers several pronounced advantages.

It not only furnishes the desired silicon, but constitutes a comparatively cheap source of calcium. Calcium has almost as strong an affinity for oxygen as aluminum, and is therefore an excellent reducing agent. By using calcium to replace some of the aluminum in the mixtures for alumino-thermic reactions, the total amount of heat generated in the mixture is not reduced, yet the amount of aluminum is reduced so that there is less danger of aluminum remaining in the metallic form in the resulting alloy. Calcium silicide in the mix therefore serves to give the advantages of a silicon content in the product, and at the same time provides a way to avoid the disadvantages of using too much aluminum.

For some purposes it may be desirable to have a higher titanium content than 20% in my improved molybdenum-titanium ferro-alloys, and this may be attained through the use of calcium silicide in the mix without too much sacrifice of economy or yield. When the mix for the alumino-thermic reaction as described, containing only rutile, roasted molybdenite, aluminum, and cryolite, was modified by using either more rutile or a higher-grade rutile so as to increase the proportion of TiO_2 to MoO_3 in the mix so as to increase the titanium content of the alloy produced, the result of the reaction was that only a negligible amount of alloy was obtained in a clean solid button, since the slag and most of the alloy were too refractory to separate well. Either a higher temperature, or an additional flux was required for good production.

Increasing the cryolite flux was not effective, as it consumed more heat in melting. The use of sodium chlorate and more aluminum produced more heat, but titanium as well as aluminum were oxidized by the chlorate, so that the aluminum content of the product came high; also the formation of additional alumina did not improve the fluidity of the slag.

The use of some magnesium in the mix with the chlorate helped in providing additional heat, but much magnesium could not be used because it reacted too explosively and blew the charge out of the crucible, and its oxide, like alumina, increased the viscosity of the slag.

I found that calcium silicide, however, with some magnesium and sodium chlorate in the mix, gave better results, permitting higher titanium contents to be obtained in the metallic products, without too high aluminum, and with reasonably high yields. The silicon improved the fluidity of the higher-titanium metal, and the calcium provided more heat in oxidizing; the calcium oxide also improved the fluidity of the slag, thereby promoting the separation of clean metal.

As examples of the effects of the hereinbefore described variations, in the mix used for the production of molybdenum-titanium ferro-alloys by the alumino-thermic method, the following data are presented. The mixtures were prepared in amounts of 870 to 970 grams each, and were milled for 15 to 16 hours in an iron ball mill, and ignited by means of an electric arc in a graphite crucible.

Designation of examples

Proportions of mix used	A	B	C	D
	Per-cent	*Per-cent*	*Per-cent*	*Per-cent*
Rutile (78% TiO_2)	23	20	20	25.8
Rutile (97% TiO_2)	23	22.3	22.3	23.7
Roasted molybdenite (93% MoO_3)	23			
Roasted molybdenite (81% MoO_3)		22.3	20	12.4
Finely divided aluminum	25.3	18.9	17.8	18.6
Finely divided magnesium		3.3	3.3	4.1
Calcium silicide		4.4	6.7	5.1
Sodium chlorate		4.4	5.5	6.2
Cryolite	5.7	4.4	4.4	4.1
	100.0	100.0	100.0	100.0

Analysis of alloy produced

	A	B	C	D
		Per-cent	*Per-cent*	*Per cent*
Titanium	Not enough for analysis.	23.28	22.28	32.40
Molybdenum	do	37.86	34.30	21.15
Silicon	do	10.97	14.35	11.35
Aluminum	do	4.90	1.98	7.09
Iron plus impurities	do	22.99	27.09	28.01
		100.00	100.00	100.00

A comparison of "Example A" with the Examples 1 and 2 first described will show how a simple increase in the titanium content of the same mix, even with increased aluminum, resulted in the separation of too small an amount of alloy, from the slag, for an analysis. Comparing these Examples 1 and 2 with "Examples B, C, and D" however, it will be noted that alloys or higher titanium content were produced by proper proportioning of the mixtures containing calcium silicide.

A comparison of the mixtures in "Examples

B and C" which are very similar except for changes in aluminum and calcium silicide, indicates how the aluminum content of the alloy produced is lowered by the substitution of more calcium silicide for some of the aluminum in the mix.

In the production of these molybdenum-titanium ferro-alloys on a larger scale, better results in regard to recoveries and lower aluminum content of the alloy may be expected, because, owing to the smaller ratio of radiating surface of the larger crucible to the bulk of its contents, there is a smaller proportion of heat lost by radiation in larger scale operation, and the charge therefore reaches a higher temperature during the reaction and holds its high temperature for a longer time. This results in a more complete reaction, so that more of the aluminum is oxidized, and more of the other metals reduced from the slag.

As an illustration of this effect, Example E is now given which was made exactly similar to the first mentioned example, but using a charge of 12,750 grams instead of 610 grams. The proportions of the mix used were the same, namely,

	Per cent
Rutile (78% TiO_2)	41.2
Roasted molybdenite (81% MoO_3)	29.3
Aluminum	23.6
Cryolite	5.9
	100.0

The alloy produced with the larger charge contained

	Per cent
Molybdenum	48.10
Titanium	15.72
Aluminum	1.50
Silicon	5.38
Iron plus impurities	29.30
	100.00

It may be noted that this Example E shows less aluminum and slightly higher molybdenum and titanium contents than the product of the small-scale reaction which I have first described in the first example. The alloy button obtained from the small charge weighed 125 grams, representing a recovery of 47% of the metallic elements (other than aluminum) introduced, while the product of the larger charge weighed 3390 grams indicating a recovery of 61% of the same elements.

I have also used calcium silicide effectively in making ferro-titanium alloys as well as nickel-titanium alloys. My invention is not to be confined to any particular method of production, although the use of calcium silicide as an aid in producing alloys of high titanium content and low aluminum by the alumino-thermic method is considered a part of my invention. My invention is also not limited to any particular composition of the improved molybdenum-titanium ferro-alloys, but covers these compounds as a broad group or family of alloys. For most purposes however, it is believed that the alloys would be most useful especially in cast iron, if the molybdenum content were about three times the titanium content, and with aluminum as low as possible, and iron not over 30%. The preferred specification of contents for a standard grade of molybdenum-titanium ferro-alloy would therefore range about as follows:—

Molybdenum	41 to 55%	(48% desired)
Titanium	12 to 20%	(16% desired)
Aluminum	Trace to 4%	(2% average)
Silicon	8 to 12%	(10% desired)
Iron plus impurities	20 to 30%	(24% average)

For treating certain grades of alloy steels, a higher proportion of titanium to molybdenum might be desirable in the ferro-alloy, and a composition similar to that stated for "Example D" above would then be called for.

By the term "balance substantially iron" occurring in the claims, I mean that the alloys called for may also contain small amounts of additional metals totaling from a trace to not more than 5%, such as manganese, copper, chromium and zirconium, as well as the addition of a trace to about 4% of one or more of the elements, carbon, phosphorus, sulphur, nitrogen, oxygen, etc.; these additions being insufficient in quantity to change substantially the characteristic properties of the said alloys.

I claim as my invention:

1. A ferro-alloy having a low melting point and freely flowing for treating molten cast iron or steel containing substantially 25 to 75% of molybdenum, substantially 5 to 45% of titanium, and the balance principally iron.

2. A ferro-alloy having a low melting point and freely flowing for treating molten cast iron or steel containing molybdenum 25–75%, titanium 5–45%, silicon trace to 25% and aluminum trace to 15% with the balance substantially iron.

3. A ferro-alloy having a low melting point and freely flowing for treating molten cast iron or steel containing molybdenum 41–55%, titanium 12–20%, silicon 8–12%, aluminum trace to 4%, and the balance substantially iron.

4. A ferro-alloy having a low melting point and freely flowing for treating molten cast iron or steel containing molybdenum about 48%, titanium about 16%, silicon about 10%, aluminum about 2%, and the balance substantially iron.

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