

## UNITED STATES PATENT OFFICE

WILLIAM C. READ, OF SCARSDALE, NEW YORK, ASSIGNOR TO ELECTRO METALLURGICAL COMPANY, A CORPORATION OF WEST VIRGINIA

## SILICOTHERMIC SMELTING PROCESS AND CHARGE THEREFOR

No Drawing.

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Ferrotungsten and ferromolybdenum are usually made directly from ore-concentrates containing tungstates or molybdates, or the corresponding trioxides. These compounds can be reduced silicothermically, that is to say, when they are suitably mixed with silicon or silicon alloys, with additional substances as explained below, a reaction initiated in the mixture will propagate itself throughout the charge without the further application of heat from extraneous sources.

In the silicothermic smelting of tungsten and molybdenum, it is necessary, or at least expedient, to add to the charge an excess of silicon over the quantity required to reduce the tungsten or molybdenum, and to incorporate with the charge an energetic oxidizer or "accelerator" to react with this excess of silicon, thereby developing additional heat to insure a complete reaction and a reguline metallic product. Sodium nitrate has heretofore been proposed for the accelerator, but the use of this compound involves several difficulties. It normally carries an objectionable proportion of water, and since it is quite fusible, and easily decomposed by heat, it is difficult to dry. The alkali base tends to volatilize at the high temperature of the silicothermic reduction, and in so doing it absorbs heat. Detrimental proportions of nitrogen may be introduced into the metal by the use of a nitrate accelerator. The cost of the nitrate is an important item; and when it is stored and handled in large quantities, the nitrate adds to the fire risk, and may possibly bring about explosions. Other available oxidizing agents are subject to the objections noted, or to others still more serious.

The present invention is a process for silicothermically smelting the metals of a group which include tungsten and molybdenum. The principal novelty of the invention resides in the use of the higher oxides of manganese as the accelerator, and of measures whereby to prevent undue contamination of the recovered metal with manganese.

I prefer to use, for the accelerator, an ore high in manganese dioxide, but any of the manganese oxides containing a higher pro-

portion of oxygen than is present in MnO have an accelerating effect on the reaction, and calcined ores in which the manganese occurs as  $Mn_2O_3$  or  $Mn_3O_4$  may be used. The indications are that if the only oxides in the charge are those of manganese and tungsten (or molybdenum) the silicon reacts first, or most energetically, with the manganese compounds, reducing them to MnO; that it then reduces the tungstic or molybdic oxide to metal; and that finally, if there is a sufficient quantity of silicon, MnO is reduced to metal. The last named reduction is an undesirable one since it contaminates the recovered metal with manganese. In attempting to adjust the proportion of silicon precisely, so as to effect the desired reduction while preventing reduction of manganese to metal, I have had but little success, the usual result being incomplete reduction of the tungsten or molybdenum, or excessive reduction of manganese to metal, or both. I have overcome the difficulty by using more silicon than is necessary to reduce the tungsten or molybdenum, and to reduce the manganese oxides to MnO, and oxidizing the excess of silicon with an iron oxide such as ore or mill-scale, thereby protecting the MnO from reduction. Like the manganese, the iron appears to be reduced in at least two stages:

- (1)  $2MnO_2 + Si = SiO_2 + 2MnO$
- (2)  $2MnO + Si = SiO_2 + 2Mn$
- (3)  $2Fe_2O_3 + Si = SiO_2 + 4FeO$
- (4)  $2FeO + Si = SiO_2 + 2Fe$

As between reactions (1) and (3), the former probably is preferential, but little or no manganese appears to be reduced to metallic form so long as a considerable proportion of FeO is present, the latter being reduced instead. When an excess of iron oxide is provided, the proportion of silicon in the charge may vary over a considerable range with no other undesirable result than to change the iron content of the alloy produced,—an inconsequential matter as compared with an incomplete recovery of the tungsten or molybdenum, or a product rendered unsalable by a high manganese content.

The following examples are typical:

I. A charge was prepared by thoroughly mixing the following components, all ground to pass a No. 100 screen.

5	Wolframite, 57.43% W	Parts	2500
	Manganese ore, 59.69% Mn, 90.24% MnO <sub>2</sub>		500
	Tungsten mill scale, 9.55% W, 57.63% Fe		450
10	Silicon metal, 97% Si		553

The charge was ignited in a steel shell lined with refractory material. The reaction was complete in eleven minutes, the slag and metal being fluid, and well separated. The following analytical results are of interest:

	Metal		Slag	
	W	81.21%	MnO	27.07%
20	Si	0.98%	SiO <sub>2</sub>	50.72%
	Mn	0.43%	FeO	13.07%

II. Ferromolybdenum was made from the following charge:

25	Commercial molybdic oxide	Parts	2000
	Manganese ore		500
	Hematite ore		500
	Ferrosilicon 59% Si		1090
30	Steel scrap		30

	Metal		Slag	
	Mo	78.08%	MnO	13.30%
	Si	1.15%	FeO	22.20%
	Mn	0.44%	Balance largely SiO <sub>2</sub>	

35 The slags produced by my process contain considerable proportions of manganese, which can of course be recovered.

Falling with tungsten and molybdenum in the periodic classification of the elements is the metal chromium. As compared with tungsten and molybdenum, chromium is very difficult to reduce silicothermically, and I have not as yet been able economically to produce chromium or ferrochrome by the method described herein. It is possible, however, to mix a suitable compound of chromium with a reducible compound of tungsten or molybdenum, and then to reduce the mixture by the method which has been described, producing, for example, an alloy of iron, tungsten and chromium free from detrimental proportions of manganese. Accordingly, I regard the invention as being applicable generally to the metals of the tungsten group.

55 In the appended claims that part of the oxygen in the accelerator which is in excess of the quantity corresponding to MnO is referred to as loosely-bound oxygen.

I claim:

60 1. A silico-thermic smelting charge comprising as essential components an oxygen-containing compound of a tungsten-group metal, manganese oxide material containing loosely bound oxygen, iron oxide material, and silicon; the quantity of manganese oxide

material being sufficient to promote a vigorous self-propagating reaction, and the quantity of silicon being so proportioned with respect to the reducible oxides present that such reaction will produce a low-manganese ferro alloy of the tungsten-group metal. 70

2. A silico-thermic smelting charge comprising as essential components an oxygen-containing compound of a tungsten-group metal, pyrolusite, iron oxide material, and silicon; the quantity of pyrolusite material being sufficient to promote a vigorous self-propagating reaction, and the quantity of silicon being so proportioned with respect to the reducible oxides present that such reaction will produce a low-manganese ferro alloy of the tungsten-group metal. 75 80

3. A silico-thermic smelting charge comprising as essential components an oxygen-containing compound of a tungsten-group metal, manganese oxide material containing loosely bound oxygen, iron oxide material, and ferro silicon; the quantity of manganese oxide material being sufficient to promote a vigorous self-propagating reaction, and the quantity of silicon being so proportioned with respect to the reducible oxides present that such reaction will produce a low manganese ferro alloy of the tungsten-group metal. 85 90

4. A silico-thermic smelting charge comprising as essential components an oxygen-containing compound of tungsten, pyrolusite, iron oxide material, and silicon; the quantity of pyrolusite being sufficient to promote a vigorous self-propagating reaction, and the quantity of silicon is so proportioned with respect to the reducible oxides present that such reaction will produce a low-manganese ferro tungsten. 95 100

In testimony whereof, I affix my signature. 105  
WILLIAM C. READ.

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