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SMELTING OF ORES

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The invention relates to the recovery of chromium, manganese and vanadium from their natural or artificial compounds with oxygen. The object of the invention is to permit close control of the composition of the metal produced, particularly with respect to the proportions of carbon and of silicon therein, and to bring about an economical utilization of materials, power and equipment.

The ferro-alloys of the above metals (which form a group having atomic weights between 50 and 55) are important articles of commerce, as are also manganese and chromium in the commercially pure state. These products are widely used for the preparation of various metals, particularly ferrous compositions such as steels and rustless irons. Simple smelting of the ores with carbon gives products of such high carbon content that they are unsuitable for many uses, and much effort has been expended in devising methods whereby the metals can be recovered in relatively carbon-free form.

According to the present invention I prepare a low-carbon silicon alloy of the metal to be recovered, and then desiliconize this product by treating it with an oxygen-containing compound of the metal to be recovered, thereby producing metal sufficiently low in both carbon and silicon. The silicon alloy can be made in various ways, for example by reducing an ore with carbon in the presence of a silicious charge. However produced, the silicon alloys in question are characteristically low in carbon. I effect the desiliconization referred to above in a self-propagating silico-thermic reaction and thus bring about an important saving in time, power and apparatus. The desiliconization of a very large quantity of silicon alloy can be carried out silico-thermically in a fraction of an hour, and often in a few minutes, and it requires no apparatus except a refractory pot or vessel to hold the charge and the reaction products.

The silico-thermic reduction of the oxides of chromium, manganese and vanadium is attended with difficulties which are not encountered when such oxides as those of tungsten and molybdenum are similarly reduced. In the case of the metals with which the present invention is concerned, the production of a low silicon product by silico-thermic reduction is incompatible with a high recovery of metal from the oxide used: a high recovery of metal can only be attained by the use of a large excess of silicon resulting in a high content of silicon in the product, which renders it unfit for many purposes. I adopt the alternative which gives metal sufficiently low in silicon, that is, I use an excess of ore or other oxygen compound; and I avoid the low recovery of metal which would otherwise result by subjecting the slag formed in the desiliconizing operation to a supplementary operation to recover its values. Preferably this latter operation is so carried out as to produce a silicon alloy suitable for the silico-thermic reaction described above. This combination of steps makes it possible to operate economically even when no metal is reduced from the ore or other metal-oxygen compound in the desiliconizing step, the ore acting merely as an oxidizing agent. It is possible, and in some cases is preferred, to increase the efficiency of the desiliconization by using a highly oxidized metal compound, for example vanadium pentoxide, vanadates, chromic anhydride, chromates, and manganese dioxide in the desiliconizing step, and to reduce little or none of such highly oxidized compound to metal.

Preferably I smelt the slag with a carbonaceous reducing agent in an electric furnace in the presence of enough silica to ensure the desired content of silicon in the alloy thereby produced. The slag is itself highly silicious but additional silicious material may be added if required. By smelting the slag in an electric furnace where the quantity of heat added to the charge and the rate of adding it are under complete control, the operation becomes very flexible, and any desired addition may be made to the charge. For example the additions may include ores, slags from other processes, and reduced metals or alloys, and a good recovery of the metal may be had with a wide variety of charges. The desiliconizing step is naturally somewhat circumscribed by the necessity for a charge which will, by a self-propagating reaction, produce a metal sufficiently low in silicon and carbon, but the use of an electric furnace smelting operation in conjunction with the self-propagating desiliconizing reactions makes the whole process highly adaptable to the various conditions which may be encountered. In other words the process turns to account the advantages inherent in silico-thermic reduction but avoids the restrictions which such a reduction usually imposes.

The silicon-bearing material and the oxygen compound which are to react in the silico-thermic stage are finely ground and intimately mixed to expedite the reaction. A more rapid reaction tends to be more nearly complete, and hence to liberate more heat, and it also tends to diminish heat losses because it curtails the interval during which radiation of heat occurs. I prefer to grind the materials at least until a large proportion will pass a one hundred mesh screen. The larger the charge for the silico-thermic step, the higher the temperature attained tends to be, the quantity of heat liberated increasing faster than the radiating surface. As is indicated by the specific examples herein, the preferred scale of operations is one in which the weight of the charge is at least several thousand pounds. The charge may generally be substantially unheated when the reaction is initiated, but an initially elevated temperature promotes the reaction. The best results follow when the charge is substantially free from moisture.

Since the reaction products and any non-reacting materials present must be brought to the same temperature, materials other than those which directly participate in the main reaction have the effect of limiting the maximum temperatures reached. In some cases there may be an excess of heat which can be usefully employed to melt iron or other metal which it is desired to incorporate into the product, but in general it is desirable to avoid unnecessary quantities of heat-absorbing substances in the charge. The exothermicity of the reaction may be increased by incorporating substances into the charge which do not contain the metal to be recovered, but which oxidize silicon energetically. The choice of an oxidizing agent for this purpose raises additional problems, of which cost is one of the most important. Sodium nitrate is a cheap and efficient solid oxidizer. Alkali metal chlorates are among the most energetic of oxidizers, but they are of little value for accelerating silico-thermic reductions because they are reduced to chlorides in the process and the chlorides boil out of the charge and absorb much heat from it. Bleaching powder is an effective accelerator under some conditions.

The percentage of silicon remaining in the purified metal may vary rather widely in different cases. Thus the percentage of vanadium incorporated into a steel is often very small, and a correspondingly small quantity of ferrovenadium is required to introduce it. The ferrovenadium may in some cases contain as high as 8 or 10% of Si (with a vanadium content of say 35%) without unduly increasing the Si content of the finished steel. On the other hand the product required may be one which contains a metal of the group under discussion and silicon in such proportions that the ratio of the former to the latter is considerably above 100. It is desirable to diminish the quantity of ore or other oxide used in the desiliconizing stage as much as the intended silicon content of the desiliconized product permits, since there is then less slag to be resmelted, and less extraneous material to absorb heat and interfere with the main reactions.

Examples of the invention as applied to vanadium and chromium follow:

A self-propagating reaction was brought about in the following charge:

	Pounds
Impure vanadium oxide	5,070
Ferrovanadium silicon	7,291
Lime	740
Sodium nitrate	2,049
Steel scrap	1,521
	16,671

The impure oxide contained 86.12% V_2O_5. The ferrovanadium silicon had the following analysis:

	Per cent
V	18.0
Si	36.5
Fe	39.5
C	0.21

The products were an alloy containing approximately 75% of the vanadium of the charge, and a slag containing the balance of the vanadium. The products analyzed as follows:

Alloy	Per cent	*Slag*	Per cent
V	35.70	V	9.48
Si	7.00	SiO_2	55.76
C	0.28		

The slag was smelted with carbon in an electric furnace to produce ferro vanadium silicon.

In an example of the process using artificial compounds instead of ores, a self-propagating reaction was brought about in the following charge:

	Pounds
Calcium chromate	1,700
Chromic anhydride (CrO_3)	255
Chrome-silicon	880
Lime	28
	2,863

The chrome-silicon had the following composition:

	Per cent
Cr	52.34
Si	46.34
Fe	0.27
C	0.05

The reaction produced metal and slag, the chromium being about equally divided between them. The products had the following composition:

Metal	Per cent	*Slag*	Per cent
Cr	95.47	Cr	23.24
Si	1.45	SiO_2	33.02
Fe	1.70	CaO	25.65
C	0.18		

The slag was crushed and mixed with silica and carbon in the following proportions:

	Parts
Slag	100
Quartzite	15
Charcoal	35

The mixture was smelted in the electric furnace and an alloy suitable for use in the self-propagating reaction was produced.

The process is particularly adapted to the preparation of manganese alloys low in silicon because of the fact that manganese dioxide, a peroxidized compound, occurs in many natural ores. The use of such ores permits the desiliconization to be effected at the expense of the loosely combined oxygen in the dioxide, the latter being reduced only to a lower oxide, in a vigorous self-propagating reaction giving a very high temperature and fluid products. Due to the excess of oxygen in the charge a very thorough elimination of slicon from the silicon alloy, for example manganese-silicon, is readily brought about. The lower oxides of manganese originally present or produced in the desiliconization combine with the silica to form a silicate slag. This slag is smelted, preferably in an electric furnace with carbon and suitable additions of silicious materials, to produce a high-silicon low-carbon manganese alloy, and this alloy can be desiliconized with a further quantity of ore in a self-propagating reaction in the manner already described.

In preparing the charge for the self-propagating reaction between the maganese-silicon alloy and the manganese dioxide ore the proportions used are approximately two molecules of MnO_2 to each atom of Si. This proportion usually gives a product sufficiently low in silicon, and if a higher silicon content is permissible a little less than this proportion of maganese dioxide can be used. Increasing the proportion of ore has the opposite effect; it gives a somewhat better elimination of silicon.

The carbon content of the desiliconized product can be predicted from that of the manganese-silicon alloy used. Since the quantity of low silicon product is less than the quantity of manganese-silicon alloy taken (little or no manganese being reduced in the desiliconization) the carbon will be concentrated in the product. An additional small quantity of carbon is usually introduced fortuitously. A manganese-silicon alloy containing 0.7% C and 24% Si is suitable for preparing a low-silicon alloy with about 1.0% C, while a maganese-silicon alloy with 1.0% carbon and 20% silicon gives a product containing about 1.5% carbon. The carbon in the product may be brought still lower by using a manganese-silicon in which the silicon is still higher and the carbon correspondingly lower.

Manganese ores are available in which practically all of the manganese present is in the form of dioxide. The content of dioxide may be very high, for example 85%, but any content of MnO_2 increases the available oxygen in the charge and hence facilitates the production of metal low in silicon. When sufficient dioxide is present it is unnecessary to add extraneous oxidizers to make the reaction self-propagating. Under some conditions the liberation of heat is unnecessarily and even detrimentally large. In such cases the excess heat may be absorbed in melting scrap metal added to the charge. Scrap in excess of 10% of the charge has been successfully melted in this way.

The slag produced may contain, for example, about 65% MnO and about 26% SiO_2. It may be crushed, mixed with carbon and silicon and smelted in the electric furnace without difficulty.

In a specific example a self-propagating reaction was brought about between an alloy and an ore of the following compositions.

Alloy	Per cent	*Ore*	Per cent
Mn	64.44	Mn (mostly as MnO_2)	56.50
Si	24.66	Fe	2.17
C	0.84		

Balance largely iron.

The charge consisted of 26,935 lbs. ore and 14,948 lbs. alloy, both ground to pass a 100 mesh screen and throughly mixed and dried. The products were ferromanganese analyzing

	Per cent
Mn	80.11
Si	1.22
C	1.25

Balance largely iron, and a slag containing 65.48% MnO.

In another example the charge consisted of 26,389 lbs. ore and 16,443 lbs. alloy. The ore was the same as in the preceding example and the alloy had the following composition:

	Per cent
Mn	68.30
Si	23.13
C	0.67

Balance largely iron.

The ferromanganese produced contained:

	Per cent
Mn	83.91
Si	1.83
C	1.08

The slag contained 62.99% MnO.

Slag from one of the examples above was mixed with silica and carbon as follows:

	Parts
Slag (crushed to pass 2½ in. screen)	400
Quartzite	50
Carbonaceous reducing agent	135
	585

The charge was smelted in an electric furnace giving a silicon-manganese alloy similar to those which have been described, and a small quantity of slag containing about 15% MnO, which was discarded.

It will appear from the foregoing description that the invention may be embodied in an extraordinary number of modified processes. A few of these processes have been particularly described to illustrate the principles involved but the invention is obviously not restricted by such examples nor except as is required by the appended claims. In these claims the term "metal" is used to embrace all metallic products regardless of the number of chemical elements present or their proportions.

The term "silicon" as used in the appended claims embraces not only the substantially pure element but also alloys thereof high enough in silicon to adapt them for use in silico-thermic charges.

I claim:

1. The process of recovering a metal of the group having atomic weights between 50 and 55 which comprises preparing a charge of at least several thousand pounds comprising an oxygen compound of said metal, silicon and a solid oxidizer which reacts more energetically with silicon than does the lowest natural oxide of said metal, the components of the charge being of such fineness that a large proportion will pass a 100 mesh screen and being intimately mixed and so proportioned as to adapt the charge to self-propagating reaction in an initially unheated environment with the production of commercially silicon-free metal; locally igniting the charge; collecting the metallic product; separately collecting the slag; and smelting the latter with electrical power to form a silicon alloy adapted to provide the silicon required in the first stage.

2. The process of recovering a metal of the group having atomic weights between 50 and 55 which comprises preparing a charge of at least several thousand pounds comprising a silicon alloy of said metal and a higher oxide of said metal, the components of the charge being of such fineness that a large proportion will pass a 100 mesh screen, and being intimately mixed and so proportioned as to adapt the charge to self-propagating reaction in an initially unheated environment with the production of a commercially silicon-free alloy but without the complete reduction to metal of a substantial part of said higher oxide; locally igniting the charge; collecting the metallic product; separately collecting the slag; and smelting the latter with electric power.

3. The process of recovering a metal of the group having atomic weights between 50 and 55 which comprises preparing a charge of at least several thousand pounds comprising an oxygen compound of said metal, silicon, and a solid oxidizer which reacts more energetically with silicon than does the lowest natural oxide of said metal, the components of the charge being of such fineness that a large proportion will pass a 100 mesh screen and being intimately mixed and so proportioned as to adapt the charge to self-propagating reaction in an initially unheated environment with the production of commercially silicon-free metal; locally igniting the charge and causing it to react without providing heat from extraneous sources; collecting the metallic product; separately collecting the slag; and smelting the latter with electrical power to form a silicon alloy adapated to provide the silicon required in the first stage.

In testimony whereof, I affix my signature.

FREDERICK M. BECKET.