May 24, 1949. P. H. ROYSTER 2,471,242

PROCESS OF TREATING TITANIFEROUS IRON ORES

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Fig. 2.

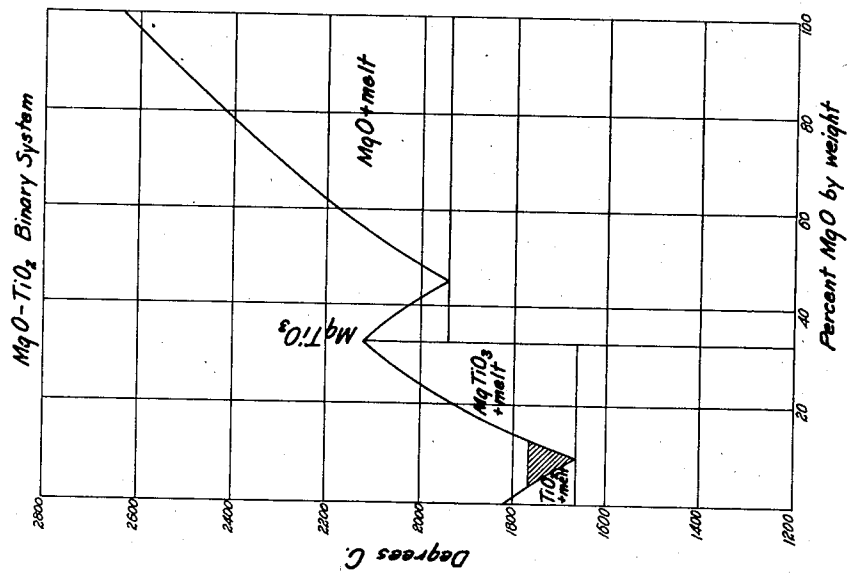
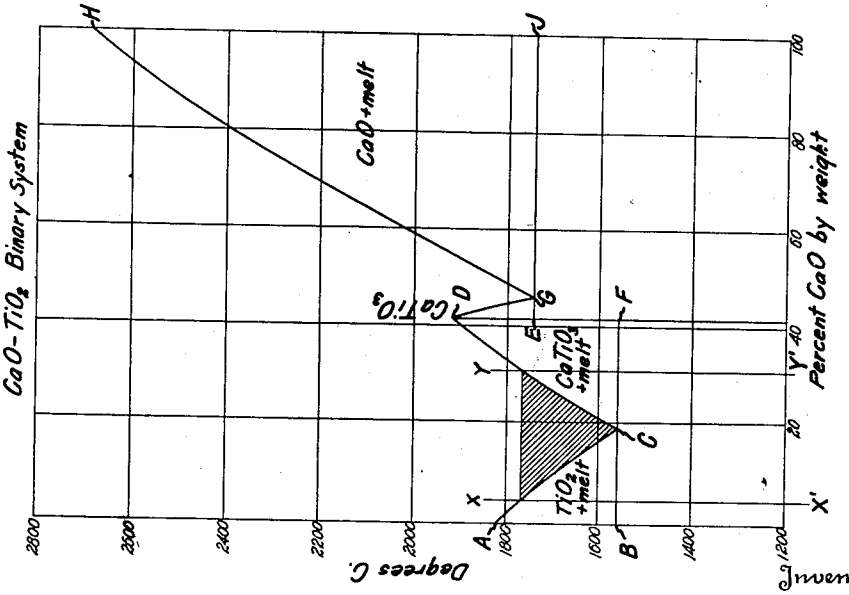


Fig. 1.



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2,471,242

PROCESS OF TREATING TITANIFEROUS IRON ORES

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10 Claims. (Cl. 75—30)

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This invention relates to the selective reduction of iron oxide from titaniferous iron ores or concentrates whereby to obtain a pig iron of merchantable quality and a slag rich in titanium oxide, and more particularly is concerned with the provision of a smelting process, of the character just described, yielding a titanium oxide-rich slag which is very poor in iron oxide and from which a titanium oxide pigment economically can be produced. In the following description and in the appended claims the expression "titaniferous iron ore" is intended to cover not only the ore per se but also concentrates thereof.

It heretofore has been widely taught that iron ores containing considerable titanium oxide could not be treated, in an electric, blast or other furnace, to make pig iron because of the alleged refractory nature of the titanium oxide, that is, the latter's supposed tendency to impart viscosity to otherwise fluid slags (F. E. Bachman, "Year Book of Amer. Iron and Steel Institute," 1914, pages 371–419). Moreover, it had been alleged that titanium oxide, in the nitrogen-containing reducing atmosphere of a pig iron furnace, forms nitride (TiN) and cyanonitride which are insoluble in slag and metal and substantially infusible, and which accumulate in the furnace, thereby impairing and halting the operation of the latter.

I am aware that it had been proposed to reduce all of the titanium and iron of a titaniferous iron ore. According to this proposal for total metallization, in the electric furnace, there would be produced a ferro-carbon-titanium alloy. It is, of course, well known that ferro-carbon-titanium alloy can be produced in an electric furnace operating at high temperature, by simultaneously reducing the greater parts of both the iron and the titanium oxides contents of the ore. In this operation, by reducing the titanium to metal, it is true that a contamination of the slag with titanium oxide is avoided, as are excessive viscosity of slag and formation of nitrides. But where, as in the present case, the object is to remove the iron as metal while recovering the major proportion of the titanium oxide in the slag, no such simple procedure is possible.

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It is an obvious suggestion—which had not eluded prior workers in this field—that there might be found a suitable flux favoring production of a slag which would contain a substantial amount of titanium oxide and which at the same time would have desirable fluidity. Due to a general unfamiliarity with the properties of liquid TiO_2, these previous attempts successfully to flux TiO_2 with basic oxides had been misdirected. Because titanium occurs in the *4th* column of the periodic table immediately under silicon, it is not surprising that its oxide, TiO_2, had been considered analogous to the "acid oxide" SiO_2, and that prior workers had thought it necessary to follow the usual fluxing rules of metallurgy, viz., a 1-to-1 combination of "acid oxide" with "basic oxide," for fluxing TiO_2. Thus Rossi (Patent No. 486,941) taught that titanium oxide "will act substantially the same part as the silica has heretofore been employed to do" in the fluxing of the charge, and—with apparent logic—proposed to add a considerable molar excess of "basic" oxides (CaO and MgO) to "neutralize" the "acid" oxides (SiO_2 and TiO_2) whereby to "insure the predominance in the slag of multiple-titanates of these bases." This same principle of mole-to-mole balancing of "acid" oxides (SiO_2 and TiO_2) with "basic" oxides (CaO and MgO) in the fluxing of titaniferous iron ores was used by van der Toorn, Patent No. 1,334,004 (page 3, lines 97–100) and by Gardner, Patent No. 1,743,885, in which latter case a molar excess of CaO over TiO_2 was advised. This widespread and long continued acceptance of the theory of maintaining a molar excess of basic oxide over TiO_2 and SiO_2—i. e., "insuring predominance of titanates"—has acted as a serious deterrent to commercial development of the process.

Difficulties with slag viscosity no less great are encountered if one attempts to follow the teaching of Borchers, Patent No. 930,344, when he advises that "no lime or other flux should be used" in reducing the iron content of a titaniferous iron ore. In such case, when the iron content has been mostly metallized the residual unfluxed oxides cannot be fused to a manageable slag by any known furnace operation which does not at

the same time result in excessive metallization of the titanium content.

As will be appreciated from a consideration of the binary system $CaO—TiO_2$ shown in Fig. 1 of the accompanying drawing, insuring a deficiency—rather than a preponderance—of basic oxide is indicated for producing a manageable slag rich in TiO_2. In fact, the location of the eutectic between rutile, TiO_2, and perofskite, $CaTiO_3$, in the immediate neighborhood of the rutile end of the diagram indicates that a surprisingly small amount of basic flux should give superior properties to the resulting fluid. The rapid rise in the liquidus temperature on the perofskite side of the eutectic makes it clear why failure has accompanied previous attempts to remove iron from titaniferous iron ore by selective reduction. It will be obvious that a considerable molar deficiency of CaO (or CaO+MgO) below the unimolecular ratio will produce an easily handled metallurgical slag. Undoubtedly, general unfamiliarity with the binary system shown in Fig. 1 must account for the persistence with which "preponderance of base" has endured and has misled so many workers in this field.

Another misconception relative to the properties of titanates has unfavorably affected progress in smelting titaniferous iron ores, namely, the general belief that TiO_2 per se has the inherent property of imparting viscosity to a slag, and that even a few per cent of TiO_2 gives excessive viscosity to mixtures of fluid oxides of any composition.

This has been found not to be true in general. For example, I have found that a melt containing 15% FeO and 74% TiO_2, when maintained at as low as 1520° C. is quite fluid, the FeO acting as an efficient fluidizing agent for the mixture. This fact is in obvious contradiction to the generally accepted theory that a high content of TiO_2 makes an oxide melt too viscous to handle. When, however, the FeO content of the above melt is progressively reduced (as by metallization of iron) the viscosity of the melt progressively increases; before the FeO content has been diminished beyond 10% the melt becomes essentially immobile even when the temperature thereof is raised to 1600° C.

I have found, however, that if a relatively small amount—not more than 10–30 molar per cent—of basic oxide (CaO, MgO or CaO and MgO) be added to the above melt, the FeO can be essentially eliminated as metallic iron without encountering any substantial difficulty with the mobility of the resulting slag. In contradistinction, if one were to follow the teachings of previous investigators by adding, in this particular case, 45.70 molar per cent of basic oxide, a slag of acceptably low viscosity cannot be produced unless a much higher temperature, e. g., a temperature above 1700° C., is resorted to—in which case the greater part of the TiO_2 is reduced along with the FeO and the resulting metal is not pig iron but rather is a high titanium ferro alloy. Since, as is well known, iron oxide in reactive contact with carbon at any temperature above 1400° C. is reduced to a small fraction of 1% when equilibrium is attained, serious difficulty is encountered in metallizing substantially all of the iron content of the above melt, at a relatively "moderate" furnace temperature, while maintaining desirable fluidity of the resulting slag.

The gist of my improved pyrometallurgical treatment of titaniferous iron ore resides in the step of maintaining a molar deficiency of basic

oxide flux adidtion with respect to the titanía content of the furnace charge whereby to hold the formation of calcium titanate to a relatively low level.

In order that the process be carried out successfully, it is necessary to operate the reduction furnace at a temperature high enough to maintain desirable slag mobility without reducing an excessive amount of TiO_2. The reduction of TiO_2 given by the free energy equation governing the reaction

$$TiO_2+2C \rightleftarrows Ti+2CO \quad (1)$$

namely

$$\log_{10} k = 1446 - \frac{29{,}700}{T} \quad (2)$$

where

$$k = \frac{(Ti)\ (CO)^2}{(TiO_2)\ (C)^2} \quad (3)$$

indicates a standard enthalpy change ($\Delta H°$) of 135,700 cal. per mol, and a standard entropy change ($\Delta S°$) of 66.25 e. u. (entropy units). In the above equations the terms "(Ti)" and "(TiO_2)" represent the molar concentrations of Ti and TiO_2 in the metal and slag, respectively, "(CO)" represents the absolute hydrostatic pressure of the CO, and "(C)" is unity—i. e., the activity of carbon in the solid phase.

It is seen from the above free energy equation 2 that when the weight per cent of TiO_2 in the slag does not exceed 75%, the weight percentage of Ti in the pig iron can be kept below 0.6% with a hearth temperature as great as 1570° C. Although this temperature is somewhat higher than the average temperature of blast furnace slags given by Royster, Joseph and Kinney in "Blast Furnace and Steel Plants," volume 7 (1919), page 445 (Trans. A. I. M. E. 1920, page 554), it is not beyond the temperature range of the standard blast furnace hearth. It should be noted, however, that the process of the present invention can be carried out satisfactorily in any of the usual types of electric furnaces, and when relatively small tonnages are contemplated, smelting in the electric furnace frequently is to be recommended.

The principles of the present process can be illustrated by considering in detail the selective smelting of a high-grade imported titanium ore having the following analysis: TiO_2 60.35%; SiO_2 0.41%; Al_2O_3 2.74%; CaO 0.85%; MgO 2.60%, Fe 22.60%.

This ore, which represents a rather considerable tonnage of material imported into this country, consists essentially of ilmenite ($FeTiO_3$) 61.40% and rutile (TiO_2) 27.95%; the titanium minerals constituting 89.35% by weight of the ore. The "acid oxides" contents, following present-day metallurgical parlance, are: $TiO_2+SiO_2+Al_2O_3$, amounting to 63.50%. The basic oxides,

$$CaO+MgO$$

total 3.45%.

In order to "flux" this ore according to conventional furnace practice and teachings of the art, to produce a so-called "neutral" slag, the furnace operator would add to each 100 lbs. of the above ore 114 lbs. of limestone analyzing: SiO_2 0.75%; Al_2O_3 0.35%; CaO 52.12%; MgO 1.50%; Fe_2O_3 0.42%; CO_2 42.84%. If a charge containing 100 lbs. of ore and 114 lbs. of limestone were smelted with carbon under the hypothetical conditions that all of the iron were reduced and none of the titanium, there would be produced 24 lbs. of pig iron and 128 lbs. of slag. The slag

would show the following analysis (in per cent by weight): TiO_2 46.59; SiO_2 0.97; Al_2O_3 2.42; CaO 46.70; MgO 3.32. The acid oxides add to 49.98% and the basic oxides to 50.02%— a slag called "neutral" for reasons which are difficult to explain and impossible to justify. This slag is predominantly calcium titanate, since the sum of the TiO_2+CaO totals 93.29%. Ignoring for the moment the 6.71% of minor constituents, the weight ratio of the oxides in the CaO+TiO_2 binary system is just fifty-fifty. The concentration of these two oxides, however, is a 58.7 molar per cent CaO and 41.3 molar per cent TiO_2, indicating an apparent molecular excess of CaO over TiO_2. Actually, of course, there is in this slag no TiO_2 present as uncombined oxide. The components of the system are: 70.3 molar per cent $CaTiO_3$ and 29.7 molar per cent aCO. The slag lies in the $CaTiO_3$+CaO binary system. It is thus seen that the fluxing methods which are taught by the prior art produce a slag in which the TiO_2 content has been diluted excessively, and one which fails to exhibit satisfactory fluidity at the temperatures specified in the present process. If, in order to attain such satisfactory fluidity, the smelting temperatures are raised above the range herein contemplated, reduction of substantial amounts of titanium occurs and the metallic product is a ferro-carbon-titanium alloy which is not contemplated in the present process.

A small minority of furnace operators, basing their metallurgy more largely upon textbooks than upon experience, have followed as a fluxing principle the theorem that the oxygen content of the basic oxides should show a one-to-one relation to the oxygen content of the acid oxides. Were this principle followed in the case of the present ore, the limestone additions would be even greater than the above, viz., would be 162 lbs. of limestone to every 100 lbs. of ore.

It is to be understood that the present invention is defined as a smelting process which produces titaniferous slags which lie in the binary system, TiO_2+$CaTiO_3$. This means that the maximum amount of limestone which can be added to the above ore and produce a slag which lies within the definition of the present invention is 81 lbs. per 100 lbs. of ore. This limitation is not arbitrary. One hundred lbs. of the ore contains 60.35 lbs of TiO_2. Eighty-one lbs. of limestone contains 42.25 lbs. of CaO. These two weights (60.35 to 42.25) are in the proportion of the molecular weights of TiO_2 and of CaO. It is necessary to restrict the additions of limestone to ore within this limit in order that the slag will contain as principal constituents TiO_2 and $CaTiO_3$. If 81 lbs. of limestone is used, the composition of the resultant slag closely approximates the analysis of pure $CaTiO_3$, which exhibits a local maximum of temperature (point D, Fig. 1).

A substantial deficiency in CaO below the $CaTiO_3$ limit is specifically recommended in carrying out the present process. The lowest melting slag in this binary system is the eutectic composition, shown in Fig. 1, containing 18.6% CaO. Very satisfactory slag and metal can be produced by using sufficient limestone to approximate a eutectic slag.

Smelting the above ore with an addition of 40 lbs. of limestone for each 100 lbs. of ore produces a slag and metal which, although requiring a somewhat higher smelting temperature than is necessary with a eutectic slag and thereby increasing somewhat the titanium content of the pig iron produced, exhibits a compensating feature in that the FeO content of the slag is, in general, less than that resulting from eutectic fluxing. When operating with 40 lbs. of limestone flux addition, the resulting slag shows approximately a fifty-fifty concentration of $CaTiO_3$ and of TiO_2 as uncombined oxide. According to Fig. 1, the liquidus of this melt is 1600° C. and its solidus is identical with that of the eutectic slag.

A smaller addition of flux than that required to produce a eutectic slag can be used. For example, an addition of 16 lbs. of limestone to 100 lbs. of ore will produce a slag exhibiting the same liquidus and solidus temperatures as that produced with 40 lbs. of limestone: in such case the slag composition lies in the low-lime side of the eutectic (hypo-eutectic). The slag resulting from the 40 lb. lime addition lies in the high-lime side of the eutectic (hyper-eutectic).

As has been stated above, an object in producing a titaniferous slag as hereindescribed is to make available a material adapted to the production of titanium pigments. It is obvious that the hypo-eutectic slags run higher in TiO_2 than the hyper-eutectic slags. I have found, however, in operating a furnace process according to the principles of the present invention, that it is possible to produce a slag containing a somewhat lower FeO-content with the hyper-eutectic than with the hypo-eutectic. Since the presence of FeO in the slag is objectionable to the pigment manufacturer, it is in many cases advantageous to employ hyper-eutectic slags, since the decreased FeO-content fully compensates for the dilution of the TiO_2 with the CaO. The over-all economy of the present smelting process is but slightly affected by the amount of limestone added, provided the maximum flux addition does not approach too closely to the $CaTiO_3$ limit, i. e., for the present ore and limestone, 81 lbs. of limestone per 100 lbs. of ore. It is, therefore, difficult to lay down fixed limits to the minimum and maximum amounts of flux required. By reference to Fig. 1 it is seen that the abscissa XX' corresponds to a 16-lb. flux addition and the abscissa YY' corresponds to the 40-lb. flux addition. In practical furnace operation little difference in operative efficiency is found in any of the slags whose compositions lie between XX' and YY'.

It is obvious that the maximum concentration of TiO_2, which is in all cases most desirable, would be obtained by smelting the ore without any flux addition at all. I have attempted to carry out such an operation, but thus far have been unable to produce an unfluxed slag which was low enough in FeO to give any economic promise. Considerable success has been attained with limestone additions of less than 10 lbs., e. g., 7 lbs. of limestone per 100 lbs. of ore. However, results which for all practical purposes were as satisfactory have been obtained in the hyper-eutectic range, and although the use of more than 40 lbs. of limestone per 100 lbs. of ore caused a considerable loss in TiO_2 values, due to the production of pig iron exhibiting a tatanium content of several per cent, it is impossible fairly to state that such operation does not fall in the range contemplated in the present invention.

From the above discussion, it is clear that the addition of an alkaline earth metal oxide flux to a titanium ore is necessary. No exact lower limit to this flux addition can properly be specified which is more specific than the phrase "a substantial addition of flux." In the same way, no more satisfactory upper limit can be specified

than is included in the phrase "a substantial deficiency of flux below that required to produce equal molar concentration of CaO and TiO_2 in the slag."

The explanation given above indicates the principles which should be employed in carrying out the present process when the flux used is a relatively pure form of limestone. It is metallurgically interesting to examine the phenomenon occurring when the above ore is fluxed with MgO in place of CaO. The cost of magnesite is many times that of limestone; therefore, from a purely economic point of view, the fluxing of titanium ores with MgO is less attractive. From a purely metallurgical standpoint, however, the process can be carried out successfully with the use of an MgO flux. Fig. 2 indicates in general that that portion of the MgO-TiO_2 binary system which lies on the TiO_2-side of the $MgTiO_3$ point shows a general resemblance to the system shown in Fig. 1. It is seen that the eutectic temperature between TiO_2 and $MgTiO_3$ is 1660° C. in contrast to the 1556° C. in eutectic temperature in Fig. 1. The discussion of the slags given above in connection with CaO can readily enough be repeated for the case of an MgO-TiO_2-slag by the use of these two figures.

From a practical standpoint, more interest attaches to the ternary system $CaO+MgO+TiO_2$, since the fluxing of titanium ore with a dolomite is frequently indicated and the cost of dolomite and dolomitic limestone is in many geographical localities somewhat cheaper than the purer form of limestone.

The metallurgical problem which the present invention attempts to solve is the treatment of titaniferous ores to produce primarily a relatively pure titanium oxide useful as a charging raw material and as a pigment. Contamination of the slag product with small amounts of oxides such as SiO_2, Al_2O_3, MgO, etc., is not serious. The presence of small percentages of FeO, MnO, V_2O_5, and the like, however, is objectionable. In practice the impurity which causes major concern is FeO. When one attempts to smelt a titanium ore in an electric furnace, it is rather simple to attain complete metallization of both the FeO and TiO_2 to form a ferro-carbon-titanium alloy. It immediately occurs to almost everyone interested in the problem that two obvious and somewhat simple methods might be used: (1) It has been widely believed possible, by restricting the energy input, to convert the FeO to pig iron and leave the TiO_2 unreduced. This, unfortunately, has been found not to be metallurgically possible. The melting point of TiO_2 is so high that when the furnace is operated hot enough to produce fluid TiO_2 objectionably large amounts of Ti will be incorporated in the metal. (2) It has been thought that restricting the carbon to an amount just sufficient to reduce the FeO would prevent reduction of TiO_2. This method also is not practical in usual electric furnace operation. The electrodes in the furnace are constructed of carbon and the highest temperature in the furnace is that of the electrodes themselves. If the temperature is high enough to melt TiO_2, excessive reduction of TiO_2 will inevitably take place through reaction with the carbon electrodes.

When it is realized that TiO_2 occurs in ores as the entity ilmenite and that the FeO is present as a part of a crystal lattice, one should not properly be surprised to learn that the atoms of metallic iron cannot bodily be removed from the ilmenite crystal while leaving the TiO_2-component of the molecule in a solid state. In order fractionally to metallize the FeO of the molecule, it is necessary first to convert the molecule to a liquid. For this reason, therefore, the controlled amount of basic flux is used in the present invention. It has been found that sufficient fluidity can be attained by the addition of this limited amount of flux without raising the temperature of the reacting ilmenite so high that objectionable amounts of TiO_2 are transferred to the metallic product.

It should be understood that the novel fluxing principle described above is the underlying feature which is characteristic of the present invention, is definitive of it, and is the operating factor which is primarily responsible for its technical success. This does not mean that the present invention can be carried out merely by complying with the fluxing principles herein explained. When the proper amount of alkaline earth metal oxide has been added to the ore, it is still necessary to control the thermal input per unit of ore to maintain the smelting zone of the furnace within the temperature range in which essentially complete reduction of FeO results without concurrent excessive reduction of TiO_2. It is also necessary to adjust the amount of carbon to prevent the accumulation of excess reducing agent. The lack of success heretofore of attempts to achieve selective reduction by limiting either the thermal input or the ratio of carbon to ore, has been caused by failure to appreciate that a substantial deficiency of basic flux below an equimolecular ratio with the TiO_2 is necessary.

Although the calculation of the heat balance for the blast furnace is somewhat tedious, it is by no means difficult. In order to illustrate in detail how the adjustment of thermal input is attained in actual furnace work, the following example of blast furnace smelting of a titanium ore may prove helpful.

A blast furnace of usual design but of small capacity with a 14 ft. 6 in. hearth is blown with 25,000 standard cu. ft. per min. of air (measured at 60° F. and 29.92 Hg) containing 3.5 grains of moisture per cu. ft., and preheated to 1180° F. The composition of the ore, stone and coke charged is as follows:

TABLE I

Ore		Limestone		Coke	
				Proximate	
Fe_2O_3	21.89	CaO	52.82	Moisture	2.20
FeO	34.30	MgO	1.25	Volatile	0.94
MnO_2	0.14	CO_2	42.86	Fixed Carbon	90.07
TiO_2	37.40	SiO_2	0.78	Ash	6.79
V_2O_5	0.28	Al_2O_3	0.35		100.00
P_2O_5	0.018	Fe_2O_3	0.74		
S	0.015	P_2O_5	0.032		
SiO_2	0.52	SO_3	0.043		
Al_2O_3	1.25	Moisture	1.13	*Ultimate*	
CaO	0.05		100.00	SiO_2	3.25
MgO	1.23			Al_2O_3	2.10
CO_2	1.36			CaO	0.65
Combined water.	0.32			MgO	0.18
Moisture	1.24			P_2O_5	0.022
	100.00			S	0.59
				Fe	0.43
Fe	41.10			Hydrogen	0.67
P	0.008			Nitrogen	0.68
Mn	0.09			Oxygen	1.95
V	0.16			Carbon	89.48
					100.00

At twenty-minute intervals the following weights are charged: ore 28,000 lbs., limestone 7800 lbs., and coke 9800 lbs. The furnace under this operation produces 394 g. t. (gross tons—2240

lbs.) per 24 hours, and 515 g. t. of slag. The pig iron produced has the following composition:

TABLE II

	Metal Analysis (by weight)	Atomic	Molecular Composition	
Fe	94.35	80.74	Fe	58.29
Si	0.12	0.21	Fe_3C	39.32
S	0.03	.04	TiC	1.02
P	0.02	.02	Fe_3V	0.73
Ti	0.46	.46	Fe_3Si	0.47
V	0.35	.33	FeS	0.10
Mn	0.11	.09	Mn_3C	0.06
C	4.56	18.11	Fe_3P	0.01
	100.00	100.00		100.00

The composition of the slag is:

TABLE III

	Analysis of Slag (by weight)	Molar (as free oxides)	Molecular Composition	
SiO_2	3.02	3.54	$CaTiO_3$	53.42 perofskite
Al_2O_3	3.53	2.44	TiO_2	30.61 brookite
TiO_2	62.95	55.19	$MgTiO_3$	7.20
CaO	24.96	31.27	$FeTiO_3$	3.17 ilmenite
MgO	2.80	4.88	$CaAl_2Si_2O_8$	3.03 anorthite
FeO	1.89	1.85	$MgAl_2O_4$	1.14 spinel
CaS	0.85	0.83	CaS	1.43
	100.00	100.00		100.00

The volume of gas discharged from the furnace is 33,400 std. cu. ft. per min. (dry basis), and the gas has the following analysis:

TABLE IV

Gas analysis (by volume)

CO_2	13.20
CO	27.80
H_2	3.50
N_2	55.50
	100.00

The temperature of the gas is 310° F, and the temperature of the slag calculated from the atomic and molecular concentrations above by Equations 2 and 3 supra is 2888° F. (1587° C.).

In smelting the ore in the operation described above, it is obvious that the thermal requirements are 6,070,000 B. t. u. per g. t. of metal. The heat generated in the furnace is 4,735,000 B. t. u. per g. t. of metal from the oxidation of coke-carbon to CO and 1,980,000 B. t. u. sensible heat brought in by the hot blast for a total of 6,720,000 B. t. u. The excess 650,000 B. t. u. per g. t. of metal is just sufficient to compensate for the heat losses in the bosh and hearth of the furnace and the sensible heat of the gas emerging at 310° F.

It should be observed that realization of the desired selective reduction in this example is accomplished by an adjustment of the thermal input to the thermal requirements for the desired smelting; but this is possible in practice only when, by careful control of the flux, the furnace hearth can be operated within the temperature range in which satisfactory metallization of iron can be achieved while concurrently maintaining the metallization of TiO_2 at a low figure. Whenever substantial tonnages of ore are to be handled it is desirable to carry out this invention in a blast furnace. When, as frequently occurs, it is desirable to treat smaller tonnages of ore, the smelting operation can be carried out at little added expense in an electric furnace.

To illustrate the details of electric smelting of the ore given above, the operation of a 7500 kv.-a. arc-furnace will be discussed.

The electrodes of this three-phase furnace are adjusted to control the current in each electrode to 87,800 amp., the potential drop at the transformer being 51.5 volts per phase. The power factor is observed to be 79.0%, indicating a thermal input of 6195 kw. The furnace is charged regularly at the rate of: 228 lbs. ore, 34 lbs. limestone, and 29 lbs. coke per minute, these charge components having the composition given above. The daily production is 65 g. t. of pig iron and 72 g. t. of slag. The heat loss through the walls of the furnace and to the water-cooled electrodes is determined, from measurements of the heat absorbed by the cooling water, to be 1092 kw. This indicates a net energy input of 5103 kw., equivalent to 1890 kw.-hr. per g. t. of metal (6,450,000 B. t. u.). With this thermal input, the metal and slag are discharged at 1575° C. (2867° F.). The flux ratio (ratio of limestone to ore) is 15%. The ore ratio (ratio of ore to coke) is 7.85. Metal and slag analyze:

TABLE V

Metal Analysis		Slag Analysis		Gas Analysis	
Ti	0.56	TiO_2	74.50	CO_2	15.72
Si	0.04	SiO_2	2.03	CO	84.28
S	0.01	Al_2O_3	3.08		100.00
P	0.02	CaO	16.38		
Mn	0.09	MgO	2.90		
V	0.34	FeO	0.96		
C	4.96	MnO	0.06		
Fe	93.98	S	0.18		
	100.00		100.09		
		Less O_2 equivalent of S	.09		
			100.00		

The furnace discharges 780 std. cu. ft. per minute of gas containing 15.72% CO_2 and 84.28% CO (dry basis). The heat capacity of the gas is only one-fourth that of the charge-materials, hence little preheat or pre-reduction takes place before the ore arrives at the smelting zone, and the gases leave the furnace at atmospheric temperature.

It is essential in carrying out the present invention in the electric furnace to adjust the energy input to the rate of charging in order to maintain a controlled thermal environment in the metal and slag bath. For example, when the rate of charging is decreased from 228 lbs. to 205 lbs. per minute of ore (i. e., 10%), the net thermal input is increased to 1790 kw. per g. t., and the slag and metal temperature is raised to 1650° C. (3002° F.).

As a result of this increase in hearth temperature, the titanium content of the metal is enhanced (i. e., to 2.25%), and the TiO_2 content of the slag is reduced (i. e., to 71.7%). This entails a minor loss of TiO_2 values in the slag and introduces an amount of Ti into the metal, which frequently restricts the marketability. When operating at the higher temperature, however, the FeO-content of the slag is reduced somewhat (i. e. to 0.62%). When this slag is treated chemically in a subsequent operation to produce a colorless pigment, the decrease in FeO is helpful. At the higher thermal input, it is desirable to reduce the ore-ratio from 7.85 to 7.00 to provide increased carbon to compensate for the inevitable metallization of TiO_2 and also to take care of the increased carbon content of the titaniferous pig iron.

If the charging rate is reduced further to 125

lbs. of ore per minute, the ore-ratio should be decreased to 4.6. Holding the flux-ratio constant at 15%, the production of metal will be 48 g. t. per day, and the net thermal input 2290 kw.-hr. per g. t. (7,850,000 B. t. u.). With increased energy input, the temperature of the slag and metal is raised to 1780° C. (3236° F.). Although it is not possible to delimit the present invention in an open-and-shut manner, it is fair enough to term this operation an upper limit of thermal input for satisfactory realization of selective reduction. The metal produced with 2290 kw.-hr. per g. t. input is not merchantable directly as pig iron, containing as it does 22.4% titanium. The metal is, in fact, a ferro-carbon-titanium alloy. Due to the transfer of such a large fraction of TiO_2 from the slag to the metal, the slag will contain only 57.2% TiO_2. The value of the slag as a source of pigment-material is sufficiently impaired to indicate that further increase in thermal input would definitely remove the furnace operation from the definitive limits of the present process.

It should be observed that when operating with the lower net thermal input (1890 kw.-hr. per g. t.) and when producing slag as given in Table V the molar concentration of this slag is 35.0% $CaTiO_3$ and 52.6% uncombined TiO_2 (i. e., 40% $CaTiO_3$ and 60% TiO_2 in the binary system CaO-TiO_2). The binary slag is diluted with 12 molar percent of unavoidable impurities (SiO_2, Al_2O_3, etc.). As a result of this dilution, the solidus for the actual slag is reduced to 1510° C. and the liquidus to 1540° C. With a bath temperature of 1780° the slag is superheated 240° C. above the liquidus (line C—D, Fig. 1), and 270° C. above the solidus (line C—F). At this high temperature, the FeO content of the slag is suppressed to less than 0.2% FeO, and the slag only slightly discolored.

The smelting operations contemplated in the present invention are somewhat unusual in the sense that the ore is converted completely into merchantable products (i. e., metallurgically useful metal and chemically useful slag). The relative amounts of each of these products (neither being logically a by-product) can be varied widely and the compositions of each can be altered by adjusting the thermal input. It is, therefore, impossible to instruct the operator to employ a precisely defined thermal input. An upper and a lower limit can be, and have been, given. The exact adjustment within this range will depend on what market he finds for his metal and his slag. The illustrative examples given above should prove sufficient guide to indicate the proper adjustments to produce the products desired.

Depending on the uses to which the metal and slag are to be put, the ore can be smelted with a net thermal input of 1890, 1970 and 2290 kw.-hr. per g. t. of metal. Each gives satisfactory operation when using a 15% flux ratio. The slags produced are located in what I have chosen to term the "eutectic valley," a region shown as the shaded area in Fig. 1. These particular slags lie in the hyper-eutectic territory of this valley (between the point "C" and the line YY').

Equally satisfactory operation can be realized by decreasing the flux ratio whereby to produce slags located in the hypo-eutectic portion of the valley (between point "C" and the line XX'). To illustrate: a flux ratio as low as 5% may be used. Holding 87,800 amp. in each electrode, at 51.5 volts, the charge rate is: 268 lbs. ore, 13 lbs. limestone and 31 lbs. coke per minute. The net thermal input is 1680 kw.-hr. per g. t. (5,720,000 B. t. u.). With this thermal input the metal and slag show a temperature of 1520° C. (2768° F.). The analyses of the slag and metal produced are:

TABLE VI

Metal Analysis		Slag Analysis	
Ti	0.38	TiO_2	82.08
Si	0.13	SiO_2	2.12
S	0.02	Al_2O_3	3.38
P	0.02	CaO	6.20
Mn	0.11	MgO	2.92
V	0.33	FeO	3.10
C	4.65	MnO	0.09
Fe	94.36	S	0.22
	100.00		100.11
		Less O_2 equivalent of S...	.11
			100.00

When the above weight-analysis is given in terms of molecular concentrations, it is seen that the slag contains 10.0% $CaTiO_2$ and 83.7% uncombined TiO_2, diluted with 6.3% silicates and aluminates. In the binary system CaO-TiO_2 the weight percentage of CaO is 7.0%, and the slag is seen to be located about 2% to the right of the line XX' in Fig. 1. The flux addition is sufficient to place the slag just inside the shaded area which defines the eutectic valley. The slag temperature is almost at the solidus itself. This is the lower limit of thermal input with which satisfactory operation can be carried out in practice.

As the ore is smelted and as its FeO content is decreased by reduction, the slag becomes increasingly stiff and sluggish. With its high TiO_2 content, it exhibits the physical property characteristic of high titania slags, i. e., although quite fluid when superheated above the solidus, it becomes mushy and almost semi-fluid when the solidus is approached. The slag at this low temperature in addition to having an objectionably high FeO content, tends to entrap globules of metallic iron which are difficult to remove even by magnetic concentration. These difficulties are readily avoided by decreasing the rate of charging of ore by 9%, i. e., 244 lbs. per minute while keeping the flux-ratio and the ore-ratio unchanged. With this operation the thermal input is increased to 1750 kw.-hr. per g. t. (5,980,000 B. t. u.). Slag and metal temperature is raised to 1628° C. (2962° F.). At this higher temperature, the titanium oxide content of the slag is lowered to 77.5%, the titanium content of the metal is increased to 4.65% and the FeO content of the slag is lowered to 1.30%. The iron content of the slag is controlled by the equation:

$$3FeO+TiC=3Fe+TiO_2+CO$$

As a result, the Fe content of the slag varies inversely as the cube root of the titanium content of the metal.

Further reduction in the FeO content of the slag can be attained of course by a further increase in thermal input. If the rate of ore feed is decreased with constant electrical input or, what is the same thing, the electrical input is increased with a constant rate of ore feed, metal and slag temperatures can be carried as high as 1710° C. (3110° F.). With such elevations in temperature the titanium oxide content of the slag is 66.6%, the titanium content of the metal will exceed 15%, and hence the metal may properly be termed a titanium alloy. The FeO content of the slag will be carried down to 0.80%. Here again the question of being able to market the

alloy is the criterion which determines the thermal input to be used.

In the binary system $MgO-TiO_2$ shown shaded in Fig. 2, a eutectic valley is found on the low MgO-side of $MgTiO_3$. The area of this valley is less extensive than the corresponding valley in the $CaO-TiO_2$ system (Fig. 1). Therefore, in the operation of the present invention the use of limestone as a flux is preferred to magnesite aside from the question of the high cost of magnesite. Moderate amounts of dolomite may of course be used. Where pure calcite is not readily available, dolomitic limestones, containing considerable amounts of magnesia, are permissible.

It should be pointed out that the present invention contemplates the smelting of ores containing as much FeO and TiO_2 as possible. The presence of SiO_2, Al_2O_3 and other acid oxides is undesirable and is avoided as far as possible. In this particular respect, the present invention is sharply distinguished from those various operations in which iron ore is smelted to produce pig iron, and wherein TiO_2 although present is considered an objectionable impurity and one which the furnaceman hopes to maintain at a minimum. Because of the widespread occurrence of titaniferous iron ores in this country, many efforts to convert them into pig iron have been made. In all cases, the dilution of titaniferous iron ore with silicious ore has been advised and the presence of the TiO_2 in the slag has been universally considered objectionable. So far as I can learn, attempts to smelt ores producing a slag containing more than 32% TiO_2 have not been successful.

The examples of practice given above have been illustrated with a particular ore which I have had occasion to investigate experimentally. It is unusually high-grade for a Fe-Ti ore. The gangue is exceptionally low ($SiO_2+Al_2O_3$ being 1.77%). The limestone and coke analyses given in Table I are the actual analyses of the materials used in the experiments. In actual practice, many Fe-Ti ores will be encountered running higher in SiO_2 and Al_2O_3, and in general coke-ash and impurities in the limestone will be higher than that shown in the examples. When the present process is carried out with such lower grades of ore, coke and limestone, slags will be produced which analyze much higher in SiO_2 and Al_2O_3. Increased amounts of such impurities interfere with the metallurgical operation and, what is more important, impair the value of the slag produced considered as a pigment material or a chemical product. Experiments to date indicate that when the TiO_2 in the slag is diluted much below 40 or 50% the overall value of the process becomes unattractive.

While the process of the present invention has been described with reference to blast furnace and electric furnace operations, it is to be understood that the process can be carried out in a fuel fired shaft-type furnace such as a cupola or other suitable furnace.

I claim:

1. In the process of smelting titaniferous iron ore with carbon and added flux consisting essentially of a basic oxide of the group consisting of calcium oxide and magnesium oxide, the improvements which consist in so proportioning the charge as to produce a slag consisting essentially of titanium oxide, basic oxides and incidental impurities, in which charge the molar ratio of TiO_2 to basic oxides is maintained within the limits 12 to 1 and 3 to 2, and smelting said charge in a furnace at a temperature between 1550° C. and 1700° C. to produce molten iron and a fluid, titanium-rich, slag.

2. The method of treating a material containing an oxidic compound of titanium and an oxidic compound of iron, which method comprises preparing a furnace charge containing said material, a quantity of carbonaceous reducing agent sufficient to reduce substantially all of the iron oxide in said material, and calcium oxide, in the form of limestone, in an amount corresponding to from about 7 to about 33 pounds of calcium oxide per each 100 pounds of titanium oxide in the charge, smelting said charge in a furnace at a temperature of about 1650° C. to produce molten iron and a fluid slag rich in titanium oxide, and separately recovering the iron and the slag.

3. Process of simultaneously producing pig iron of low titanium content and high titania slag low in iron, which comprises smelting a titaniferous iron ore with carbon and with an added flux consisting essentially of oxide of calcium in an amount, with respect to the titanium dioxide content of the charge, equivalent to a weight percentage of CaO in the binary system $CaO-TiO_2$ of from about 12 to about 25, and maintaining the charge at a temperature, between 1500° and about 1650° C., adapted to liquefy the same and to secure metallization of substantially all of the iron content thereof while minimizing the concurrent reduction of the titanium dioxide content thereof.

4. Process of producing simultaneously pig iron of low titanium content and a high titania slag low in iron from a titaniferous iron ore which comprises smelting the titaniferous iron ore with carbon and a basic flux of the group consisting of limestone and dolomite, the content of basic oxide in the charge being equivalent to 10 to 30 molar percent of basic oxide of the group consisting of CaO and MgO, based on the titanium oxide content of said charge, maintaining the charge at a temperature, between 1550° C. and 1700° C., adapted to liquefy the same and to secure metallization of substantially all of the iron content thereof while minimizing concurrent reduction of the titanium oxide content thereof, and separately recovering the molten iron and the fluid slag.

5. The method of treating a material containing an oxidic compound of titanium and an oxidic compound of iron, which method comprises preparing a furnace charge containing said material, a quantity of a carbonaceous reducing agent sufficient to reduce substantially all of the iron oxide in said material, and a quantity of calcium oxide and magnesium oxide sufficient to flux said charge and to form, when said charge is smelted, a slag containing about 62% titanium oxide, the remainder, except for incidental impurities, being calcium oxide and magnesium oxide; and smelting said charge in a furnace at a temperature of about 1650° C. to produce molten iron and a fluid titanium-rich slag of such composition.

6. The method of treating a material containing an oxidic compound of titanium and an oxidic compound of iron, which method comprises preparing a furnace charge containing said material, a quantity of carbonaceous reducing agent sufficient to reduce substantially all of the iron oxide in said material, and a quantity of calcium oxide sufficient to flux said charge and to form, when said charge is smelted, a slag containing

about 74% titanium oxide calculated as TiO_2, the remainder, except for incidental impurities, being calcium oxide; and smelting said charge in a furnace at a temperature of about 1650° C. to produce molten iron and a fluid, titanium-rich slag of such composition.

7. Process of smelting titaniferous iron ore in the blast furnace, which comprises charging the furnace with the ore, coke and limestone, blasting the charge with a preheated air blast, adjusting the thermal input to maintain a temperature such that the charge is liquefied, said temperature being not in excess of 1700° C., and adjusting the limestone content of the charge to maintain the molar ratio of TiO_2 to basic oxide flux, calculated as CaO equivalent, in the charge within the limits 12 to 1 and 3 to 2, whereby there are produced a fluid pig iron low in titanium and a fluid slag rich in titanium oxide and poor in iron oxide, and separately removing the pig iron and the slag from the blast furnace.

8. Process of smelting titaniferous iron ore containing not more than about 1.25% by weight of alumina in an electric furnace, which comprises charging the furnace with the ore, coke and limestone, adjusting the electrical input to maintain a temperature such that the charge is liquefied, said temperature being not in excess of 1700° C., and adjusting the limestone content of the charge to maintain the molar ratio of TiO_2 to CaO in the charge within the limits 12 to 1 and 3 to 2, whereby there are produced a fluid pig iron low in titanium and a fluid slag rich in titanium oxide and poor in iron oxide, and separately removing the pig iron and the slag from the electric furnace.

9. The method of treating a material containing an oxidic compound of titanium and an oxidic compound of iron, which method comprises preparing a furnace charge consisting essentially of said material, a quantity of carbonaceous reducing agent sufficient to reduce substantially all of the iron oxide in said material, and limestone, the limestone being present in an amount corresponding to from 16 to 40 pounds of a limestone containing 52.8% by weight of CaO per each 100 pounds of said material analyzing 37.4% by weight of TiO_2, smelting said charge in a furnace at a temperature in excess of 1550° C. but not exceeding 1700° C. to produce molten iron and a fluid slag rich in titanium oxide, and separately recovering the iron and the slag.

10. A metallurgical slag having the following approximate composition:

	Percent
Titanium oxide ----------calc. as TiO_2--	63
Calcium oxide ----------	25
Magnesium oxide ----------	2.8
Iron oxide ----------calc. as FeO--	1.9
Silicon dioxide ----------	3.0
Aluminum oxide ----------	3.5
Calcium sulphide ----------	0.85
MnO ----------	0.06

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