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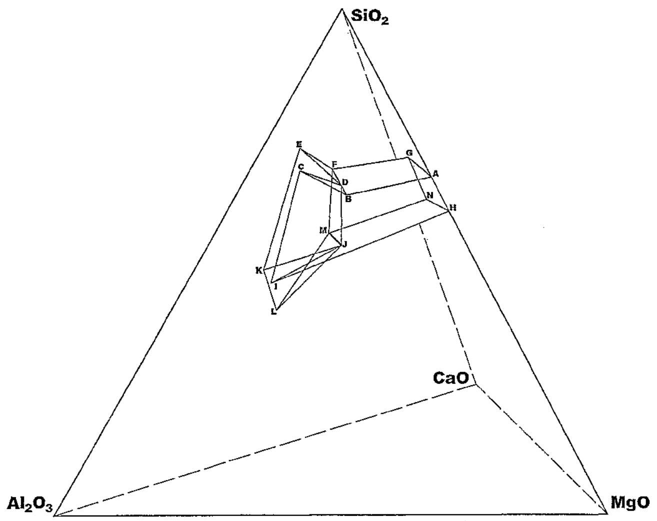
(54) Title: PROCESS FOR EXTRACTING CRYSTALLINE TITANIUM OXIDES



(57) Abstract: A process for extracting crystalline TiO_2 from a titanium oxides-bearing material is provided. First one produces a molten slag of a mixture of titanium oxides-bearing material comprising Ti_x0_y, and fluxing agents comprising SiO_2 and metal oxides from a group including CaO, MgO and $A1_20_3$, wherein the fluxing agents are present in the molten slag in an amount to adjust the molar ratio of CaO, MgO, $A1_2O_3$ and SiO_2 in the molten slag to substantially favour formation of a secondary silicate phase subsequent to fortnation of a primary crystalline TiO_2 phase when the molten slag is cooled. The TiO_2 concentration in the molten slag must be sufficient to afford crystalline TiO_2 when the molten slag is cooled. The molten slag is then cooled at a slow rate between the liquidus and the solidus of the molten slag to promote crystallisation of TiO_2 and the crystalline TiO_2 so formed is liberated and separated from the solidified slag. The process is particularly applicable to titanium bearing slags produced as a byproduct in reductive smelting process for treatment of ferrous oxides containing titanium oxides.

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TITLE

PROCESS FOR EXTRACTING CRYSTALLINE TITANIUM OXIDES

FIELD OF THE INVENTION

The present invention relates to a process for extracting crystalline titanium oxides, in particular to extracting crystalline titanium oxides from titanium oxides-bearing material also containing ferrous oxides.

BACKGROUND OF THE INVENTION

It is known to require the extraction of various titanium oxide species (Ti_XO_Y) in crystalline form from ores and other materials bearing these titanium oxides. Known processes for extraction of titanium oxides include the Becher process, in which ilmenite is subjected to a reductive process to reduce the iron oxide content to metallic iron, and then reoxidising the metallic iron in an aqueous solution to separate the metallic iron from the ilmenite to produce a synthetic rutile product and separate iron oxide waste product; and the conventional titanium slag process where ferrous ores of titanium are reductively smelted to produce an enriched titanium oxide slag and a pig iron byproduct.

The Becher and conventional titanium slag processes both require feedstock that is low in CaO, MgO, Al_2O_3 and SiO_2 in order to produce synthetic rutile and titanium slag that have a sufficiently low content of CaO, MgO, Al_2O_3 and SiO_2 to be acceptable as feedstock in the chloride process for producing titanium dioxide pigment. Both processes enrich the titanium oxide content, and consequently the CaO, MgO, Al_2O_3 and SiO_2 contents, only by depletion of the iron oxide content.

The chloride process generally requires a feedstock having a TiO_2 content above 75% and an auxiliary oxide content substantially no more than as follows: CaO 0.15%, MgO 1.0%, Al_2O_3 1.5%, SiO_2 2.0%, MnO 1.8%, and V_2O_5 0.7%.

The low CaO, MgO, Al_2O_3, and SiO_2 feedstock impurity concentration requirement means that only a minor portion of the available resources of titanium oxides-bearing materials are able to be exploited.

A titanium slag production process is practiced at Richards Bay Iron and Titanium (Republic of South Africa), QIT-Fer et Titane (Canada), and Tinfos (Norway). The Becher process is practiced by Iluka. These production facilities produce a high TiO_2 content slag that has up to 85% TiO_2 and at least 10% FeO with only up to total of 10% CaO, MgO, Al_2O_3, and SiO_2. Typically, these slags cannot be tapped from the furnace if the FeO content is too low. The feedstocks and coal that is used in the process is chosen to minimise CaO, MgO, Al_2O_3, and SiO_2.

The present invention attempts to provide an alternative method for extracting TiO_2 in a crystalline form from titanium oxides-bearing materials that have levels of CaO and/or MgO and/or Al_2O_3 and/or SiO_2 that make them generally make them unacceptable as feedstock for either the Becher process or the conventional titanium slag process.

SUMMARY OF THE INVENTION

In accordance with a first aspect of the invention there is provided a process for extracting crystalline TiO_2 from a titanium oxides-bearing material comprising the steps of:

a) providing a molten slag of a mixture of titanium oxides-bearing material comprising Ti_xO_y, and fluxing agents comprising SiO_2 and metal oxides from a group including CaO, MgO and Al_2O_3, wherein the fluxing agents are present in the molten slag in an amount to adjust the molar ratio of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag to substantially favour formation of $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof subsequent to formation of crystalline TiO_2 when the molten slag is cooled, the TiO_2 concentration in the molten slag being sufficient to afford crystalline TiO_2 when the molten slag is cooled;

b) cooling the molten slag at a slow rate between the liquidus and the solidus of the molten slag to promote crystallisation of TiO_2; and

c) separating the crystalline TiO_2 formed in step b) from the solidified slag.

DESCRIPTION OF THE FIGURES

The present invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a three-dimensional composition diagram of the range of relative % composition of CaO, MgO, Al_2O_3 and SiO_2, in the molten slag, exclusive of the TiO_2 concentration, which substantially favours formation of silicate mineral phases $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof in accordance with a preferred embodiment of the present invention;

Figure 2 is four scanning electron microscope (SEM) micrographs of slag samples A-D at low magnification from Example 1 in accordance with the present invention;

Figure 3 is a SEM micrograph of slag sample A shown at higher magnification than in Figure 2;

Figure 4 is six SEM micrographs of slag samples A1-G at low magnification from Example 2 in accordance with the present invention; and

Figure 5 is a flow chart of the present invention conducted in relation to reductive smelting of titanium oxides-bearing material also containing ferrous oxides.

DESCRIPTION OF THE INVENTION

The present invention is based on the discovery that a molten slag comprising a mixture of Ti_xO_y and CaO, MgO, Al_2O_3 and SiO_2, wherein CaO, MgO, Al_2O_3 and SiO_2 are in particular molar ratios, will differentially solidify to afford a plurality of crystalline phases, where a primary crystalline phase comprises crystalline TiO_2 in the form of rutile and a secondary silicate phase substantially comprises silicate mineral species $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof, when the molten slag is cooled at a slow rate between the liquidus and the solidus of the molten slag, provided that the TiO_2 content of the molten slag composition is sufficiently high for crystalline TiO_2 to form.

Therefore, crystalline TiO_2 can be produced from a titanium oxides-bearing material by heating a mixture of titanium oxides-bearing material comprising Ti_xO_y, and fluxing agents comprising SiO_2 and metal oxides from a group including CaO, MgO and Al_2O_3 to high temperatures to afford a molten slag. The fluxing agents are present in the molten slag in an amount to adjust the molar ratio of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag to substantially favour formation of silicate mineral species $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof subsequent to formation of crystalline TiO_2 when the molten slag is cooled. However, the TiO_2 concentration in the molten slag must also be sufficient to afford crystalline TiO_2 when the molten slag is cooled.

Thus, it is an important consideration in formation of the molten slag composition that adjustment of the molar ratios of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag to substantially favour formation of silicate mineral $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$ or a mixture thereof by addition of the fluxing agents does not, in fact, dilute the TiO_2 concentration in the molten slag to a level where little or no crystalline TiO_2 is formed when the molten slag is subject to slow cooling solidification.

The minimum TiO_2 content of the molten slag sufficient for crystalline TiO_2 to form varies depending on the relative proportions of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag, and varies from about 25% to about 50%.

In a preferred embodiment of the invention, the molten slag comprises calcium oxide (CaO), magnesium oxide (MgO), aluminium oxide (Al_2O_3), silicon dioxide (SiO_2), and titanium oxides (Ti_xO_y). Referring to Figure 1, in the preferred embodiment of the invention the molten slag contains CaO, MgO, SiO_2 and Al_2O_3 in the molar ratios of CaO, MgO, Al_2O_3 and SiO_2 as provided in the polygonal prism defined by vertices A-N (see Table 1 below) in addition to at least the minimum concentration of TiO_2 for crystalline TiO_2 to form during slow cooling solidification.

TABLE 1: VERTEX COORDINATES FOR FIGURE 1

(C = CaO; M = MgO; A = Al_2O_3; S = SiO_2)

Vertex	Weight %				Empirical Molecular Formula
	CaO	MgO	Al_2O_3	SiO_2	
A	0.00	33.47	0.00	66.53	M_3S_4
B	0.00	20.04	16.90	63.06	$M_9A_3S_{19}$
C	0.00	9.10	23.03	67.86	MAS_5
D	8.77	12.61	15.95	62.67	$C_3M_6A_3S_{20}$
E	10.81	0.00	19.66	69.52	CAS_6
F	23.67	0.00	14.34	61.99	$C_9A_3S_{22}$
G	20.27	14.57	0.00	65.16	CMS_3
H	0.00	40.15	0.00	59.85	MS
I	0.00	15.36	38.85	45.79	MAS_2
J	11.71	16.83	21.29	50.18	CM_2AS_4
K	20.16	0.00	36.65	43.19	CAS_2
L	30.45	0.00	36.92	32.63	$C_3A_2S_3$
M	32.95	0.00	19.97	47.08	C_3AS_4
N	25.90	18.61	0.00	55.49	CMS_2

It is particularly envisaged that the process of the present invention is a beneficial enhancement to a reductive smelting process performed with titanomagnetite utilised for ironmaking, for example the Waikato North Heads vanadiferous titanomagnetite iron sand concentrate processed by New Zealand Steel, wherein a low-grade non-conventional titanium oxides-bearing slag is produced as a byproduct of the production of pig iron. In the reductive smelting process, a carbonaceous reductant, such as coal is required to reduce any iron oxides contained in the feedstock. The resultant ash of the coal or other carbonaceous reductant inherently contains CaO, MgO, Al_2O_3 and SiO_2. Thus, any titanium oxides-bearing slag produced by the reductive smelting process will also contain additional amounts of CaO, MgO, Al_2O_3 and SiO_2 as a result of ash entrainment, in addition to certain amounts of CaO, MgO,

Al_2O_3 and SiO_2 inherently present in the gangue of the titanium oxides-bearing material.

It is unlikely that a molten slag formed merely from the titanium oxides-bearing material (TOBM), regardless of whether it is a byproduct of the reductive smelting process, would have appropriate inherent molar proportions of CaO, MgO, Al_2O_3 and SiO_2 to coincide with the preferred molten slag composition as defined in Figure 1. Accordingly, it is thus necessary to adjust the concentrations of some of the oxides, particularly those that are deficient in the slag, to the preferred molar ratios of CaO, MgO, Al_2O_3 and SiO_2 with fluxing agents comprising CaO, MgO, Al_2O_3 and SiO_2.

Addition of CaO and MgO fluxes can be made as oxides or carbonates, the latter subsequently needing to be burnt to the oxide form during either or both the iron oxide reduction and smelting steps of the reductive smelting process. Flux additions in the form of sulphates will be deleterious to the process of the present invention.

One or more or all of the fluxes may be subject to preparation by conventional treatments. These may include but are not limited to drying, grinding, burning of carbonate forms to oxide forms, and agglomeration.

Flux additions can be made at three successive stages in the process of the present invention, including but not limited to during blending of the TOBM feedstock (and optionally the reductant) for the process and/or during smelting and/or prior to slow cooling solidification of the molten slag. Staggering the addition of the fluxes may be beneficial.

However, if as a result of making the requisite flux additions to achieve the requisite proportions the TiO_2 content of the molten slag is diluted by too much then crystalline rutile will not form when the molten slag is slow cooled.

In another embodiment of the invention, the molten slag may contain oxide impurities that may have originated as accessory oxides or/and accessory minerals in the titanium oxides-bearing material or/and fluxing agents or/and ash from the carbonaceous reductant(s). Typical oxides encountered include oxides of vanadium, chromium, manganese, zinc, sodium and potassium. The present invention proposes, where practicable, binding these oxide impurities as impurities within the silicate mineral phases. This is achieved by appropriate variation in the amounts of CaO, MgO, Al_2O_3 and SiO_2 present in the slag.

For example, if divalent manganese oxide (MnO) is present, it may be bound with CaO and SiO_2 to form the silicate mineral species $CaO.MnO.2SiO_2$. This will manifest itself as an elemental impurity within the $CaO.MgO.2SiO_2$ phase. Accordingly, the number of moles of MgO required in the slag may be reduced by the number of moles of MnO present. Similarly, if chromium is present as trivalent chromium oxide (Cr_2O_3) then it readily substitutes for Al_2O_3 and may be accomodated by equating the number of moles of Cr_2O_3 as the same number of moles of Al_2O_3 and cause the trivalent chromium oxide to manifest itself as an impurity within the respective silicate mineral phase.

It may be further required to create other silicate mineral species to bind with particular metal oxides present, in order to preferentially retain these oxides within the silicate mineral phase, and thus prevent them becoming impurities within the TiO_2 crystals.

The preferred percentage proportions of CaO, MgO, Al_2O_3, and SiO_2 in the molten slag in which crystallisation of titanium oxide is evidenced is shown in Figure 1. It will be appreciated that the preferred percentage proportions of CaO, MgO, Al_2O_3, and SiO_2 in the composition diagram of Figure 1 is equivalent to 100%. In other words the minimum concentration of TiO_2 in the molten slag is understood to be in addition to the CaO, MgO, Al_2O_3, and SiO_2 components in the molten slag. It will be understood that location of the composition boundary shown within the composition diagram of Figure 1 is approximate. Additionally, it will be appreciated that the location of the boundary in the composition diagram of Figure 1 may vary to accommodate the types and quantity of impurity oxides present in the molten slag.

The titanium oxides-bearing materials that may be used in the process of the present invention include, but are not limited to non-ferrous ores of titanium such as rutile (naturally occurring or synthetic), anatase, brookite, perovskite, titanate (also known as sphene) or geikielite. Rutile, anatase and brookite are polymorphs of TiO_2. The process of the present invention can also be used in relation to titanium ores containing iron oxides including, but not limited to, leucoxene, ilmenite (conventional or altered), ülvospinel, titanomaghemite, titanomagnetite, and vanadiferous titanomagnetite provided that the titanium ores containing iron oxides undergo standard reduction and melting or smelting processes, and which may include subjecting the titanium ores containing iron oxides to an oxidising roast. At the conclusion of this process pig iron is tapped from a smelting furnace and processed according to known techniques. Molten slag is also tapped from the smelting furnace, and it is this tapped molten slag which is subject to treatment according to the present invention.

The suitability of any titanium oxides-bearing material must be assessed on general criteria as described in more detail as follows. The titanium oxides-bearing material is typically comprised of TiO_2, iron oxides (but not always), and other oxides. The other oxides are typically but not exclusively CaO, MgO, Al_2O_3 and SiO_2. Three examples of TiO_2 source materials that do not specifically contain iron are the minerals perovskite [$CaTiO_3$], geikielite [$MgTiO_3$], and Titanate (also known as Sphene) [$CaTiSiO_5$].

Perovskite and titanate (sphene) cannot be used solely as the addition of requisite fluxes would dilute their TiO_2 content to less than that required to adequately form crystalline TiO_2 on slow cooling solidification. However, they may be used as combined sources of TiO_2 and flux with other materials.

Thus, in all titanium oxides-bearing material it is necessary that following any beneficiation the ratio of TiO_2 content be sufficiently high relative to the combined CaO, MgO, Al_2O_3 and SiO_2 contents present naturally or as gangue in the source material and present as ash in the carbonaceous reductant so that the molten slag subsequently created together with any requisite fluxing additions of CaO, MgO, Al_2O_3 and SiO_2 has sufficiently high TiO_2 content. If a TiO_2 source material contains various other metal oxides then these may also have to be allowed for. For example, if the molten slag is predominantly comprised of TiO_2, CaO, Al_2O_3 and SiO_2 then any Cr_2O_3 content may be treated as equivalent to Al_2O_3.

For example, a titanium oxides-bearing material that is by itself unsuitable for this process is the Waikato North Heads vanadiferous titanomagnetite ironsand concentrate currently utilised for ironmaking at New Zealand Steel. Alternatively, if the ratio of TiO_2 were to be raised sufficiently by blending with requisite quantities of one or more high grade sources of TiO_2, such as Ilmenite, Leucoxene or Rutile, then it will be suited for the process of the present invention. Alternatively, the fine concentrate that would be produced by conventional beneficiation of the hard rock vanadiferous titanomagnetite present at Balla Balla in Western Australia would be suitable as the titanium oxides-bearing material for the process of the present invention.

Accordingly, two or more TOBMs may be blended and used in the process of the present invention. Blending of the CaO, MgO, Al_2O_3 and SiO_2 contained in the TOBMs can advantageously minimise the addition of the fluxing agents.

To promote crystallisation of TiO_2 the molten slag is cooled at a slow rate between the liquidus and the solidus of the molten slag. When the molten slag has solidified, the crystalline TiO_2 can then be extracted from the solidified slag by various separation techniques.

Typically, the TiO_2 rutile crystals will first be liberated from the solidified slag by breaking up, crushing and grinding the solidified slag to a particle size suitable to commence separation techniques. Typically the largest particle size at which separation of the rutile crystals from the silicate mineral phases of the solidified slag can commence is approximately 1mm, because usually the bulk of rutile crystals formed are less than 1mm in size. Breaking, crushing and grinding are performed by conventional means.

By way of example, breaking up of the solidified body of slag can be performed with a pneumatic or hydraulic powered breaking tool to produce lumps of slag less than 1000mm in size. These lumps are then crushed in a jaw crusher to less than 150mm in size. These subsequent lumps are then crushed in a cone crusher to less than 32mm in size, then ground using high-pressure grinding rolls (HPGR) to less than 1mm in size.

HPGR has the beneficial characteristic of breaking materials along grain boundaries between phases. If the phases are similar in hardness then similar size particles of the different phases will be produced. If the phases have different hardnesses then the harder the phase the larger the relative particle size will be.

Separation of the rutile crystals from the silicate phase minerals in the ground slag will be performed by conventional mineral particle separation methods, and usually augmented with finer grinding at intermediate stages to further liberate the rutile crystals.

Mineral particle separation methods typically work by exploiting the physical properties as shown in Table 2 (size, density, electrical conductivity, magnetic susceptibility, etc.) of the minerals that are being separated.

Table 2. Physical properties of primary and secondary mineral phases formed in the slag.

Mineral	**Hardness**	**Magnetic susceptibility**	**Density**	**Electrical conductivity**
TiO_2	6 – 6.5	Low	4.2+	High
$CaAl_2Si_2O_8$	6 – 6.5	Low	2.76	Low
$CaMgSi_2O_6$	5 – 6	Low	3.3	Low
$Mg_2Si_2O_6$	7 – 7.5	Low	2.3	Low
$Mg_2Al_4Si_5O_{18}$	5 - 6	Low	3.2+	Low

Because all the mineral phases have low magnetic susceptibility then magnetic separation is not viable, except as a precautionary measure to remove any tramp metallic iron prills that may be present in the crushed slag.

Given the expected similar particle sizes and significantly higher density of rutile then gravity separation methods can be used to separate the denser rutile particles from the less dense silicate mineral phase particles. Gravity separation methods that could be employed include wet separation methods such as cones, spirals and shaking tables and dry separation methods such as air tables.

Because the electrical conductivity of rutile is high and that of all the silicate mineral phases formed in the slag is low then high tension (electrostatic) separation methods can also be employed.

In the case where one or more of the silicate mineral phases in the solidified slag is acid soluble then acid can be used to remove these phases, usually in a final liberation step. By way of example the silicate mineral phase $CaAl_2Si_2O_8$ is known to be soluble in hydrochloric acid. Thus, where minor quantities of $CaAl_2Si_2O_8$ remain attached to the rutile crystals, either on the surface or within exposed cavities in the bodies of the rutile crystals, then hydrochloric acid can be used to dissolve the residual $CaAl_2Si_2O_8$.

Thus a suitable combination of breaking, crushing and grinding liberation methods, and gravity and electrostatic separation methods, and in some cases acid treatment for a final clean-up, will be effective in accomplishing liberation and separation of the rutile crystals.

The liberation and separation processes as described above will produce a substantial proportion of particles that will be part rutile and part silicate mineral phase. While successively finer grinding will eventually liberate the rutile from the silicate mineral phases it will usually be more effective to recycle some or all of this proportion back into the smelting step. Without recycling, this proportion will become tailings and the rutile content will be lost when the tailings portion is disposed of.

It will be understood that there is a natural limitation to the portion that can be recycled in that the total mass of materials leaving the process (rutile, tailings, process gases, yield losses, etc) must balance with the total mass of materials entering the process (TOBM, carbonaceous reductant, the fluxing agents, etc).

The crystals of mineral rutile formed by the process of the present invention are of relatively high purity although they typically comprise less than 100% TiO_2. Laboratory scale trials of the process of the present invention have produced rutile crystals with TiO_2 content in excess of 99.0% and as high as 99.8%.

Size and conformation of the crystals of rutile vary with the TiO_2 content and the relative proportions of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag. Laboratory-scale tests have produced rutile crystals as large as 1000μm in length and smaller than 10μm in length.

Similarly, rutile crystal conformation has been observed to vary from cubic to dendritic to approximately filamentous, as shown in Figures 2 and 3. The molar ratios of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag that result in an optimum rutile crystal conformation (cubic) are not necessarily the same as the molar ratios of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag that maximise the rutile crystal size and in turn are not necessarily the same as the ratios that maximise TiO_2 recovery as crystalline rutile. Up to a point, higher TiO_2 content in the molten slag promotes the formation of larger rutile crystals.

The rate of cooling of the molten slag also affects the rutile crystal size. Cooling at a rate of approximately 2 degrees centigrade or less during solidification is advantageous but not mandatory. Quench cooling where solidification takes place in a few seconds or less will prevent the formation of crystals of rutile. Cooling at a rate well in excess of 2 degrees centigrade per minute, for example 5 degrees centigrade per minute, does not necessarily prevent formation of crystals of rutile but the faster rate of cooling will typically result in rutile crystals that are substantially smaller in size than would otherwise be obtained by slower cooling. This is typical of diffusion rate control, where the rate of diffusion of TiO_2 in the molten slag towards solidifying crystals in conjunction with the cooling rate influences the size and number of rutile crystals that are formed. Diffusion rate will vary also with the relative proportions of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag.

While the formation of fewer and larger rutile crystals is desired and thermodynamically preferred, fewer and larger rutile crystals can only form if the rate of diffusion of TiO_2 in the liquid slag surrounding the rutile crystals initially formed during the slow cooling period exceeds the rate of rutile crystal formation dictated by the rate at which the solidifying slag is cooling. If the cooling rate of the solidifying slag is too high then the liquid slag surrounding existing rutile crystals will become supersaturated in respect of its TiO_2 content and new rutile crystals will begin to form so as to restore the concentration of TiO_2 in the surrounding liquid slag to its equilibrium concentration. Thus the slower the cooling rate the greater the potential for existing rutile crystals to grow bigger without new rutile crystals forming.

Slow cooling need only proceed during solidification. Slow cooling the molten slag at temperatures substantially above the liquidus and below the solidus temperature does not have any effect.

Slow cooling of the molten slag may be effected by natural means or by controlled means, provided that the cooling rate is slow enough so as to promote the formation of rutile crystals. Slow cooling practice may employ any technique that may be advantageous to improving rutile crystal morphology and/or size, including but not limited to direction solidification by means of directional cooling.

It will be appreciated that the optimum rate at which the solidifying slag is cooled will be sensitive to the temperature difference between the liquidus and the solidus. In relation to a slag composition where a large difference between the liquidus and solidus exists, a faster cooling rate may be acceptable and yield TiO_2 crystals, whereas in cases where a small difference between the liquidus and solidus exists, a very slow cooling rate may be required to afford crystalline TiO_2.

The formation of crystals of mineral rutile during slow cooling solidification is not substantially affected by the presence of other oxides so long as they are present at sufficiently low concentrations. By way of example, the presence of a minor amount of Fe_2O_3 has little or no effect on the formation of crystals of rutile because at low concentrations Fe_2O_3 will be analogous to Al_2O_3 and can be incorporated as if it were Al_2O_3 into the Al_2O_3-bearing mineral species that form subsequent to the formation of rutile crystals. This substitutional behaviour is the method by which most if not all of the other common and sometimes uncommon minor quantities of accessory oxides that are attendant in the raw titanium oxides-bearing materials, reductant and fluxes are accommodated.

The efficiency of recovery of the rutile crystals from the solidified slag is highly dependant on crystal size and conformation. One method of promoting fewer and larger crystals of rutile to form is to seed the liquid slag with rutile crystals and cool it at sufficiently slow rate so that only the seed crystals grow.

If the slag is at its liquidus temperature then the TiO_2 is at its saturation level. Decreasing the slag temperature will cause the slag to become supersaturated in TiO_2 and rutile crystals will begin to precipitate. Increasing the slag temperature will cause the slag to become under-saturated in TiO_2. Any rutile seed crystals that are added to an under-saturated molten slag will be at least partially dissolved up to the point that the new TiO_2 equilibrium saturation level is achieved. Only if the quantity of rutile crystals added to an under-saturated slag is in excess of that required to saturate it in TiO_2 will seeding be achieved. Accordingly, multiple methods of achieving seeding can be chosen.

Firstly, the TiO_2 content of the molten slag in the furnace can be controlled such that at the operating temperature the slag is both saturated in TiO_2 and crystals of rutile will pre-exist in the slag before commencement of cooling.

Secondly, a molten slag that is close to saturation can be produced and just prior to commencement of the slow cooling step it is possible to stir in some rutile crystals that where previously extracted, ensuring that sufficient seed crystals are added to the molten slag allow for any portion thereof that will be dissolved in saturating the molten slag with TiO_2.

Thirdly, the slag can be allowed to cool, or be deliberately cooled, to just above its liquidus temperature and some rutile crystals could be stirred in.

There are advantages and disadvantages to all methods. The advantage of the first method is that it maximises the TiO_2 productivity, but the disadvantage is that the denser rutile crystals may stratify in the slag. The disadvantage of the second method is that it is usually very difficult to control smelting processes to achieve a slag temperature in conjunction with a high TiO_2 content. The disadvantage of the third method is that the TiO_2 productivity of the furnace will be lower and slag temperature will have to be monitored. The advantages of the second and third methods will be that the rutile crystals that are added to the molten slag prior to the slow cooling step will be of a controllable size, number, quantity, etc.

The process of the present invention will now be further illustrated by means of the following Examples.

Example 1

Four slags, designated A, B, C and D, were prepared by mixing the prescribed proportions of pre-dried Reagent Grade Al_2O_3, $CaCO_3$, MgO, TiO_2 and SiO_2 in accordance with Table 3

Table 3. Composition of slags A to D.

	Slag A	**Slag B**	**Slag C**	**Slag D**
Component	**Mass %**	**Mass %**	**Mass %**	**Mass %**
Al_2O_3	9.49			
CaO	12.0	18.3	15.4	12.2
MgO	8.51	13.8	11.5	9.15
TiO_2	26.3	24.9	37.4	49.7
SiO_2	43.1	42.3	35.3	28.0
CaO/SiO_2	0.28	0.43	0.44	0.44
MgO/SiO_2	0.20	0.33	0.33	0.33

These mixtures were then individually pre-melted in platinum crucibles at 1550°C using a muffle furnace. During the pre-melting, the samples were held at 1550°C for 1 hour and then rapidly quenched on an inclined steel plate. The recovered quenched slags were then crushed and pulverised in a WC ring mill.

About 1 gram of each pre-melted slag was weighed and placed into a small platinum crucible. The crucibles were then placed on a ceramic pedestal with an embedded Pt/Pt-13% Rh (R-Type) thermocouple to monitor the sample temperature. The pedestal was placed into a $MoSi_2$ resistance heated vertical tube furnace at room temperature and the furnace was then sealed with gas tight water-cooled end caps. High purity Ar (99.997%) was then introduced into the furnace tube at a flow rate of 0.5 l/min to flush and maintain an inert atmosphere inside the furnace. The samples were then heated at 3°C/min to 1550°C. After being held at 1550°C for 3 hours, the samples were cooled to 800°C at 2°C/min and the to room temperature at 3°C/min.

The solidified samples were then removed from the furnace and the crucibles cut away from the samples. Large crystals were observed on the surface of samples A, C and D and the resultant samples were quite porous and crumbly. Sample B had no visible crystals on the surface.

A small piece of each slag sample was mounted and polished for optical/scanning electron microscopy (SEM) analysis. The SEM images of the polished sections of the four samples at low magnification are shown in Figure 2. The presence of light crystalline phase(s) is apparent in slags A, C and D. It is also apparent that the crystals in slag D are considerably larger than those for slags A and C.

Each sample was also examined by SEM-EDS at higher magnification, for identification of phases present and their chemical composition. Figure 3 shows the micrograph for slag A with the composition of phases listed in Table 4. According to SEM-EDS measurements, the bright angular phase is rutile (TiO_2) and the matrix is a silicate phase containing low concentration of TiO_2.

Table 4. Composition of phases marked by points 1 and 2 in Figure 3.

Element	**Point 1**		**Point 2**	
	Mass %	**Atom %**	**Mass %**	**Atom %**
O	38.16	**64.81**	45.13	**61.13**
Mg	0	**0**	6.23	**5.55**
Al	0.12	**0.12**	6.41	**5.15**
Si	0.12	**0.12**	25.51	**19.69**
Ca	0.24	**0.16**	10.66	**5.76**
Ti	61.41	**34.84**	5.66	**2.56**

Example 2

Several slags were prepared by mixing the prescribed proportions of pre-dried Reagent Grade Al_2O_3, $CaCO_3$, MgO, TiO_2 and SiO_2 in accordance with Table 5

Table 5. Composition of slag samples (in mass %) used for melting and cooling tests.

Sample	**A1**	**A2**	**B**	**C**	**D**	**E**	**F**	**G**
CaO	13.0	13.0	16.4	16.4	16.8	16.8	11.2	11.2
MgO	9.1	9.1						
SiO_2	27.8	27.8	40.7	40.7	17.4	17.4	23.3	23.3
Al_2O_3			10.0	10.0	9.9	9.9	19.8	19.8
TiO_2	49.8	33.2	31.9	21.2	55.5	36.9	45.5	31.0
Ti_2O_3		16.7		10.8		18.6		14.5
CaO/ SiO_2	0.47	0.47	0.40	0.40	0.97	0.97	0.48	0.48

These mixtures were then individually pre-melted in platinum crucibles at 1600°C using a muffle furnace. During the pre-melting, the samples were held at 1600°C for 1 hour and then rapidly quenched on an inclined steel plate. The recovered quenched slags were then crushed and pulverised in a WC ring mill.

About 1.5 gram of the pre-melted slags were weighed and placed into small platinum crucibles. The crucibles were then placed on a ceramic pedestal with an embedded Pt/Pt-13% Rh (R-Type) thermocouple to monitor the sample temperature. The pedestal was placed into a $MoSi_2$ resistance heated vertical tube furnace at room temperature and the furnace was then sealed with gas tight water-cooled end caps. High purity Ar (99.997%) was then introduced into the furnace tube at a flow rate of 0.5 l/min for 30 minutes to flush the tube, then the flow was reduced to 0.1 l/min. The samples were then heated at 3°C/min to 1600°C. After being held at 1600°C for 3 hours, the samples were cooled to 800°C at 2°C/min and the to room temperature at 3°C/min.

The solidified samples were then removed from the furnace and the crucibles cut away from the samples. Large crystals were observed on the surface of samples B, D, E and F.

A small piece of each slag sample was mounted and polished for optical/SEM analysis and the remaining portion of the slag sample was pulverised using an agate mortar and pestle and submitted for X-Ray Diffraction (XRD). Powdered samples of the slags were measured on a Philips X'Pert Diffractometer using Copper Kα radiation with a 1° divergence slit on the incident beam and a 0.3 mm receiving slit, a 1° anti-scatter slit and a graphite monochromator on the diffracted beam. Data collected from 5 to 70° 2θ using a step size of 0.02° 2θ at 0.4 seconds per step. The data was analysed using XPLOT for Windows, Version 1.34 and the database of the International Centre for Diffraction Data, ICDD PDF-4/FullFile 2003, Version 3.00. The phases identified by the XRD for each of the samples are listed in Table 6. It is apparent that all solidified samples contained rutile and other silicate mineral phases depending on the chemical composition of the slag samples. The SEM images of the polished samples at low magnification are shown in Figure 4.

Table 6. Phases identified by XRD analysis of slow cooled slags.

Slag	**Rutile** **[TiO_2]**	**Perovskite** **[$CaTiO_3$]**	**Diopside*** **[$CaMgSi_2O_6$]**	**Titanite** **[$CaTiSiO_5$]**	**Dmistein-bergite**** **[$CaAl_2Si_2O_8$]**	**Quartz** **[SiO_2]**	**Glassy phase**
A1	Major		Medium			Trace	
A2	Major		Minor			Trace	
B	Major			Pos.Trace			Present
C	Major						Present
D	Major	Major			Trace		Present
E	Major	Major			Trace	Pos.Trace	Present
F	Major	Pos. Trace			Major	Trace	
G	Major	Pos. Trace			Major	Trace	

*A clinopyroxene phase is present in samples A1 and A2. It closely resembles the XRD pattern of the clinopyrxene subgroup phase, augite, although according to the SEM-EDS analysis the elemental composition of this phase does not contain iron.

**Dmisteinbergite is a Feldspar group mineral that is polymorphous with anorthite, although its XRD pattern is distinct from that of anorthite.

In example 1 slags D, C and B had successively less TiO_2 content. The rutile crystals in slag C are smaller than in slag D and no rutile crystals are detectable in slag B. This is an example of a minimum TiO_2 content being required to form rutile crystals.

Slag A has the same TiO_2 content as slag B, but because the proportions of CaO, MgO, Al_2O_3 and SiO_2 have been altered rutile crystals were able to form.

As hereinbefore mentioned it is particularly envisaged that the process of the present invention will be used in conjunction with a reductive smelting process performed on ferrous ores of titanium, wherein a titanium oxides-bearing slag is produced as a byproduct in the formation of pig iron. A description of this particular embodiment of the present invention will now be provided with reference to the flow chart of Figure 5.

There is shown in Figure 5 a flow chart detailing the treatment of ferrous ores of titanium according to an alternative embodiment of the present invention. The ores that may be treated by this process come from a group comprising titanium and iron oxides, including titanomagnetite, titanomaghemite, ülvospinel, ilmenite, leucoxene, and vanadiferous titanomagnetite. A similar process may be employed with partially processed materials having an iron oxide content, such as titanium slags and beneficiated ilmenites.

Typically, these ores first undergo a standard reduction melting or smelting process to produce pig iron and a molten slag. The process of the present invention is thus performed in relation to the molten slag so formed.

Referring to Figure 5, the TOBM feedstock is sampled, analysed and characterised by well-known techniques. Importantly, the relative concentrations of CaO, MgO, Al_2O_3 and SiO_2 in the gangue of the TOBM are determined. The TOBM may additionally undergo beneficiation and/or concentration to increase the titanium oxides content of the TOBM.

Carbonaceous reductant is required to reduce any iron oxides contained in the TOBM to pig iron. The TOBM may also contain various other accessory metal oxides that will be partially reduced or wholly reduced to the metallic state including, but not limited to, V_2O_5 or MnO. The carbonaceous reductants typically comprise coal. The carbonaceous reductant is also sampled, analysed and characterised at the outset of the process to, amongst other things, determine the relative concentrations of CaO, MgO, Al_2O_3 and SiO_2 in the carbonaceous reductant. Accordingly, various coals or/and other carbonaceous reductants may be blended to achieve a desired composite molar ratios of Cao, MgO, Al_2O_3 and SiO_2.

Based upon the results of the chemical analyses conducted on the TOBM feedstock and the carbonaceous reductant, fluxing agents can be added to the feedstock at the outset of the process to adjust the molar ratios of CaO, MgO, Al_2O_3 and SiO_2 in the subsequent molten slag to appropriate values to afford a molten slag composition that favours formation of crystalline TiO_2 when the molten slag is slow cooled between the liquidus and the solidus of the molten slag, as described previously. Preferably the molar ratios of CaO, MgO, Al_2O_3 and SiO_2 will be adjusted in accordance with Figure 1.

The titanium oxide(s) bearing material(s) and carbonaceous reductant(s) and all or some or none of the fluxing agents and any binders are then blended together in a controlled manner.

If the blended materials are to be formed into green balls or briquettes then it is usual to add one or more binder materials to improve cohesion and strength. In the case of green balls binders might be added, and any CaO added as a fluxing agent, if present in a sufficient amount, will also act as a binder when the water is added.

Blending is achieved by conventional methods, either on a continuous basis or a batch basis or a combination of both. Thus not all of the above listed materials will necessarily be mixed together at the same time.

The requisite reductant requirement for the TOBMs is determined on a semi-empirical basis. Carbonaceous reductants are characterised by their fixed carbon content. The TOBMs will be characterised by their reducible oxide contents. For example in the case of an ilmenite the reducible oxide will be FeO and sometimes some accessory Fe_2O_3.

The requisite reductant requirement will also be dependent upon the type of equipment in which the oxide reduction is performed. By way of examples, if the blended mix is neither balled nor briquetted and the coal in the blended mix is devolatilised before oxide reduction is performed in a rotary kiln then a certain fixed carbon to reducible oxides ratio requirement, and thereby coal requirement, will be established. Alternatively, if the blended feed is briquetted, the coal is not devolatilised and oxide reduction is performed in a rotary hearth furnace then the fixed carbon requirement, and thereby coal requirement, will be lower than for the previous example.

By way of further example, if any requisite CaO flux requirement is furnished by way of $CaCO_3$ then extra thermal energy will be required to burn the $CaCO_3$ to CaO, thereby further increasing the coal requirement.

Ultimately then the coal or other reductant requirement can only be established on a case by case basis in accordance with the nature and composition of all the raw materials and the specific process route that is employed, bearing in mind that no one process route is uniquely advantageous as it too is usually tailored to suit the locally accessible raw materials.

The blended feedstock materials may themselves undergo sampling, analysis and determination of molar ratios of CaO, MgO, Al_2O_3 and SiO_2, these analytical results being used in conjunction with other relevant analyses to jointly determine the requisite additions of fluxing agents at later stages in the process.

Referring to Figure 5, in cases where the carbonaceous reductant is conventional lignite/brown coal (e.g. from the Latrobe Valley in Victoria, Australia), an additional subsequent treatment process (as described in Australian Patent No. 703821) in relation to the blended feedstock materials may be advantageously included in the system. Lignite has a very high moisture content, which is mainly inherent. A patented process has been developed to release this moisture, making it an ideal carbonaceous reductant for ferrous ores such as titanomagnetite and ilmenite. Thus, when using high inherent moisture content lignite/brown coal as the carbonaceous reductant, then after Blending/Mixing the feedstock materials, it is envisaged that they would undergo this patented process.

Alternatively, the lignite/brown coal could be pre-processed as part of the carbonaceous reductant preparation/beneficiation step described earlier.

After blending the feedstock materials, the mixture may undergo briquetting or balling depending on the means by which the iron oxide reduction is performed. When oxide reduction is to be performed in a rotary hearth furnace (RHF), balling or briquetting of the feedstock materials is typically required. As to which is employed, if either, will usually be determined by the operating requirements of the RHF or other iron oxide reduction means, as specified by the equipment supplier.

When oxide reduction is performed in a rotary kiln, balling or briquetting are not usually required.

Balling is carried out on one or more balling discs and requires the addition of water and usually but not always a binder. CaO fluxing agents can be used as a binder.

Briquetting is carried out in a briquetting machine and usually requires the addition of a binder and sometimes the addition of water.

The feedstock may then undergo a drying or pre-heating process step. When the moisture content of the feedstock is high, such as in green balls produced in balling, or in the case that high moisture content lignite/brown coal is used as the carbonaceous reductant, it may be advantageous or desirable to reduce the moisture content by drying before further processing.

Drying occurs in two stages because water is usually present as both free and inherent moisture. Free moisture can be driven off at temperatures below 100 degrees centigrade. Inherent moisture in coal must be driven off at temperatures in excess of 105 degrees centigrade. Water of hydration that might be present with other materials has to be driven off at the respective 'ignition temperatures', which are usually substantially higher and more likely to be performed during the subsequent oxide reduction step or/and smelting step.

Drying may be achieved by means of (but not limited to) a travelling grate, rotary kiln, rotary hearth, or a multiple hearth.

Drying could even be done in more than one step so that low grade waste heat is used to drive off free moisture at temperatures below 105 degrees centigrade. Inherent moisture in coal could then be driven of in a second dryer that is fired (using natural gas or combustible process by-product gas(es) such as volatiles that are driven off during devolatilisation) to raise the mixture temperature to above 105 degrees centigrade as required.

In the case of coal (or any other carbonaceous reductant) that has a high volatiles content it may be advantageous or desirable to heat the coal prior to oxide reduction to drive of a proportion of the volatiles. This may be achieved by means of, but not limited to, a travelling grate, rotary kiln, rotary hearth, or a multiple hearth. Because drying and devolatilisation may be achieved in the same type of plant then it is possible to simultaneously combine these two process steps.

The proportion of volatiles driven off is dependant on the temperature.

The volatiles driven off, and other combustible process gases that might be produced in the subsequent smelting step, etc., can be utilised in a number of ways including, being burnt to provide process heat for drying, preheating, etc, being burnt to raise steam for power cogeneration to supply power for the process and auxiliary equipment (eg. conveyors, crushers, electric furnace(s) if used, etc.).

It is generally advantageous to reduce the iron oxide(s) (wholly or partially) prior to the smelting step. When the iron oxide(s) are to be reduced prior to smelting reduction can be achieved by conventional processing in a travelling grate, rotary kiln, rotary hearth, or a multiple hearth.

One of the above iron oxide reduction means is usually employed because iron oxide reduction using carbonaceous reductant is an energy intensive process and if reduction is completed together with the melting of the slag and the resultant pig iron during the smelting step with an electric furnace then the electricity requirement is usually prohibitively costly. Thus, preferably most if not all of the oxide reduction is done by one of the above iron oxide reduction means where the process heat is provided by combusting some or all of the process gases, and sometimes some additional natural gas or pulverised coal. Thus the smelting step only requires enough energy input to complete any reduction and afford high enough temperatures to produce the molten slag and the liquid pig iron.

In the case of leucoxene or rutile feed materials, where there is little iron oxide material present in the feedstock, the capital cost of installing the previously described reduction equipment would be disadvantageous so the modest amount of reduction required would simply be done in the smelting step at a slightly higher operating cost.

The reduced feedstock material may then be sampled, analysed and characterised for determination of relative molar quantities of CaO, MgO, Al_2O_3, and SiO_2. Requisite amounts of fluxing agents can either be added to the reduced feedstock material before smelting commences or during smelting. Smelting may be batchwise or continuous..

At the conclusion of batch smelting, or at appropriate intervals during continuous smelting, pig iron is tapped from the smelting furnace and is processed according to known techniques. Molten slag is also tapped from the smelting furnace, and it is this slag which is subject to treatment according to the present invention.

It is envisaged that during tapping of the slag following smelting a sample of the molten slag will be taken. The sample of slag will be analysed by standard techniques to determine its composition. The actual composition of slag tapped will be compared with both the intended composition of slag prior to slow cooling solidification and the intended composition of slag tapped if that differs from the intended composition of slag prior to cooling.

Any difference in the actual and intended composition of the slag tapped will be used as the basis for adjusting the relative molar amounts of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag being smelted to substantially favour formation of silicate mineral species $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof subsequent to formation of crystalline TiO_2 when the molten slag is cooled, by adjusting the addition of fluxing agents to the smelting vessel.

Any difference in the actual and intended composition of slag prior to slow cooling solidification and the mass of slag will be used as the basis for determining the requisite mass additions of fluxing agents prior to slow cooling to substantially favour formation of silicate mineral species $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof subsequent to formation of crystalline TiO_2 when the molten slag is cooled.

As a result of the highly reducing nature of the smelting step a proportion of the TiO_2 in the molten slag is usually reduced to Ti_2O_3. Typically, the slag includes titanium oxides in a plurality of oxidation states, for instance TiO_2, Ti_3O_5, Ti_2O_3, TiO, Ti_3O_2, Ti_2O, and Ti_3O, following the reduction of the iron oxides to metallic iron. By way of example, in the case of New Zealand Steel slag, which typically contains 35% TiO_2 equivalent (and is insufficient to form Rutile crystals given the bulk slag composition), up to one third of the TiO_2 can be reduced to Ti_2O_3 during the smelting step.

When rutile crystal formation occurs during slow cooling solidification of the molten slag some or all of the Ti_2O_3 will behave as if it were chemically equivalent to Al_2O_3. Thus, the decrease in the proportion of TiO_2 in the slag may reduce the recovery of TiO_2 as crystalline rutile dependent on the molar ratio of CaO, MgO, Al_2O_3 and SiO_2.

Following removal of the slag from the smelting vessel it will therefore be advantageous to oxidise any Ti_2O_3 and other sub-oxidesto TiO_2. This will be achieved by bubbling gaseous oxygen through the molten slag. Bubbling air, as an alternate source of oxygen, through the molten slag will be disadvantageous as the nitrogen content of air will result in the formation of Titanium Oxy Nitride (TiON). Simultaneously, other partially reduced oxides present in the slag will be oxidised. By way of example any FeO will be oxidised to Fe_2O_3. By way of further example any VO or V_2O_3 will be oxidised to V_2O_5.

After oxidation any flux additions required to make final adjustments to achieve the intended proportions of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag can be made. There are three reasons to make flux additions at this point.

Firstly, to fine tune the molar ratios of CaO, etc. because the actual molten slag composition frequently differs from the intended molten slag composition.

Secondly, having analysed the molten slag, a determination of its impurity oxide contents e.g. Fe_2O_3, V_2O_5, Cr_2O_3, Mn_2O_3, etc can be made. While these will not necessarily associate with TiO_2 when forming rutile crystals, it is best to promote their incorporation in the silicate mineral phases, on a substitutional basis. So final determination of the intended proportions of CaO, MgO, Al_2O_3 and SiO_2 can be made following slag analysis prior to this step.

Thirdly, for example, some slag compositions have substantial SiO_2 content which makes the slag both acidic and more viscous. Thus, in cases where it is desirable to have high SiO_2 content and to achieve it SiO_2 additions have to be made then all or part of the addition could be delayed until this final adjustment step so that the smelting step will involve a less acidic and less viscous slag than would otherwise be the case.

The requisite additions will be determined on the basis of the mass of the slag and the difference between the analysed composition of the slag sample taken before oxidation and the intended slag composition.

Addition of fluxing agents at this step will be made using the oxide forms only (ie. no carbonates).

The present invention envisages that a portion of the crystalline titanium oxides which is extracted according to methods such as those described above may be recycled for seeding as previously described on the basis of mass of slag, composition and temperature.

The molten slag is now cooled in a controlled fashion, at a rate sufficiently slow to enable the formation of crystalline TiO_2.

During slow cooling, the slag solidifies into a primary crystalline titanium dioxide phase (rutile) and a secondary silicate phase substantially comprising silicate mineral species $CaAl_2Si_2O_8$ or $CaMgSi_2O_6$ or $Mg_2Si_2O_6$ or $Mg_2Al_4Si_5O_{18}$, or a mixture thereof, when the molten slag is cooled at a slow rate between the liquidus and the solidus of the molten slag, provided that the TiO_2 content of the molten slag composition is sufficiently high enough for crystalline TiO_2 to form.

Typically, the molten slag is allowed to slow cool at a rate of approximately 2°C per minute substantially between the liquidus and the solidus of the molten slag. Cooling at these rates results in the formation of crystalline titanium oxide.

Following the controlled cooling of the slag to a solid state, the crystalline rutile can be recovered by liberating and separating as described previously.

Modifications and variations as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.

CLAIMS

1. A process for extracting crystalline TiO_2 from a titanium oxides-bearing material comprising the steps of:

a) providing a molten slag of a mixture of titanium oxides-bearing material comprising Ti_xO_y, and fluxing agents comprising SiO_2 and metal oxides from a group including CaO, MgO and Al_2O_3, wherein the fluxing agents are present in the molten slag in an amount to adjust the molar ratio of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag to substantially favour formation of $CaAl_2Si_2O_8$, $CaMgSi_2O_6$, $Mg_2Si_2O_6$, $Mg_2Al_4Si_5O_{18}$, or a mixture thereof subsequent to formation of crystalline TiO_2 when the molten slag is cooled, the TiO_2 concentration in the molten slag being sufficient to afford crystalline TiO_2 when the molten slag is cooled;

b) cooling the molten slag at a slow rate between the liquidus and the solidus of the molten slag to promote crystallisation of TiO_2; and

c) separating the crystalline TiO_2 formed in step b) from the solidified slag.

2. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to claim 1, characterised in that a minimum TiO_2 concentration in the molten slag sufficient to afford crystalline TiO_2 when the molten slag is cooled is from about 25% to about 50%.

3. The process according to claim 2, characterised in that the minimum TiO_2 concentration in the molten slag sufficient to afford crystalline TiO_2 when the molten slag is cooled is about 35% wherein the silicate mineral phase is $CaMgSi_2O_6$.

4. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the rate of cooling of the molten slag between the liquidus and the solidus of the molten slag is up to about 5 degrees Centigrade per minute.

5. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to claim 4, characterised in that the rate of cooling of the molten slag between the liquidus and the solidus of the molten slag is up to about 2 degrees Centigrade per minute.

6. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the molten slag is seeded with crystalline TiO_2 before commencement of step b) by seeding the molten slag with crystalline TiO_2 or by producing the molten slag at step a) wherein the molten slag inherently contains crystalline TiO_2.

7. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the molten slag is oxidised before commencement of step b) to convert Ti_2O_3 and other sub-oxides of titanium to TiO_2.

8. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the fluxing agents are added to the titanium oxides-bearing material prior to formation of the molten slag and/or during formation of the molten slag and/or prior to commencement of step b).

9. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that carbonate salts of CaO and MgO can be added as fluxing agents.

10. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the crystalline TiO_2 formed in step b) is separated from the solidified slag by liberating the crystalline TiO_2 from the solidified slag by breaking, crushing and grinding the solidified slag followed by performing separation methods on the ground solidified slag including gravity separation methods, high tension electrostatic separation methods, or acid treatment separation methods.

11. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the molten slag is a byproduct of a reductive smelting process for iron oxide ores contained in the titanium oxides-bearing material.

12. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to any one of the preceding claims, characterised in that the titanium oxides-bearing material include, but are not limited to, non-ferrous ores of titanium such as rutile (naturally occurring or synthetic), anatase, brookite, perovskite, titanate (sphene) or geikielite, beneficiated ores, or titanium bearing slags; or titanium oxides-bearing materials containing iron oxides including, but not limited to, leucoxene, ilmenite (conventional or altered), ülvospinel, titanomaghemite, titanomagnetite, and vanadiferous titanomagnetite.

13. The process for extracting crystalline TiO_2 from a titanium oxides-bearing material according to claim 11, characterised in that the iron oxides contained in the titanium oxides-bearing material undergo standard reduction and/or a smelting process comprising subjecting the iron oxides contained in the titanium oxides-bearing material to reduction of iron oxides to metallic iron and subsequent melting to afford the molten slag and pig iron.

14. A process for extracting crystalline TiO_2 from a titanium oxides-bearing material comprising the steps of:

a) providing a molten slag of a mixture of titanium oxides-bearing material comprising Ti_xO_y, and fluxing agents comprising SiO_2 and metal oxides from a group including CaO, MgO and Al_2O_3, wherein the fluxing agents are present in the molten slag in an amount to adjust the molar ratio of CaO, MgO, Al_2O_3 and SiO_2 in the molten slag as provided in the polygonal prism of Figure 1 as defined by vertices A-N coordinates defined in Table 1 to favour formation of crystalline TiO_2 when the molten slag is cooled, the TiO_2 concentration in the molten slag being sufficient to afford crystalline TiO_2 when the molten slag is cooled;

b) cooling the molten slag at a slow rate between the liquidus and the solidus of the molten slag to promote crystallisation of TiO_2; and

c) separating the crystalline TiO_2 formed in step b) from the solidified slag.

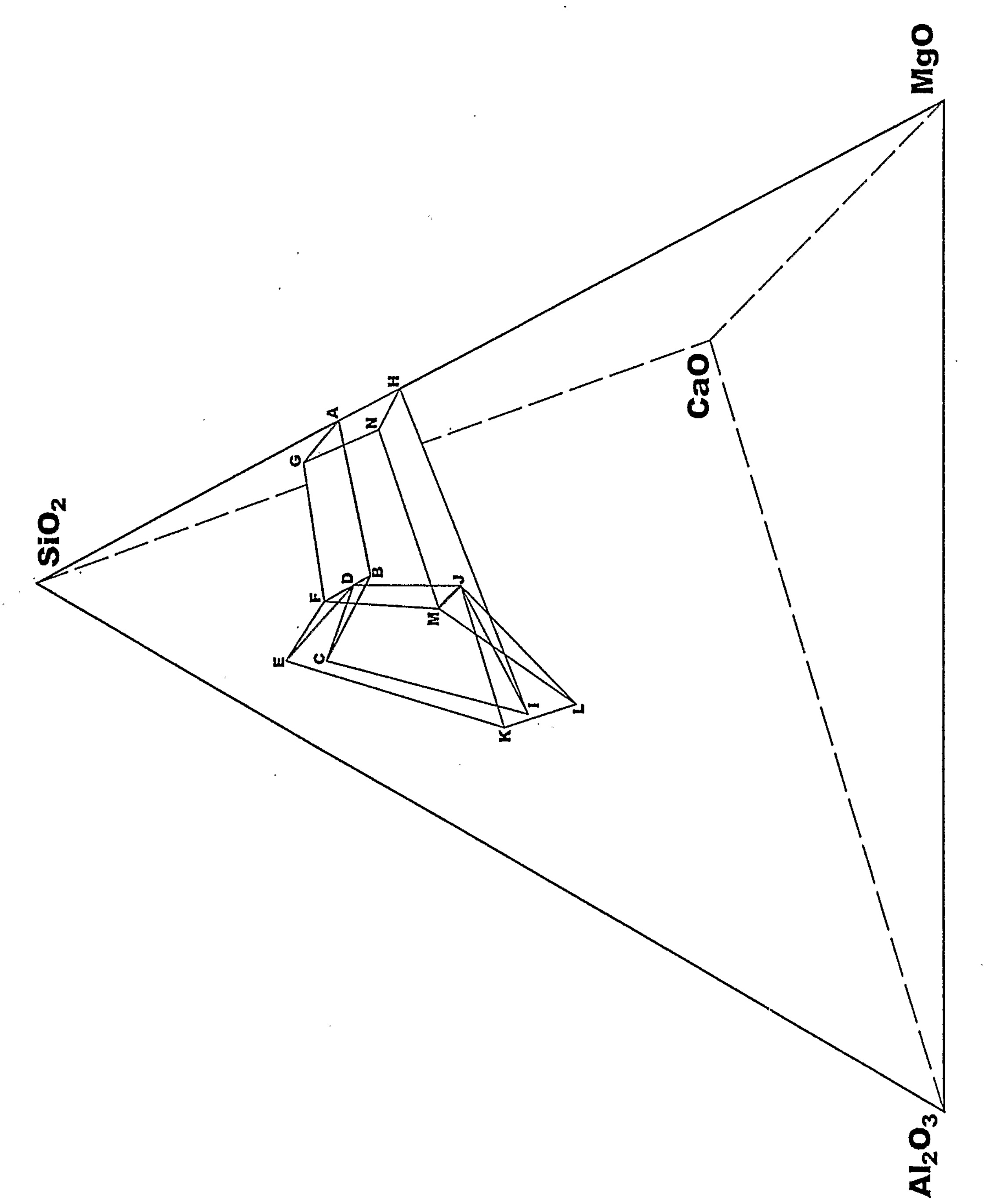


Figure 1

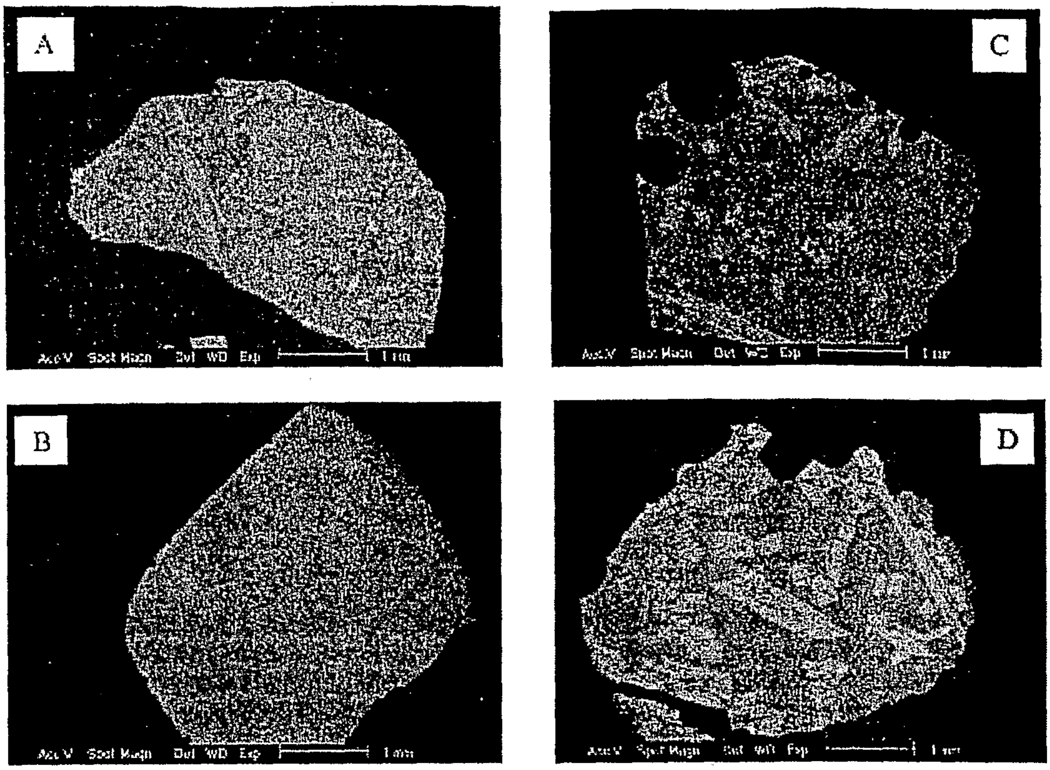


Figure 2. Scanning electron microscope (SEM) micrograph of slag samples A-D at low magnification.

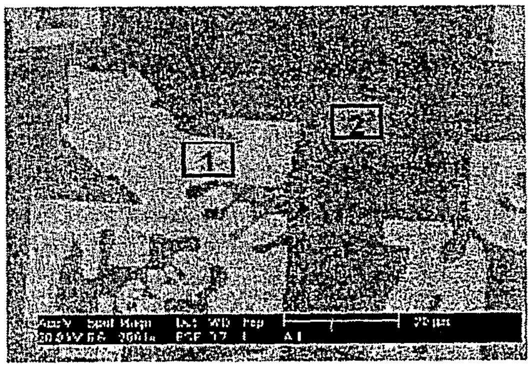


Figure 3. SEM micrograph of slag sample A shown at higher magnification.

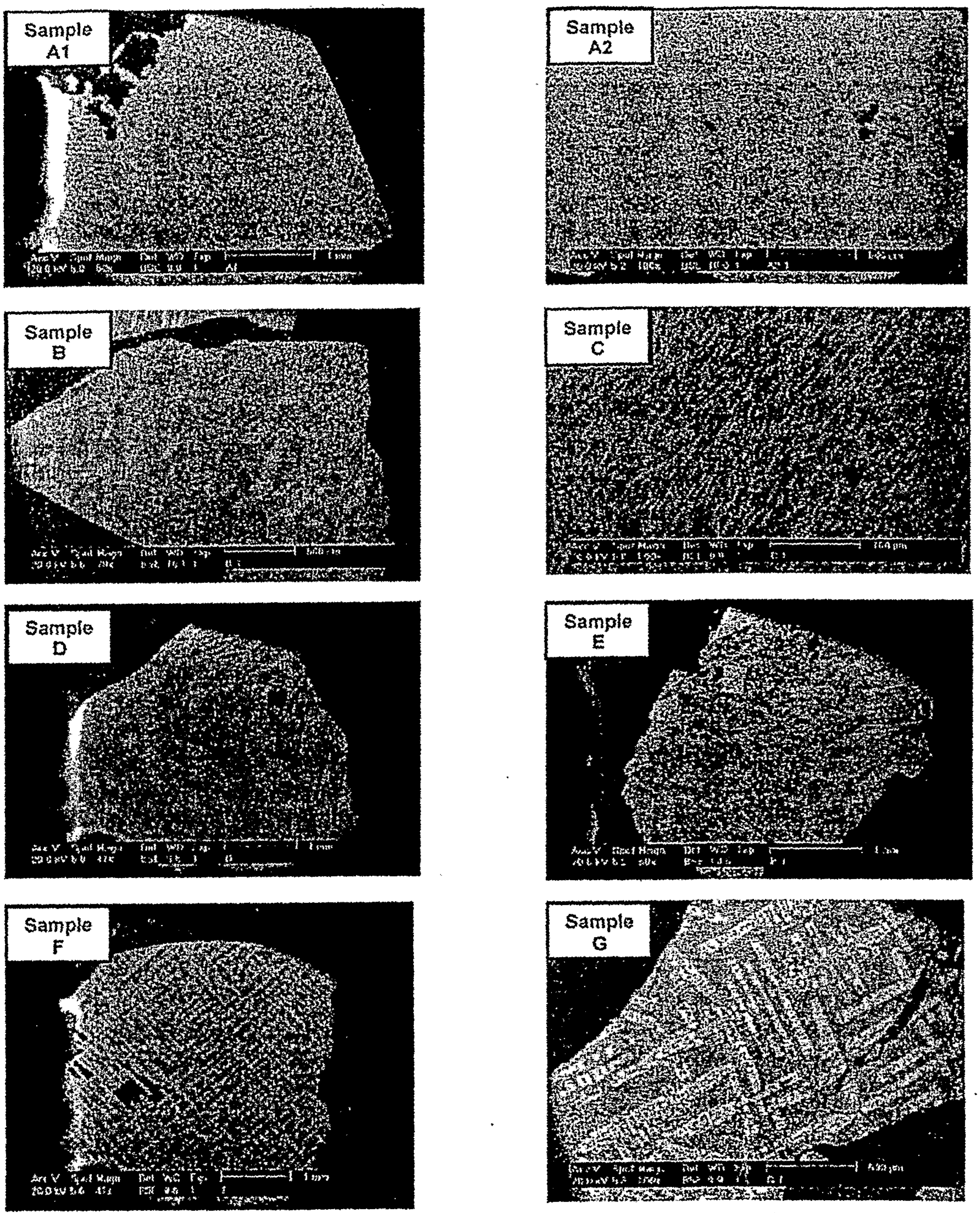
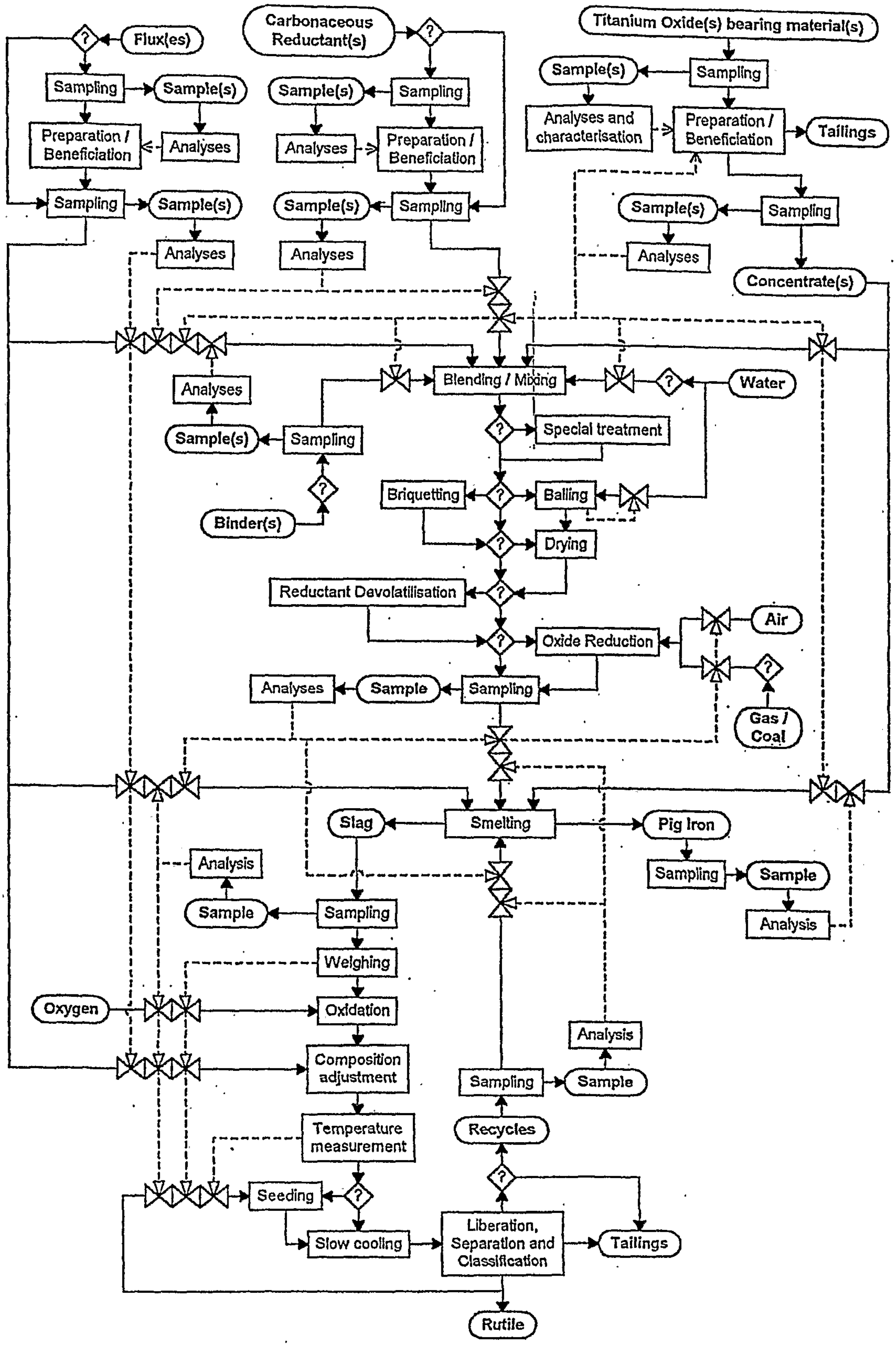


Figure 4. SEM micrograph of slag samples A1-G at low magnification.


Flux(es)
?
Sampling
Sample(s)
Preparation / Beneficiation
Analyses
Sampling
Sample(s)
Analyses
Carbonaceous Reductant(s)
?
Sample(s)
Sampling
Analyses
Preparation / Beneficiation
Sample(s)
Sampling
Analyses
Titanium Oxide(s) bearing material(s)
Sample(s)
Sampling
Analyses and characterisation
Preparation / Beneficiation
Tailings
Sample(s)
Sampling
Analyses
Concentrate(s)
Analyses
Blending / Mixing
?
Water
Sample(s)
Sampling
Special treatment
?
Binder(s)
Briquetting
?
Balling
?
Drying
Reductant Devolatilisation
?
?
Oxide Reduction
Air
?
Gas / Coal
Analyses
Sample
Sampling
Slag
Smelting
Pig Iron
Sampling
Sample
Analysis
Analysis
Sample
Sampling
Weighing
Oxygen
Oxidation
Composition adjustment
Temperature measurement
Seeding
?
Slow cooling
Liberation, Separation and Classification
Tailings
?
Recycles
Sampling
Sample
Analysis
Rutile

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001188

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ^{7}: C22B 34/12, 7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI: C22B 34/12, 7/04 and keywords (titan+, slag+, flux+, silic+, calc+ magnes+, alumin+, SiO2, CaO, MgO, Al2O3)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2815272 A (ARMANT et al) 3 December 1957 See whole document	1-14
A	US 4078039 A (GUEGUIN) 7 March 1978 See whole document	1-14
A	US 5910621 A (HARRIS et al) 8 June 1999 See whole document	1-14
A	Scandinavian Journal of Metallurgy 14 (1985) 33-43, Phase Relations and Oxygen Potentials in the FE-TI-MG-O System, Krzyszof Borowiec and Terkel Rosenqvist See whole document	1-14

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search
8 October 2004

Date of mailing of the international search report
12 OCT 2004

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/001188

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 1995/007366 (TECHNOLOGICAL RESOURSES PTY LTD) 16 March 1995 See whole document	1-14
A	EP 460319 A1 (QIT-FER ET TITANE INC) 11 December 1991 See whole document	1-14