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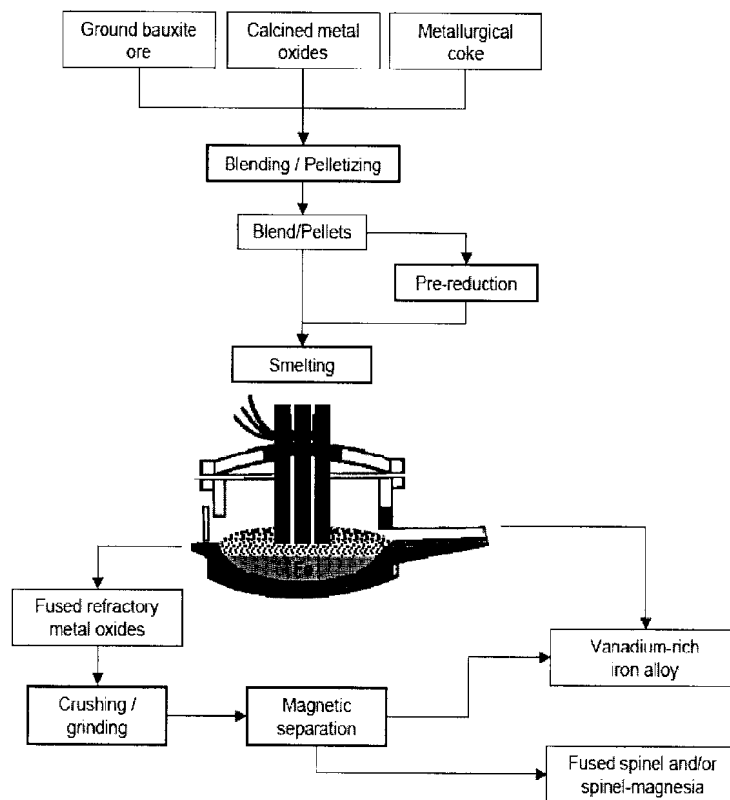
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(54) Titre : PROCÉDE DE REDUCTION PYROMETALLURGIQUE A HAUTE TEMPERATURE POUR LA RECUPERATION D'OXYDES DE METAUX REFRACTAIRES FONDUS ET LA PRODUCTION D'ALLIAGES DE FER RICHES EN VANADIUM A PARTIR DE RESIDUS MINIERS OU DE DECHETS METALLURGIQUES PRODUITS DURANT LA VALORISATION DE LAITIERS DE DIOXYDE DE TITANE

(54) Title: HIGH TEMPERATURE PYROMETALLURGICAL REDUCTION PROCESS FOR THE RECOVERY OF FUSED REFRACTORY METAL OXIDES AND THE PRODUCTION OF VANADIUM-RICH IRON ALLOYS FROM MINING RESIDUES OR METALLURGICAL WASTES BY PRODUCED DURING THE BENEFICIATION AND UPGRADING OF TITANIA SLAGS



(57) **Abrégé/Abstract:**

A process for producing vanadium-rich iron alloys and fused refractory metal oxides is described. The process comprises submitting mining residues or metallurgical wastes to a pyrometallurgical reductive treatment to produce a molten vanadium-rich



(57) **Abrégé(suite)/Abstract(continued):**

iron alloy and a fused refractory metal oxide; separating the molten vanadium-rich iron alloy from the fused refractory metal oxide; and recovering the molten vanadium-rich iron alloy and the fused refractory metal oxide.

ABSTRACT OF THE DISCLOSURE

A process for producing vanadium-rich iron alloys and fused refractory metal oxides is described. The process comprises submitting mining residues or metallurgical wastes to a pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide; separating the molten vanadium-rich iron alloy from the fused refractory metal oxide; and recovering the molten vanadium-rich iron alloy and the fused refractory metal oxide.

TITLE

HIGH TEMPERATURE PYROMETALLURGICAL REDUCTION PROCESS FOR THE RECOVERY OF FUSED REFRACTORY METAL OXIDES AND THE PRODUCTION OF VANADIUM-RICH IRON ALLOYS FROM MINING RESIDUES OR METALLURGICAL WASTES BY PRODUCED DURING THE BENEFICIATION AND UPGRADING OF TITANIA SLAGS

FIELD

[0001] The present disclosure relates to a high temperature pyrometallurgical reduction process for the recovery of fused refractory metal oxides and the production of vanadium-rich iron alloys. More specifically, but not exclusively, the present disclosure relates to a high temperature pyrometallurgical reduction process for the recovery of fused refractory metal oxides and the production of vanadium-rich iron alloys from mining residues or metallurgical wastes by-produced during the beneficiation and upgrading of titania slags.

BACKGROUND

[0002] **Titanium Feedstock for TiO₂ Pigment Production**

[0003] Titanium is the ninth most abundant element in the Earth's crust. Among the various titanium-based products, titanium dioxide (TiO₂) holds, with an annual world production approaching 6 millions tons, the greatest industrial and commercial significance. Titanium dioxide is a high-volume chemical commodity used as a white pigment in paints, plastics, papers, inks, *etc.*

[0004] Titanium because of its strong chemical reactivity with oxygen occurs naturally as an oxide, titanate and/or silicate. Titanium dioxide (TiO_2) occurs usually as rutile and in a lesser extent as anatase and brookite. Among the titanates, those comprising iron such as ilmenite [FeTiO_3], hemo-ilmenite [$\text{FeTiO}_3\text{-Fe}_2\text{O}_3$], or titanomagnetite [$(\text{Ti,Fe})\text{Fe}_2\text{O}_4$] are the most common.

[0005] Ilmenite is the most important source of titanium dioxide by tonnage, accounting for more than ninety percent of the TiO_2 supplied to the world market. Ilmenite is mined either as hard-rock ilmenite (30-46 wt.% TiO_2) or as weathered and altered ilmenites (46-62 wt.% TiO_2) in beach sands [1].

[0006] Ilmenites are commercially upgraded by an electrothermal smelting or slagging process performed at high temperature in an electric arc furnace (EAF) using anthracite coal as the reductant. This process yields a titaniferous slag, also called titanium slag or titania slag, along with pig iron as a co-product. Commercial titanium slags contain typically from 70-90 wt.% TiO_2 . Ilmenite ores are also upgraded to synthetic rutiles containing from 92-95 wt.% TiO_2 by processes comprising the reduction of iron oxides with sub-bituminous coal at moderately high temperatures in rotary kilns, followed by the removal of iron by leaching with strong mineral acids. Rutile, which exhibits a high TiO_2 content (93-96% TiO_2), is recovered along with zircon as a co-product during the beneficiation of ilmenite from beach sands.

[0007] The production of white titanium dioxide pigment is based on two major commercial processes. The traditional "*Sulphate Process*" involves digesting hard rock ilmenite or titanium slag in concentrated sulfuric acid; pure TiO_2 is obtained by selective hydrolysis of the titanium-bearing liquors. The modern "*Chloride Process*" [2] comprises fluidizing a mixture of titanium-rich feedstocks such as beach sand ilmenite, titanium slag, synthetic rutile or natural rutile with petroleum coke at high

temperatures ranging from 950°C to 1200°C in a stream of chlorine gas to produce a gaseous mixture of metal chlorides, including titanium tetrachloride (TiCl₄) and other metal chlorides originating from impurities present in the feedstock. The TiCl₄ is further separated and purified from the other metal chlorides by selective condensation, fractional distillation, or countercurrent extraction and subsequently converted to pure TiO₂ by contacting it with oxygen at high temperatures. The chlorine gas is recovered during the oxidation step and recycled back to the chlorinator.

[0008] One of the main technical requirements for the sulphate process is that the feedstock must be soluble in concentrated sulfuric acid. For the chloride process, the main technical requirements are a low content of alkaline-earth metal oxides and silica, as well as a particle size distribution compatible with the fluidization procedure.

[0009] Although the smelting of hard rock ilmenites yields a titanium slag suitable for the sulphate process, the smelting does not remove sufficient amounts of impurities, especially calcium and magnesium oxides, to render it suitable as a feedstock for the chloride process. A further upgrading of the titanium slag by a process including sizing, magnetic separation, oxidation, reduction, acid leaching and finally calcination is often required [3, 4]. Such a process has been commercialized under the trademark UGS™. The upgraded titanium slag produced becomes a high-grade feedstock suitable for the chloride process.

[0010] The UGS™ process also provides for the regeneration of hydrochloric acid, by pyrohydrolysis of the spent hydrochloric acid solution containing the dissolved metal chlorides. The regenerated hydrochloric acid is recycled back to the leaching step. The pyrohydrolysis step is typically conducted at temperatures of about

900°C, either in a fluidized bed or in a circulating bed reactor. A significant amount of calcined metal oxides are also produced which are currently disposed off and landfilled.

[0011] The calcined metal oxides are typically in the form of dense solid pellets having an essentially spherical shape and a particle size distribution (PSD) such as illustrated in **Table 1**. The average PSD comprises particles (about 65 wt.%) having a size ranging from about 425 μm to about 850 μm (20-35 mesh). Their apparent density, as determined by a helium pycnometer, is 4,000 kg.m^{-3} and their bulk density 1,700 kg.m^{-3} . Each pellet is typically composed of concentric layers of metal oxides that form during the flash evaporation of the water and the subsequent hydrolysis of the metal chlorides.

[0012] **Table 1:** Particle size distribution of calcined metal oxides as produced by the UGSTM process.

Particle Size ($d/\mu\text{m}$)	Mass Fraction (wt. %)
-200	5
200-355	15
355-500	20
500-710	30
710-1000	25
+1000	5
$D_{p50} = 550 \mu\text{m}$	

[0013] Typical chemical compositions and composition ranges for calcined metal oxides as produced by the UGSTM process are illustrated in **Table 2**.

[0014] **Table 2:** Chemical compositions and composition ranges for calcined metal oxides as produced by the UGS™ process.

Metal Oxide or Element	Mass fraction Range (wt. %)	Typical Mass Fraction # 1 (wt. %)	Typical Mass Fraction # 2 (wt. %)
Fe ₂ O ₃	40.0 – 70.0	53.76	47.20
MgO	15.0 – 40.0	25.97	31.57
Al ₂ O ₃	5.0 – 20.0	12.84	13.55
V ₂ O ₅	0.1 – 3.0	1.83	1.86
CaO	0.1 – 3.0	1.35	1.99
Mn ₂ O ₃	0.1 – 3.0	1.17	1.45
Cr ₂ O ₃	0.1 – 2.0	0.78	0.84
Cl (chloride)	0.05 – 2.0	1.08	0.72
SiO ₂	0.1 – 2.0	0.88	0.13
TiO ₂	0.05 – 0.9	0.58	0.66
Na (chloride)	0.01 – 0.2	0.09	0.07
K (chloride)	0.01 – 0.3	0.17	0.14
Co ₂ O ₃	0.001 – 0.003	0.016	0.016
CuO	0.001 – 0.03	0.013	0.013
NiO	0.001 – 0.03	0.010	0.010

[0015] Because of the high iron, magnesium, and aluminum oxide content, the synthetic mineral phases identified in the calcined metal oxides belong mainly to the spinel group of chemical formula A^{II}B^{III}₂O₄ wherein A^{II} = Mg²⁺, Fe²⁺, Mn²⁺, Ni²⁺ and wherein B^{III} = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mn³⁺, Co³⁺. The most common phases are in order of importance: magnesioferrite or pleonaste (MgFe₂O₄), donathite (MgFeAlO₄), spinel *senso-stricto* (MgAl₂O₄), and hercynite (FeAl₂O₄). The remaining uncombined free magnesia is usually found as free periclase (MgO), also containing minute amounts of

calcia (CaO) that is not combined with silica as calcium silicate (CaSiO₃). The chloride residues are usually found as kalsiohalites (Na_{0.6}K_{0.4}Cl). Because of isomorphic substitutions, the spinel-type phase also comprises in its crystal lattice small amounts of V, Mn, Cr, Ni and Co, sometimes even forming a single phase such as coulsonite (FeV₂O₄) or chromite (FeCr₂O₄). As a general rule, the calcined metal oxides are strongly ferromagnetic and exhibit a brownish color.

[0016] Because of the particular chemistry of the calcined metal oxides, the valuable content that can be recovered therefrom is considerably more than the value of the iron metal content. The reduction of one tonne of calcined metal oxides “*as received*”, having the chemical composition as exemplified by “Mass Fraction #1” in **Table 2**, by means of either a high temperature pyrometallurgical process (*e.g.* smelting) using a conventional reductant (*e.g.* coal, coke, hydrogen, natural gas, smelter gas or synthetic gas), or by a metallothermic process using reactive metals as the reductant (*e.g.* magnesium, magnesium alloys, ferrosilicon, aluminum, aluminum alloys), yields 407.54 kilograms of a molten vanadium-rich iron alloy. The chemical composition of this vanadium-rich iron alloy was as follows: 92.26 wt.% Fe, 2.52 wt.% V, 2.00 wt.% Mn, 1.31 wt.% Cr, 1.01 wt.% Si, 0.85 wt.% Ti as well as 300 ppm Co and 200 ppm Ni.

[0017] Assuming a theoretical yield of 100%, there remains 407.40 kilograms of refractory metal oxides following the reduction having the following chemical composition: 64.67 wt.% magnesia (MgO), 31.97 wt.% alumina (Al₂O₃), and 3.36 wt.% calcia (CaO). If the alumina and magnesia are chemically combined as spinel (MgAl₂O₄), the refractory mass contains about 44.61 wt.% of spinel (*i.e.* 181.74 kg; incorporating most of the titania as an impurity), and about 55.39 wt.% of fused magnesia (MgO) (*i.e.* 225.66 kg; including most of the calcia).

[0018] Based on the market price for pig iron (900 US\$/tonne), vanadium (80 US\$/kg), chromium (11 US\$/kg), and manganese (4.5 US\$/kg) [*Metal Bulletin Monthly*, June 9, 2008, Number 9050], the price of the vanadium-rich iron alloy is evaluated at \$3,080 US\$/tonne (*i.e.* 1,255 US\$/tonne of calcined oxides “*as received*”). Based on the price of fused spinel (500 US\$/tonne) and electrofused magnesia (600 US\$/tonne) [*Industrial Minerals*, January 2008], the refractory metal oxide recovered can be evaluated at about \$226 US\$/tonne of calcined metal oxides “*as received*” or 555 US\$/tonne of fused refractory metal oxides.

[0019] Because of their elevated content in vanadium, manganese and chromium, the vanadium-rich iron alloys are suitable as master alloys in the steel industry for the manufacture of high-strength low alloy steels (HSLA) and tool steels as well as powders in various powder metallurgical processes.

[0020] Because of the high temperatures involved during the pyrometallurgical reduction process, both periclase and spinel are produced in the molten state and, once cooled, yield an intimate mixture of fused and purer refractory products. Most of the silica, typically found as an impurity, is either lost as volatile silicon monoxide (SiO) during partial reduction or is totally reduced into elemental silicon which, along with titanium metal, enters the liquid iron alloy.

[0021] Another important and unique characteristic that pertains to both the calcined metal oxides “*as received*” and the refractory metal oxides produced following thermal reduction, is their high refractoriness. Regarding the calcined metal oxides “*as received*”, all the phases exhibit a high melting point: periclase (*m.p.* 2,820°C), magnesioferrite (*m.p.* 1,800°C), hercynite (*m.p.* 1,780°C), and chromite (*m.p.* 2,075°C). This refractory behavior distinguishes them from any type of iron ore commercially available and from most of the vanadium-rich slags (*e.g.* BF-slag, LD-slag, and EAF-

slag) by-produced during the pre-treatment of vanadium-rich hot metal. This refractoriness precludes the use of conventional smelting processes that require the addition of a fluxing agent (*e.g.* quartzite, silica sand, lime, and limestone) to allow the formation of a molten silicate slag having a low solidus temperature, and that separates easily from the liquid iron metal. Following thermal reduction, the remaining non-reduced metal oxides are more refractory because they are essentially composed of 50-70 wt.% magnesia or periclase (*m.p.* 2,820°C) and 30-50 wt.% spinel (*m.p.* 2,135°C). Hence, high temperatures are required during the pyrometallurgical reduction process to melt these refractory metal oxides. Suitable and practical temperatures typically range from about 1,500°C to about 3,500°C. Based on the MgO-Al₂O₃ phase diagram [5], it is possible to predict that a molten mixture comprising 70 wt.% magnesia and 30 wt.% alumina will yield, after cooling, an intimate mixture of crystallites consisting of periclase and spinel. This mixture can be used as a raw material in the manufacture of refractories and castables.

[0022] It is possible to modify the chemistry of the initial charge of calcined metal oxides “*as received*” to lower the temperature of the molten refractory metal oxide slag. This can be achieved by adding either ground bauxite ore or by adding metallurgical grade alumina. The addition of either ground bauxite ore, or metallurgical grade alumina provides the additional alumina required to yield a final refractory product composed of 100 wt.% fused spinel. In order to achieve a reduction in the temperature of the molten refractory metal oxide slag, a suitable alumina to magnesia mass ratio is required (*e.g.* Al₂O₃/MgO = 2.530).

[0023] There thus remains a need for a novel, simple and cost effective process providing for the recovery of valuables from mining residues and metallurgical wastes such as calcined metal oxides produced as by-products in the UGSTM process or similar processes for the beneficiation and upgrading of titanium slags.

[0024] The present description refers to a number of documents, the contents of which are herein incorporated by reference in their entirety.

SUMMARY

[0025] The present disclosure broadly relates to a novel process for the recovery of valuables from mining residues and metallurgical wastes. In an embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from mining residues and metallurgical wastes. In a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from mining residues or metallurgical wastes by-produced during the beneficiation an upgrading of titania slags from hard rock or beach sand ilmenites. In a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from calcined metal oxides. In a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from calcined metal oxides by-produced during the beneficiation an upgrading of titania slags from hard rock or beach sand ilmenites. In yet a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from calcined metal oxides produced as by-products in the UGSTM process or similar processes for the beneficiation and upgrading of titanium slags. In yet a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory metal oxides from mining residues or metallurgical wastes by-produced during the production of pig iron and steelmaking. In yet a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for

producing vanadium-rich iron alloys and fused refractory metal oxides from calcined metal oxides by-produced during the pyrohydrolysis or spray roasting of spent pickling acids.

[0026] In an embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory ceramic materials from mining residues or metallurgical wastes. In a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory ceramic materials from mining residues or metallurgical wastes by-produced during the beneficiation and upgrading of titania slags from hard rock or beach sand ilmenites. In an embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory ceramic materials from calcined metal oxides. In an embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory ceramic materials from calcined metal oxides by-produced during the beneficiation and upgrading of titania slags from hard rock or beach sand ilmenites. In yet a further embodiment, the present disclosure relates to a high temperature pyrometallurgical reduction process for producing vanadium-rich iron alloys and fused refractory ceramic materials from calcined metal oxides produced as by-products in the UGSTM process or similar processes for the beneficiation and upgrading of titanium slags.

[0027] In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on mining residues or metallurgical wastes. In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on mining residues or metallurgical wastes by-produced during the beneficiation and upgrading of titania slags. In an

embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on mining residues or metallurgical wastes by-produced during the beneficiation and upgrading of titania slags from hard rock or beach sand ilmenites. In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on calcined metal oxides. In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on calcined metal oxides by-produced during the beneficiation and upgrading of titania slags. In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on calcined metal oxides by-produced during the beneficiation and upgrading of titania slags from hard rock or beach sand ilmenites. In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed on calcined metal oxides produced as by-products in the UGSTM process or similar processes for the beneficiation and upgrading of titanium slags.

[0028] In an embodiment of the present disclosure, the present disclosure relates to a process comprising submitting mining residues or metallurgical wastes to a high temperature pyrometallurgical reductive treatment followed by a casting, tapping, teeming or pouring step to produce a material suitable for upgrading into a vanadium-rich iron alloy and a fused refractory metal oxide feedstock. In an embodiment of the present disclosure, the present disclosure relates to a process comprising submitting calcined metal oxides to a high temperature pyrometallurgical reductive treatment followed by a casting, tapping, teeming or pouring step to produce a material suitable for upgrading into a vanadium-rich iron alloy and a fused refractory ceramic feedstock. In a further embodiment of the present disclosure, the mining residues or metallurgical wastes are mixed with ground bauxite ore or with metallurgical grade alumina prior to being submitted to the high temperature pyrometallurgical reduction process. In a further embodiment of the present disclosure, the high temperature pyrometallurgical

reduction process comprises electrothermal carbothermic smelting. In yet a further embodiment of the present disclosure, the high temperature pyrometallurgical reduction process comprises metallothermic reduction.

[0029] In an embodiment of the present disclosure, the electrothermal carbothermic smelting process produces a fused refractory metal oxide containing material and a molten vanadium-rich iron alloy comprising vanadium, manganese, chromium, silicon, and titanium. In an embodiment of the present disclosure, the electrothermal carbothermic smelting process produces a fused refractory ceramic material and a molten vanadium-rich iron alloy comprising vanadium, manganese, chromium, silicon, and titanium.

[0030] In an embodiment of the present disclosure, the metallothermic reduction process produces a fused refractory metal oxide containing material and a molten vanadium-rich iron alloy comprising vanadium, manganese, chromium, silicon, and titanium. In an embodiment of the present disclosure, the metallothermic reduction process produces a fused refractory ceramic material and a molten vanadium-rich iron alloy comprising vanadium, manganese, chromium, silicon, and titanium.

[0031] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and fused refractory metal oxides, the process comprising:

[0032] submitting mining residues or metallurgical waste oxides to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide material; and

[0033] recovering the molten vanadium-rich iron alloy and the fused refractory metal oxide material.

[0034] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and fused refractory ceramic materials, the process comprising:

[0035] submitting mining residues or metallurgical waste oxides to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory ceramic material; and

[0036] recovering the molten vanadium-rich iron alloy and the fused refractory ceramic material.

[0037] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and fused refractory metal oxides, the process comprising:

[0038] submitting mining residues or metallurgical waste oxides to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide material;

[0039] casting the molten vanadium-rich iron alloy; and

[0040] separating the cast vanadium-rich iron alloy from the fused refractory metal oxide material.

[0041] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and fused refractory ceramic materials, the process comprising:

[0042] submitting mining residues or metallurgical waste oxides to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory ceramic material;

[0043] casting the molten vanadium-rich iron alloy; and

[0044] separating the cast vanadium-rich iron alloy from the fused refractory ceramic material.

[0045] In an embodiment of the present disclosure, the separating step comprises separation by gravity.

[0046] In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment is performed at temperatures ranging from 1,500°C to 3,500°C.

[0047] In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment comprises electrothermal carbothermic smelting.

[0048] In an embodiment of the present disclosure, the high temperature pyrometallurgical reductive treatment comprises metallothermic reduction.

[0049] In an embodiment of the present disclosure, the recovering step comprises a casting, teeming, pouring or tapping step.

[0050] In an embodiment of the present disclosure, the vanadium-rich iron alloy comprises elements selected from the group consisting of iron, vanadium, chromium, manganese, silicon, titanium, nickel and cobalt.

[0051] In an embodiment of the present disclosure, the fused refractory metal oxide material comprises elements selected from the group consisting of magnesium, aluminum and calcium oxides.

[0052] The foregoing and other objects, advantages and features of the present disclosure will become more apparent upon reading of the following non restrictive description of illustrative embodiments thereof, given by way of example only with reference to the accompanying drawings, and which should not be interpreted as limiting the scope of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0053] In the appended drawings:

[0054] **FIG. 1** shows a flowchart illustrating an exemplary carbothermic process for producing a vanadium-rich iron alloy and a fused refractory ceramic material from calcined metal oxides according to an embodiment of the present disclosure; and

[0055] **FIG. 2** shows a flowchart illustrating an exemplary aluminothermic process for producing a vanadium-rich iron alloy and a fused refractory ceramic

material from calcined metal oxides according to a further embodiment of the present disclosure.

DETAILED DESCRIPTION

[0056] In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention pertains.

[0057] The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one”, but it is also consistent with the meaning of “one or more”, “at least one”, and “one or more than one”. Similarly, the word “another” may mean at least a second or more.

[0058] As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”) or “containing” (and any form of containing, such as “contain” and “contains”), are inclusive or open-ended and do not exclude additional, unrecited elements or process steps.

[0059] The term “about” is used to indicate that a value includes an inherent variation of error for the device or the method being employed to determine the value.

[0060] As used in this specification, the term “reducible oxides” refers to metal oxides susceptible to high temperature pyrometallurgical reduction. Non-limiting examples of such oxides include oxides of iron, chromium, vanadium, manganese, titanium, silicon, nickel and cobalt.

[0061] As used in this specification, the term “non-reducible oxides” refers to metal oxides not susceptible to high temperature pyrometallurgical reduction. Non-limiting examples of such oxides include oxides of magnesium, aluminum, and calcium.

[0062] As used in this specification, when referring to a titanium slag obtained from hard rock ilmenite, the term “impurity” essentially refers to oxides of magnesium, calcium, silicon, aluminum, vanadium, manganese, chromium, and metallic iron. When referring to a titanium slag obtained from a beach sand ilmenite, the term “impurity” essentially refers to manganese and radioactive elements (*e.g.* uranium and thorium).

[0063] In an embodiment, the present disclosure relates to a process for producing molten vanadium-rich iron alloys and fused refractory metal oxide materials from mining residues or metallurgical wastes. The process comprises submitting the mining residues or metallurgical wastes to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide material followed by the recovery of the molten vanadium-rich iron alloy and the fused refractory metal oxide material. In an embodiment of the present disclosure, the recovery step comprises a casting, teeming, pouring or tapping step. Other recovery procedures are known in the art (*e.g.* recovery by means of magnetic separation) and are within the capacity of a skilled technician.

[0064] In an embodiment, the present disclosure relates to a process for producing molten vanadium-rich iron alloys and fused refractory metal oxide materials from mining residues or metallurgical wastes. The process comprises submitting the mining residues and/or metallurgical wastes to a high temperature pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide material followed by gravity separation of the molten product. The products obtained (*i.e.* vanadium-rich iron alloy and fused refractory metal oxides) can be directly used or further upgraded depending on the application.

[0065] In an embodiment, the present disclosure relates to a process for producing a molten vanadium-rich iron alloys and fused refractory metal oxide materials from calcined metal oxides. In an embodiment, the present disclosure relates to a process for producing a molten vanadium-rich iron alloys and fused refractory metal oxide materials from calcined metal oxides produced as by-products in the UGSTM process. In an embodiment, the process comprises submitting the calcined metal oxides to a pre-reduction step, either during or after being discharged from the pyrohydrolyser, by contacting these oxides with either a gaseous or solid reducing agent. This pre-reduction step provides for at least a partial reduction of the reducible oxides.

[0066] In an embodiment, the present disclosure relates to a process for producing molten vanadium-rich iron alloys and a material composed of fused refractory metal oxides from calcined metal oxides. The process comprising submitting the calcined metal oxides to a high temperature pyrometallurgical reductive treatment using either a gaseous reducing agent, a solid reducing agent or mixtures thereof.

[0067] It has been surprisingly discovered that the calcined metal oxides, obtained from the pyrohydrolysis of the dissolved metal chlorides containing spent acid

solution resulting from the UGSTM process, can be effectively submitted to a high temperature pyrometallurgical reductive treatment to provide a molten vanadium-rich iron alloy comprising significant amounts of manganese, chromium, silicon and titanium, in addition to producing a mixture of magnesia and spinel. Following casting, the vanadium-rich iron alloy and the product comprising the fused refractory metal oxides are recovered.

[0068] In an embodiment of the present disclosure, the high temperature pyrometallurgical reduction step is performed using a gaseous reducing agent selected from the group consisting of hydrogen, natural gas, carbon monoxide, gaseous hydrocarbons, synthesis gas [*i.e.* syngas; mixture of carbon monoxide (CO) and hydrogen (H₂)] and smelter gas. Other suitable gaseous reducing agents are known in the art and are within the capacity of a skilled technician. In a further embodiment of the present disclosure, the high temperature pyrometallurgical reduction step is performed using a solid reducing agent including but not limited to carbon-based materials selected from the group consisting of charcoal, coal, carbon black, petroleum, metallurgical cokes, and graphite. Other suitable solid reducing agents are known in the art and are within the capacity of a skilled technician. In yet a further embodiment of the present disclosure, the high temperature pyrometallurgical reduction step is performed using reducing agents used in metallothermic processes, such reducing agents being selected from the group consisting of ferrosilicon, magnesium metal and alloys thereof, and aluminum metal and alloys thereof. In yet a further embodiment of the present disclosure, the high temperature pyrometallurgical reduction is performed at temperatures ranging from about 1,500°C to about 3,500°C.

[0069] Under the highly reductive conditions prevailing in the high temperature pyrometallurgical reduction process of the present disclosure, in addition to the elevated carbon activity (when carbon is used as the reductant), any molten reduced

iron metal further promotes the reduction of manganese, chromium and vanadium, thus further enhancing the separation of these elements and significantly preventing the partitioning between the molten iron alloy and the molten refractory slag. Because of the higher reducing capabilities of aluminum and magnesium, this effect becomes even more pronounced when a metallothermic process is employed.

[0070] In an embodiment of the present disclosure, the high temperature pyrometallurgical reduction is performed using a vertical shaft furnace in which the calcined metal oxides are on a fluidized bed, a fixed bed, a circulating bed or a moving bed. Further non-limiting examples of suitable apparatuses include an induction furnace, an electric arc furnace (EAF) (either of the tapping or tilting type and operating either on direct or alternate current), a vertical shaft furnace with water-cooled walls such as those used in the production of ferroalloys by either aluminothermic, magnesiothermic or silicothermic processes, and a furnace equipped with a plasma torch. Other suitable apparatuses are known in the art, and are within the capacity of a skilled technician.

[0071] The separation of the molten products following high temperature pyrometallurgical reduction can be performed by tapping, teeming, casting or pouring, depending on the type of furnace used.

[0072] Following cooling, the product comprising the fused refractory metal oxides may be comminuted (*e.g.* crushing and/or grinding), and subsequently submitted to magnetic separation in order to remove any entrapped iron alloy. Such iron alloy can be recycled to the furnace or added to the molten iron alloy during the tapping, casting, pouring or teeming step. Suitable comminution equipment is known in the art and is within the capacity of a skilled technician. Non-limiting examples of suitable comminution equipment include a hammer mill and a roller mill. In

applications wherein a high purity refractory metal oxide product is required, iron contamination of the refractory metal oxide product is alleviated by means of acid leaching. The leachate can be recycled to a pyrohydrolyser.

[0073] In an embodiment of the present disclosure, the high temperature pyrometallurgical reduction is performed on calcined metal oxides obtained from the pyrohydrolysis of the spent hydrochloric acid solution resulting from the UGSTM process or similar processes for the beneficiation and upgrading of titania slags.

[0074] In an embodiment of the present disclosure, the high temperature pyrometallurgical reduction is performed on calcined metal oxides obtained from the pyrohydrolysis of a spent hydrochloric acid solution generated from the upgrading of chloride-type titanium slags having a titanium dioxide content ranging from about 76 to about 86 wt.% TiO₂ using the UGSTM process. In a further embodiment of the present disclosure, the high temperature pyrometallurgical reduction is performed on calcined metal oxides obtained from the pyrohydrolysis of a spent acid solution generated from the beneficiation and upgrading of titania slags from beach sand ilmenites by the Benelite or the Becher process.

EXPERIMENTAL

[0075] A number of examples are provided hereinbelow, illustrating the efficiency of the process of the present disclosure in the preparation of vanadium-rich iron alloys and fused refractory metal oxides from mining residues or metallurgical waste oxides.

[0076] **Example 1: Electrothermal Carbothermic Reduction**

[0077] About one kilogram of calcined metal oxides “*as received*”, by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in **Table 2** (fraction #1), was pre-mixed in a V-blender with fine metallurgical coke (about 150 grams). The blend was fed into a benchscale electric arc furnace (EAF) operating in DC mode and using a graphite electrode. Because of the extreme temperatures and elevated corrosiveness of the molten refractory slag, the EAF was equipped with a water-cooled jacketed shell and a thick baseplate made of copper. The reduction process was initiated by directly arcing the base plate and feeding the blend until the crucible was full. The EAF was then operated by submerging the graphite electrode into the highly electrically insulating molten refractory metal oxide slag but without contacting the highly conductive pool of molten iron alloy underneath. Because the molten refractory metal oxide slag comprises both fused spinel and magnesia, the operating temperatures are typically located at about 2,900°C or higher. During the reduction process, the feed materials float over the molten spinel, decreasing the thermal losses by radiation, while the droplets of the dense liquid iron alloy sink by gravity, settling at the bottom of the furnace where they coalesce and form a pool of molten iron alloy. After about 30 minutes of continuous operation the entire charge was treated and the reduction process considered complete. The electric power was turned off, the graphite electrode lifted and the molten mass allowed to cool. About 400 grams of vanadium-rich iron alloy was recovered along with about 400 grams of fused spinel and magnesia. Following cooling and demoulding, the fused refractory mass of spinel and magnesia was crushed and ground and subsequently submitted to a magnetic separation step to remove any tiny entrapped droplets of iron alloy. Chemical analysis of the solidified iron alloy ingot gave the following elemental composition: 89.14 wt.% Fe, 2.43 wt.% V, 1.93 wt.% Mn, 1.27 wt.% Cr, 0.98 wt.% Si, 0.82 wt.% Ti and 3.38 wt.% C. Chemical analysis of the

refractory mass of fused metal oxides exhibited the following chemical composition: 55 wt.% fused magnesia, 45 wt.% fused spinel.

[0078] **Example 2: Electrothermal Carbothermic Reduction using bauxite**

[0079] About one kilogram of calcined metal oxides “*as received*”, by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in **Table 2** (fraction #1), was pre-mixed in a V-blender with fine metallurgical coke (about 225 grams) and ground bauxite ore (820 grams; 65 wt.% Al_2O_3 , 25 wt.% Fe_2O_3 , 5 wt.% SiO_2 , 4 wt.% TiO_2 and 1 wt.% CaO). The blend was fed into a benchscale electric arc furnace (EAF) operating in DC mode and using a graphite electrode. Because of the extreme temperatures and elevated corrosiveness of the molten refractory slag, the EAF was equipped with a water-cooled jacketed shell and thick baseplate made of copper. The reduction process was initiated by directly arcing the base plate and feeding the blend until the crucible was full. The EAF was then operated by submerging the graphite electrode into the highly electrically insulating molten refractory metal oxide slag but without contacting the highly conductive pool of molten iron alloy underneath. Because the molten refractory metal oxide slag was comprised of only fused spinel (*m.p.* 2,175°C), it was possible to operate at temperatures typically located at about 2,200°C or higher. At these operating temperatures, the total energy, that is the specific energy (*i.e.*, sensible and latent enthalpies per unit mass) required to raise the temperature of the entire charge (*i.e.* calcined metal oxides + bauxite + coke) and the specific energy required to perform the reduction of all reductible metal oxides, is about 1.32 kWh/kg. During the reduction process, the feed materials float over the molten spinel, decreasing the thermal losses by radiation, while the droplets of the dense liquid iron alloy sink by gravity, settling at the bottom of the furnace where they coalesce and form a pool of molten iron alloy. After

about 45 minutes of continuous operation the entire charge was treated and the reduction process considered complete. The electric power was turned off, the graphite electrode lifted and the molten masses allowed to cool. About 600 grams of vanadium-rich iron alloy was recovered along with about 940 grams of electrofused spinel. Following cooling and demoulding, the electrofused mass of spinel was crushed and ground and submitted to a magnetic separation step to remove any tiny entrapped droplets of iron alloy. Chemical analysis of the solidified iron alloy ingot gave the following elemental composition: 88.53 wt.% Fe, 2.93 wt.% Ti, 1.66 wt.% V, 1.32 wt.% Mn, 1.28 wt.% Si, 0.86 wt.% Cr and 3.40 wt.% C.

[0080] **Example 3: Electrothermal Carbothermic Reduction using alumina**

[0081] About one kilogram of calcined metal oxides “*as received*”, by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in Table 2 (fraction #1), was pre-mixed in a V-blender with fine metallurgical coke (about 150 grams) and metallurgical grade alumina (525 grams; 99.95 wt.% Al₂O₃). The blend was fed into a benchscale electric arc furnace (EAF) operating in DC mode and using a graphite electrode. Because of the extreme temperatures and elevated corrosiveness of the molten refractory slag, the EAF was equipped with a water-cooled jacketed shell and thick baseplate made of copper. The reduction process was initiated by directly arcing the base plate and feeding the blend until the crucible was full. The EAF was then operated by submerging the graphite electrode into the highly electrically insulating molten refractory metal oxide slag but without contacting the highly conductive pool of molten iron alloy underneath. Because the molten refractory metal oxide slag was comprised of only fused spinel (*m.p.* 2,175°C), it was possible to operate at temperatures typically located at about 2,200°C or higher. At these operating

temperatures, the total energy, that is the specific energy (*i.e.* sensible and latent enthalpies per unit mass) required to raise the temperature of the entire charge (*i.e.* calcined metal oxides + alumina + coke) and the specific energy required to perform the reduction of all reducible metal oxides, is about 1.23 kWh/kg. During the reduction process, the feed materials float over the molten spinel, decreasing the thermal losses by radiation, while the droplets of the dense liquid iron alloy sink by gravity, settling at the bottom of the furnace where they coalesce and form a pool of molten iron alloy. After about 45 minutes of continuous operation the entire charge was treated and the reduction process considered complete. The electric power was turned off, the graphite electrode lifted and the molten masses allowed to cool. About 408 grams of vanadium-rich iron alloy was recovered along with about 930 grams of electrofused spinel. Following cooling and demoulding, the electrofused mass of spinel was crushed and ground and submitted to a magnetic separation step to remove any tiny entrapped droplets of iron alloy. Chemical analysis of the solidified iron alloy ingot gave the following elemental composition: 88.29 wt.% Fe, 2.41 wt.% V, 1.91 wt.% Mn, 1.25 wt.% Cr, 0.97 wt.% Si, 0.82 wt.% Ti and 4.31 wt.% C.

[0082] Example 4: Aluminothermic Reduction

[0083] About one kilogram of calcined metal oxides "*as received*", by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in **Table 2** (fraction #1), was ground in a ball mill to a particle size less than 200 mesh (75 μm), oven dried at 150°C and then carefully mixed with secondary aluminum metal powder (220 grams). A first batch of the blend (100 grams) was introduced at the bottom of a cast iron vertical crucible and ignited by means of a priming mixture of sodium nitrate (NaNO_3), aluminum metal powder and magnesium turnings. Because of the high temperatures occurring during the process, the walls and base plate of the crucible were water cooled

while a carbon hearth was installed at the bottom of the vessel to collect the molten iron alloy. After starting the aluminothermic reduction process, the remainder of the blend was charged at a constant feed rate to ensure that the surface of the melt was always covered by a thin layer of solid material to reduce heat losses by radiation. During the reduction process, droplets of dense liquid iron alloy sink by gravity, settling at the bottom of the hearth where they coalesce and form a pool of molten iron alloy. After about 15 minutes of continuous operation the entire charge was treated and the reduction process considered complete. The crucible was allowed to cool for few hours. Upon demoulding, a block composed of a mixture of fused corundum and spinel overlaying an ingot of vanadium-rich iron alloy was recovered. About 400 grams of vanadium-rich iron alloy were recovered along with about 1.1 kilograms of fused corundum and spinel. The fused mass of corundum and spinel was crushed and ground and submitted to a magnetic separation step to remove any tiny entrapped droplets of iron alloy. Chemical analysis of the solidified iron alloy gave the following elemental composition: 91.81 wt.% Fe, 2.50 wt.% V, 1.99 wt.% Mn, 1.30 wt.% Cr, 1.00 wt.% Si, 0.85 wt.% Ti, and 0.5 wt.% Al.

[0084] It is to be understood that the present disclosure is not limited in its application to the details of construction and parts as described hereinabove. The disclosure is capable of other embodiments and of being practiced in various ways. It is also understood that the phraseology or terminology used herein is for the purpose of description and not limitation. Hence, although the present disclosure has been described hereinabove by way of illustrative embodiments thereof, it can be modified, without departing from the spirit, scope and nature of the subject disclosure as defined in the appended claims.

REFERENCES

1. F. Cardarelli – *Materials Handbook. A Concise Desktop Reference*. Springer, London, **2008**, pp. 276-280.
2. U.S. Patent 4,078,039.
3. WO 04/104239.
4. U.S. Patent 5,830,420.
5. Alper, A. M., McNally, R. N., Ribbe, P. G. and Doman, R. C.; *Journal American Ceramic Society*, **45(6)**, **1962**, 264.

WHAT IS CLAIMED IS:

1. A process for producing vanadium-rich iron alloys and fused refractory metal oxide, the process comprising:

a) submitting mining residues or metallurgical wastes to a pyrometallurgical reductive treatment to produce a molten vanadium-rich iron alloy and a fused refractory metal oxide;

b) separating the molten vanadium-rich iron alloy from the fused refractory metal oxide; and

c) recovering the molten vanadium-rich iron alloy and the fused refractory metal oxide.

2. The process according to claim 1, further comprising the step of mixing the mining residues or metallurgical wastes with a reducing agent.

3. The process according to claim 2, further comprising the step of submitting the mining residues or metallurgical wastes to a pre-reduction step to produce a partially reduced material that is subsequently submitted to the pyrometallurgical reductive treatment.

4. The process according to claims 2 or 3, further comprising the steps of comminuting the fused refractory metal oxide to produce a comminuted material and submitting the comminuted material to magnetic separation.

5. The process according to claim 4, wherein the pyrometallurgical reduction step comprises either an electrothermal carbothermic process, or a metallothermic process.

6. The process according to claim 5, wherein the metallothermic process comprises an aluminothermic process, a magnesiothermic process or a silicothermic process.

7. The process according to claim 6, wherein the pyrometallurgical reductive treatment is performed at temperatures ranging from 1,500°C to 3,500°C.

8. The process according to claim 6, wherein the pyrometallurgical reductive treatment is performed using a reductant selected from the group consisting of a solid reductant, a liquid reductant, a gaseous reductant or mixtures thereof.

9. The process according to claim 8, wherein the vanadium-rich iron alloy comprises elements selected from the group consisting of iron, vanadium, manganese, chromium, silicon, titanium nickel and cobalt.

10. The process according to claim 8, wherein the fused refractory metal oxide comprises elements selected from the group consisting of magnesium, aluminum and calcium oxides.

11. The process according to claim 1, wherein the pyrometallurgical reduction step is performed on mining residues or metallurgical wastes by-produced during the beneficiation or upgrading of titania slags.

12. The process according to claim 1, wherein the pyrometallurgical reduction step is performed on mining residues or metallurgical wastes by-produced during the production of pig iron and steel making.

13. The process according to claim **1**, wherein the pyrometallurgical reduction step is performed on mining residues or metallurgical wastes by-produced during the pyrohydrolysis or spray roasting of spent pickling acids.

14. The process according to claims **11**, **12** or **13**, wherein the mining residues or metallurgical wastes are calcined metal oxides.

15. The process according to claim **4**, wherein the magnetic separation removes iron alloy from the fused refractory metal oxide.

16. The process according to claim **15**, wherein the magnetic separation is performed using a magnetic flux ranging from 0.01 Tesla to 0.1 Tesla.

17. The process according to claim **8**, wherein the reductant is a solid reductant.

18. The process according to claim **17**, wherein the solid reductant is selected from the group consisting of carbon-based materials, ferrosilicon, magnesium metal, alloys of magnesium metal, aluminum metal, alloys of aluminum metal and mixtures thereof.

19. The process according to claim **18**, wherein the carbon-based materials are selected from the group consisting of charcoal, coal, carbon black, petroleum, metallurgical cokes, and graphite.

20. The process according to claim **1**, wherein the separation step is selected from the group consisting of casting, teeming, pouring and tapping.

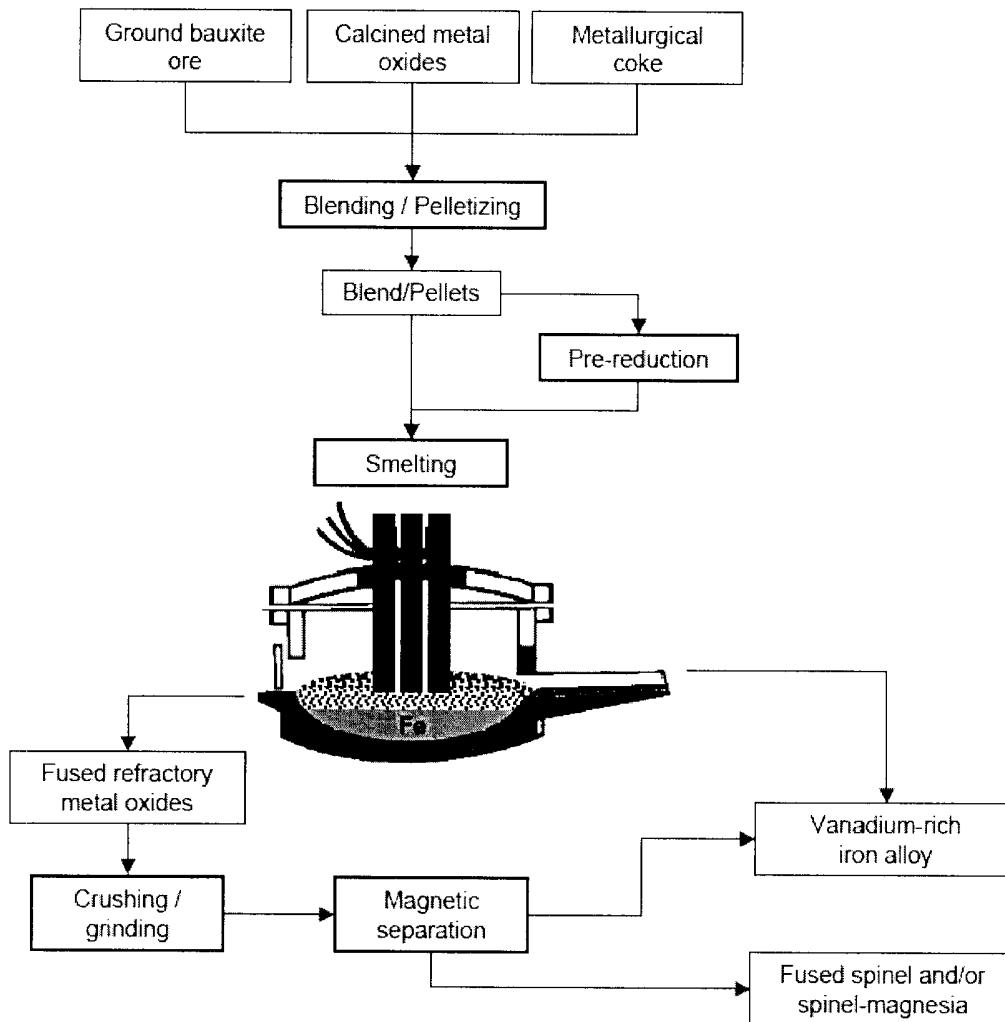


FIG. 1

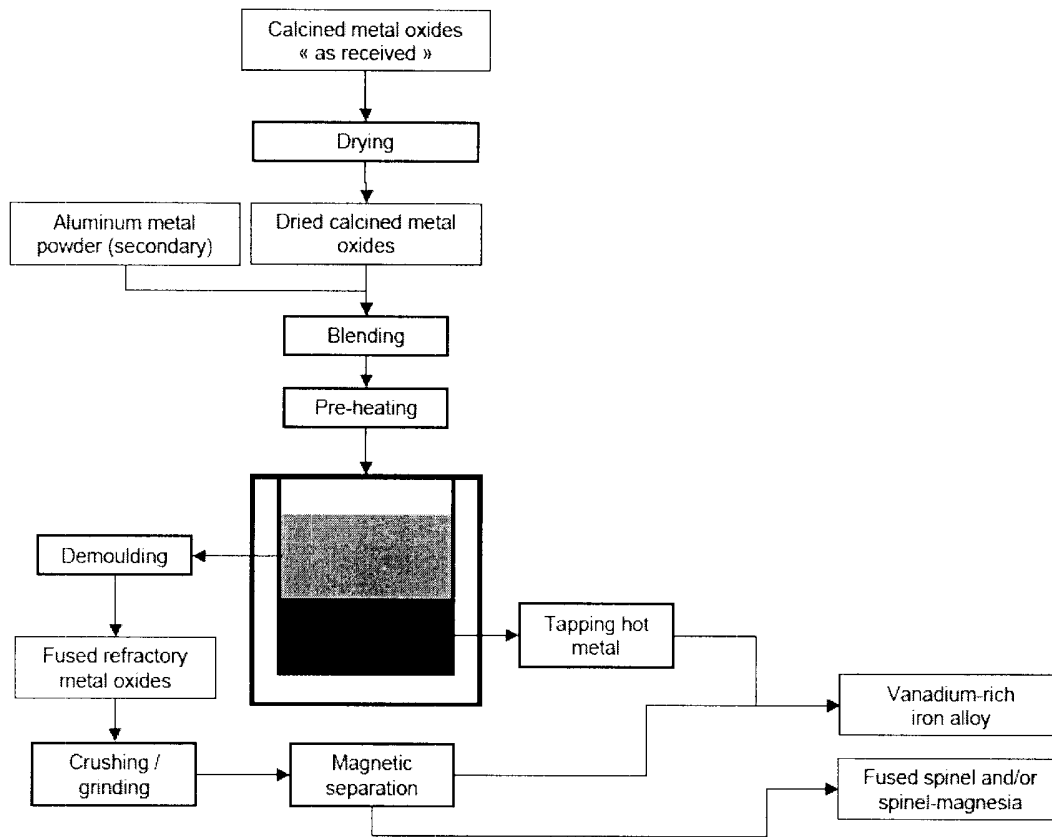


FIG.2

