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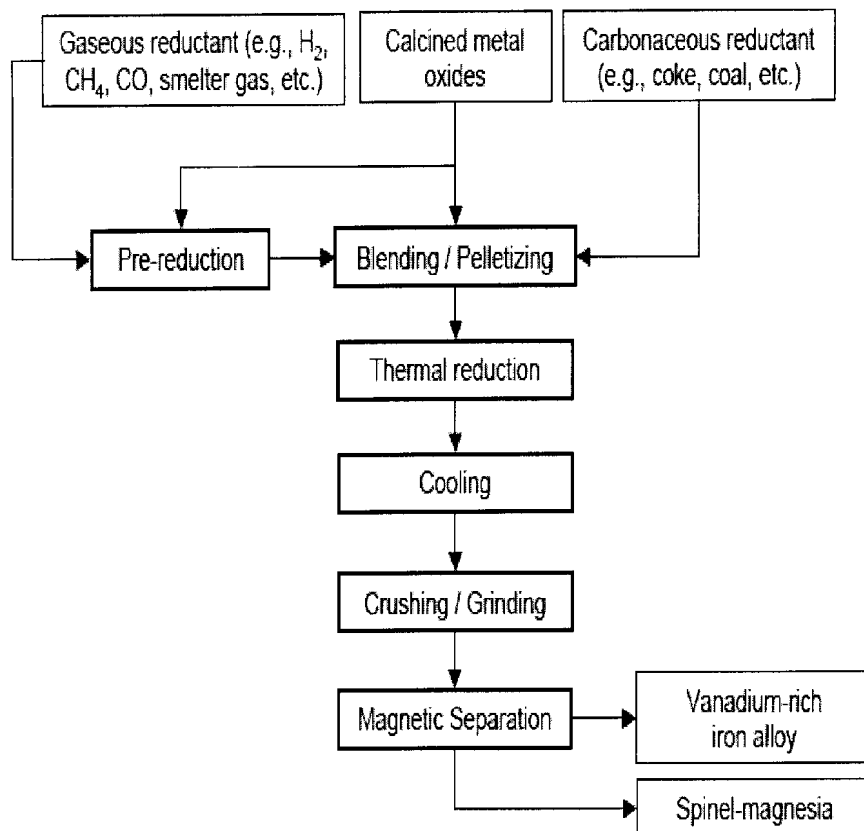
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(54) Titre : PROCEDE DE REDUCTION THERMIQUE POUR LA RECUPERATION D'OXYDES DE METAUX REFRACTAIRES ET LA PRODUCTION D'ALLIAGES DE FER RICHES EN VANADIUM A PARTIR DE RESIDUS MINIERES OU DE DECHETS METALLURGIQUES PRODUITS DURANT LA VALORISATION DE LAITIERS DE DIOXYDE DE TITANE
(54) Title: THERMAL REDUCTION PROCESS FOR THE RECOVERY OF 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 refractory metal oxides is described. The process comprises submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to produce a reduced material; submitting the



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

reduced material to at least one magnetic separation step to produce magnetic fractions of differing magnetic susceptibilities; and recovering the magnetic fractions.

ABSTRACT OF THE DISCLOSURE

A process for producing vanadium-rich iron alloys and refractory metal oxides is described. The process comprises submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to produce a reduced material; submitting the reduced material to at least one magnetic separation step to produce magnetic fractions of differing magnetic susceptibilities; and recovering the magnetic fractions.

TITLE

THERMAL REDUCTION PROCESS FOR THE RECOVERY OF 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 thermal reduction process for the recovery of refractory metal oxides and the production of vanadium-rich iron alloys. More specifically, but not exclusively, the present disclosure relates to a thermal reduction process for the recovery of 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 (TiO₂) occurs

usually as rutile and in a lesser extent as anatase and brookite. Among the titanates, those comprising iron such as ilmenite $[\text{FeTiO}_3]$, 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 temperatures 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 (TiCl_4), and other

metal chlorides originating from impurities present in the feedstock. The TiCl_4 is further separated and purified from the other metal chlorides by selective condensation, fractional distillation, or countercurrent extraction and subsequently converted to pure TiO_2 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 particle size distributions 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 UGSTM. The upgraded titanium slag produced becomes a high-grade feedstock suitable for the chloride process.

[0010] The UGSTM 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 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 UGSTM 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 $A^{II}B^{III}_2O_4$ wherein $A^{II} = Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}$ and wherein $B^{III} = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mn^{3+}, Co^{3+}$. The most common phases are in order of importance: magnesioferrite or pleonaste ($MgFe_2O_4$), donathite ($MgFeAlO_4$), spinel *senso-stricto* ($MgAl_2O_4$), and hercynite ($FeAl_2O_4$). 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 ($CaSiO_3$). 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

(FeV_2O_4) or chromite (FeCr_2O_4). 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 its 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**, using a conventional reductant (*e.g.*, coal, coke, hydrogen, natural gas, smelter gas or synthetic gas), yields 399.95 kilograms of a vanadium-rich iron alloy. The chemical composition of this vanadium-rich iron alloy was as follows: 94.02 wt.% Fe, 2.56 wt.% V, 2.04 wt.% Mn, 1.33 wt.% Cr as well as 300 ppm Co and 200 ppm Ni.

[0017] Assuming a theoretical yield of 100%, there remains 416.20 kilograms of refractory metal oxides following the reduction having the following chemical composition: 62.40 wt.% magnesia (MgO), 30.85 wt.% alumina (Al_2O_3), 3.24 wt.% calcia (CaO), 2.11 wt.% silica (SiO_2), and finally 1.39 wt.% titania (TiO_2). If the alumina and magnesia are chemically combined as spinel (MgAl_2O_4), the refractory mass contains about 44.44 wt.% of spinel (*i.e.* 184.96 kg; incorporating most of the titania as an impurity), and about 53.45 wt.% of fused magnesia (MgO) (*i.e.* 222.44 kg; incorporating most of the calcia and finally 2.11 wt.% of free silica).

[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 3,135 US\$/tonne (*i.e.* 1,254 US\$/tonne of calcined oxides “*as received*”). Based on the price of spinel (500 US\$/tonne) and dead burned magnesia (350 US\$/tonne) [*Industrial Minerals*, January 2008], the refractory metal oxide recovered

can be evaluated at about 409 US\$/tonne of magnesia spinel refractories (*i.e.* 170 US\$/tonne of calcined metal oxides “*as received*”).

[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] 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.* 2820°C), magnesioferrite (*m.p.* 1800°C), hercynite (*m.p.* 1780°C), and chromite (*m.p.* 2075°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 (*m.p.* 2820°C) and 30-50 wt.% spinel (*m.p.* 2135°C). Hence, at the temperatures used during the thermal reduction process, typically between 500°C to 1500°C, these refractory metal oxides remain in the solid state and, because of their high market value, no suitable fluxing agents or additives can be used to lower the melting temperature without jeopardizing their chemistry.

[0021] 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.

[0022] The present description refers to a number of documents, the contents of which are herein incorporated by reference in their entirety.

SUMMARY

[0023] 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 process for producing vanadium-rich iron alloys and refractory metal oxides from mining residues or metallurgical wastes. In a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides from mining residues or metallurgical wastes by-produced during the beneficiation and upgrading of titania slags from hard rock or beach sand ilmenites. In a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides from calcined metal oxides. In a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides 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 process for producing vanadium-rich iron alloys and 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 process for producing vanadium-rich iron alloys and 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 process for producing vanadium-rich iron alloys and refractory metal oxides from calcined metal oxides by-produced during the pyrohydrolysis or spray roasting of spent pickling acids.

[0024] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials from mining residues or metallurgical wastes. In a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and 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 a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials from calcined metal oxides. In a further embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and 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 process for producing vanadium-rich iron alloys and 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.

[0025] In an embodiment, the present disclosure relates to a process comprising submitting mining residues or metallurgical wastes to a reductive thermal treatment followed by magnetic separation. In a further embodiment, the products following magnetic separation are further upgraded into iron alloys and a refractory metal oxide feedstock.

[0026] In an embodiment, the present disclosure relates to a process comprising submitting calcined metal oxides to a reductive thermal treatment followed by magnetic separation. In a further embodiment, the products following magnetic separation are further upgraded into iron alloys and a refractory ceramic feedstock.

[0027] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides, the process comprising:

[0028] submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to provide magnetic fractions of differing magnetic susceptibilities; and

[0029] recovering the magnetic fractions.

[0030] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials, the process comprising:

[0031] submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to provide magnetic fractions of differing magnetic susceptibilities; and

[0032] recovering the magnetic fractions.

[0033] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides, the process comprising:

[0034] submitting calcined metal oxides to at least one reductive thermal treatment to provide magnetic fractions of differing magnetic susceptibilities; and

[0035] recovering the magnetic fractions.

[0036] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials, the process comprising:

[0037] submitting calcined metal oxides to at least one reductive thermal treatment to provide magnetic fractions of differing magnetic susceptibilities; and

[0038] recovering the magnetic fractions.

[0039] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides, the process comprising:

[0040] submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to provide a reduced material;

[0041] submitting the reduced material to at least one magnetic separation step to provide magnetic fractions of differing magnetic susceptibilities; and

[0042] recovering the magnetic fractions.

[0043] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials, the process comprising:

[0044] submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to provide a reduced material;

[0045] submitting the reduced material to at least one magnetic separation step to provide magnetic fractions of differing magnetic susceptibilities; and

[0046] recovering the magnetic fractions.

[0047] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides, the process comprising:

[0048] submitting calcined metal oxides to at least one reductive thermal treatment to provide a reduced material;

[0049] submitting the reduced material to at least one magnetic separation step to provide magnetic fractions of differing magnetic susceptibilities; and

[0050] recovering the magnetic fractions.

[0051] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory ceramic materials, the process comprising:

[0052] submitting calcined metal oxides to at least one reductive thermal treatment to provide a reduced material;

[0053] submitting the reduced material to at least one magnetic separation step to provide magnetic fractions of differing magnetic susceptibilities; and

[0054] recovering the magnetic fractions.

[0055] In an embodiment of the present disclosure, the reductive thermal treatment is performed at a temperature ranging from 500°C to 1,500°C.

[0056] In an embodiment, the reductive thermal 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 a further embodiment, the reductive thermal 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 yet a further embodiment, the reductive thermal treatment is performed on calcined metal oxides produced as by-produced in the UGSTM process or similar processes for the beneficiation and upgrading of titanium slags.

[0057] In an embodiment of the present disclosure, the reductive thermal treatment is performed at a temperature ranging from 500°C to 1,500°C or below the melting point or solidus temperature of the iron alloy.

[0058] In an embodiment of the present disclosure, the magnetic separation is performed using a magnetic flux ranging from about 0.01 Tesla to about 0.1 Tesla.

[0059] In an embodiment of the present disclosure, the magnetic fractions of differing magnetic susceptibilities comprise a fraction consisting of a vanadium-rich iron alloy and reducible elements and a fraction consisting of refractory metal oxides and non-reducible elements.

[0060] In an embodiment of the present disclosure, the fraction consisting of a vanadium-rich iron alloy and reducible elements comprises a higher magnetic susceptibility relative to the fraction consisting of refractory metal oxides and non-reducible elements.

[0061] In an embodiment of the present disclosure, the fraction consisting of a vanadium-rich iron alloy and reducible elements comprises vanadium, chromium, manganese, nickel and cobalt. In an embodiment of the present disclosure, the fraction consisting of refractory metal oxides and non-reducible elements comprises magnesium, aluminum, calcium, titanium and silicon oxides.

[0062] 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

[0063] In the appended drawings:

[0064] FIG. 1 shows a flowchart illustrating an exemplary process for producing a vanadium-rich iron alloy and refractory metal oxides (*e.g.* spinel magnesia) from mining residues or metallurgical waste oxides according to an embodiment of the present disclosure; and

[0065] FIG. 2 shows a flowchart illustrating an exemplary process for producing a vanadium-rich iron alloy and refractory metal oxides (*e.g.* spinel magnesia) from mining residues or metallurgical waste oxides according to a further embodiment of the present disclosure.

DETAILED DESCRIPTION

[0066] 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.

[0067] 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.

[0068] 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.

[0069] 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.

[0070] As used in this specification, the term “reducible oxides” refers to metal oxides susceptible to reductive thermal treatment. Non limiting examples of such oxides include oxides of iron, chromium, vanadium, manganese, nickel and cobalt.

[0071] As used in this specification, the term “non-reducible oxides” refers to metal oxides not susceptible to reductive thermal treatment. Non limiting examples of such oxides include oxides of magnesium, aluminum, titanium, silicon and calcium.

[0072] As used in this specification, when referring to a titanium slag obtained from a 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).

[0073] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides from mining residues or metallurgical waste oxides such as calcined metal oxides. In an embodiment, the process comprises subjecting the mining residues or metallurgical waste oxides to at least one reductive thermal treatment step and at least one magnetic separation step.

[0074] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides from mining residues and/or metallurgical waste metal oxides. In an embodiment, the process comprises subjecting the mining residues and/or metallurgical waste metal oxides to at least one reductive thermal treatment step. Following cooling, the reduced material is subjected to a comminution step including crushing and grinding. The comminuted material is then subjected to a magnetic separation procedure to provide magnetic fractions of differing magnetic susceptibilities. The magnetic fractions are subsequently recovered and analyzed. The products obtained (*i.e.* vanadium-rich iron alloys and refractory metal oxides) can be directly used or further upgraded depending on the application.

[0075] In an embodiment, the present disclosure relates to a process for producing vanadium-rich iron alloys and refractory metal oxides from calcined metal oxides produced as by-products in the UGSTM process. In an embodiment, the process comprises subjecting the calcined metal oxides to a pre-reduction step, either during or after being discharged from the pyrohydrolyser, by contacting the oxides with either a gaseous or solid reducing agent. This pre-reduction step provides for at least a partial reduction of the reducible oxides.

[0076] 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 reduced at relatively low temperatures to produce particles or platelets of an iron alloy containing significant amounts of vanadium, manganese and chromium, leaving a mixture of free magnesium oxide and spinel. In an embodiment of the present disclosure, the particles and/or platelets are subjected to a comminution step to provide a material that is readily subjected to magnetic separation. In an embodiment of the present disclosure, the magnetic separation is performed by means of a hand magnet.

[0077] In an embodiment of the present disclosure, the reductive thermal treatment 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)], producer gas, water gas 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 reductive thermal treatment 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 reductive thermal treatment step is performed at temperatures ranging from about 500 to about 700°C when using hydrogen gas as the reducing agent. In yet a further embodiment of the present disclosure, the reductive thermal treatment is performed at temperatures ranging from about 900 to about 1500°C when using carbon-based materials as the reducing agent.

[0078] In an embodiment of the present disclosure, the reductive thermal treatment step is performed using a vertical shaft furnace in which the calcined metal oxides are on a fluidized bed, a circulating bed or a moving bed. Further non-limiting examples of suitable apparatuses include a rotary hearth furnace, a multiple heart furnace, a rotary kiln, a reverberatory furnace and an induction furnace. Other suitable apparatuses are known in the art, and are within the capacity of a skilled technician.

[0079] Comminution of the reduced material (following reductive thermal treatment) provides for the substantial liberation of the iron alloy from the refractory metal oxides. Suitable comminution equipment is known in the art and is within the capacity of a skilled technician. Depending on the type of magnetic separator used to

sort the iron alloy from the refractory metal oxides, the comminution step can be performed in either dry or wet conditions by means of sand milling.

[0080] The magnetic separation can be performed in a single step or multiple steps, in either dry or wet mode, using either a permanent magnet or an electromagnet. In an embodiment of the present disclosure, the median magnetic fractions are recycled back for a further reductive thermal treatment step.

[0081] In an embodiment of the present disclosure, the reductive thermal treatment step is performed on calcined metal oxides obtained from the pyrohydrolysis of the spent acid solution resulting from the UGSTM process.

[0082] In an embodiment of the present disclosure, the reductive thermal treatment step is performed on calcined metal oxides obtained from the pyrohydrolysis of a spent 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 reductive thermal treatment step 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 using the Benelite or the Becher process.

EXPERIMENTAL

[0083] 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 refractory metal oxides from mining residues or metallurgical waste oxides.

[0084] **Example 1**

[0085] A mass of calcined metal oxides (100 grams), 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 thoroughly mixed with carbon black (20 grams) as reductant. The mixture was then introduced into a magnesia crucible (2" by 5") prepared by slip casting (Custom Ceramics Inc.) and covered by a lid. The loaded crucible was introduced into a box furnace (Blue M, Lindberg) and maintained at 1100°C over a period of 2 hours. Following cooling, the agglomerated mixture was ground in a pulverizer (Retsch) to produce a powder having a particle size < 200 mesh (<75 µm). Any excess carbonaceous material (*i.e.* carbon black) was removed from the ground material by pouring it into a separatory funnel comprising carbon tetrachloride. Following decantation, the carbon-free material was dried in an oven kept at 80°C, cooled and subjected to magnetic separation using a hand magnet (Gilson). About 40 grams of an iron alloy powder was recovered along with about 40 grams of a white powder comprising refractory metal oxides. Chemical analysis of the iron alloy powder revealed the following elemental composition: 93 wt.% Fe, 2.5 wt.% V, 2.0 wt.% Mn, 1 wt.% Cr and 1.5 wt.% C. Chemical analysis of the white powder comprising refractory metal oxides revealed the following composition: 62 wt.% MgO, 31 wt.% Al₂O₃, 3 wt.% CaO, 2 wt. % SiO₂ and 1 wt.% TiO₂. X-ray diffraction analysis revealed periclase and spinel as major phases.

[0086] **Example 2**

[0087] A mass of calcined metal oxides (100 grams), by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in **Table 2** (fraction #2) was thoroughly mixed with metallurgical coke (20 grams) as reductant. The mixture was then

introduced into a magnesia crucible (2" by 5") prepared by slip casting (Custom Ceramics Inc.) and covered by a lid. The loaded crucible was introduced into a box furnace (Blue M, Lindberg) and maintained at 1000°C over a period of 2 hours. Following cooling, the agglomerated mixture was ground in a pulverizer (Retsch) to produce a powder having a particle size < 200 mesh (<75 µm). Any excess carbonaceous material (*i.e.* carbon black) was removed from the ground material by pouring it into a separatory funnel comprising carbon tetrachloride. Following decantation, the carbon-free material was dried in an oven kept at 80°C, cooled and subjected to magnetic separation using a hand magnet (Gilson). About 36 grams of an iron alloy powder was recovered along with about 48 grams of a slightly yellowish powder comprising refractory metal oxides. Chemical analysis of the iron alloy powder revealed the following elemental composition: 93 wt.% Fe, 3.0 wt.% V, 2.5 wt.% Mn, 1.0 wt.% Cr and 0.5 wt.% C. Chemical analysis of the slightly yellowish powder comprising refractory metal oxides revealed the following composition: 66 wt.% MgO, 28 wt.% Al₂O₃, 4 wt.% CaO, 0.4 wt. % SiO₂ and 1.6 wt.% TiO₂. X-ray diffraction analysis revealed periclase and spinel as major phases.

[0088] **Example 3**

[0089] A mass of calcined metal oxides (100 grams), 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 introduced into a vitreous silica tube (1" diameter) and fluidized by a stream of synthetic smelter gas [a mixture of 15 vol.% hydrogen and 85 vol.% carbon monoxide free of deleterious sulfur-bearing compounds (*e.g.*, H₂S, COS)]. The loaded tube was heated using a vertical furnace (Lindberg) and maintained at 1000°C over a period of 2 hours. Following cooling, the pellets were ground in a pulverizer (Retsch) to produce a powder having a particle size < 200 mesh (<75 µm). The ground material was subjected to magnetic

separation using a hand magnet (Gilson). About 40 grams of an iron alloy powder was recovered along with about 40 grams of a white powder comprising refractory metal oxides. Chemical analysis of the iron alloy powder revealed the following elemental composition: 93.5 wt.% Fe, 2.5 wt.% V, 2.0 wt.% Mn, 1.5 wt.% Cr and 0.5 wt.% C. Chemical analysis of the white powder comprising refractory metal oxides revealed the following composition: 62 wt.% MgO, 31 wt.% Al₂O₃, 3 wt.% CaO, 2 wt. % SiO₂ and 1 wt.% TiO₂. X-ray diffraction analysis revealed periclase and spinel as major phases.

[0090] **Example 4**

[0091] A mass of calcined metal oxides (100 grams), 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 introduced into a magnesia boat prepared by slip casting (Custom Ceramics Inc.). The loaded magnesia boat was introduced into a gas-tight tubular retort made of heat resistant austenitic stainless steel (AISI 310). The retort was heated using a horizontal tube furnace (Lindberg) and maintained at 900°C over a period of 2 hours while a stream of pure hydrogen gas was passing through it. Following cooling, the pellets were ground in a pulverizer (Retsch) to produce a powder having a particle size < 200 mesh (<75 μm). The ground material was subjected to magnetic separation using a hand magnet (Gilson). About 40 grams of an iron alloy powder was recovered along with about 40 grams of a white powder comprising refractory metal oxides. Chemical analysis of the iron alloy powder revealed the following elemental composition: 94 wt.% Fe, 2.5 wt.% V, 2.0 wt.% Mn, and 1.5 wt.% Cr. Chemical analysis of the white powder comprising refractory metal oxides revealed the following composition: 62 wt.% MgO, 31 wt.% Al₂O₃, 3 wt.% CaO, 2 wt. % SiO₂ and 1 wt.% TiO₂. X-ray diffraction analysis revealed periclase and spinel as major phases.

[0092] **Example 5**

[0093] A mass of calcined metal oxides (100 grams), by-produced during the pyrohydrolysis of a spent aqueous acid solution containing metal chlorides and having the chemical composition reported in **Table 2** (fraction #2) was thoroughly mixed with bituminous coal (13 grams) as reductant and ground using a Braun pulverizer to a particle size < 200 mesh (<75 μm). The blend was then introduced into a magnesia crucible (2" by 5") prepared by slip casting (Custom Ceramics Inc.) and covered by a lid. The loaded crucible was introduced into a box furnace (Blue M, Lindberg) and maintained at 1000°C over a period of 2 hours. Following cooling, the agglomerated mixture was ground in a pulverizer (Retsch) to produce a powder having a particle size < 200 mesh (<75 μm). Any excess carbonaceous material (*i.e.* carbon black) was removed from the ground material by pouring it into a separatory funnel comprising carbon tetrachloride. Following decantation, the carbon-free material was dried in an oven kept at 80°C, cooled and subjected to magnetic separation using a hand magnet (Gilson). About 36 grams of an iron alloy powder was recovered along with about 48 grams of a slightly yellowish powder comprising refractory metal oxides. Chemical analysis of the iron alloy powder revealed the following elemental composition: 93 wt.% Fe, 3.0 wt.% V, 2.5 wt.% Mn, 1.0 wt.% Cr and 0.5 wt.% C. Chemical analysis of the slightly yellowish powder comprising refractory metal oxides revealed the following composition: 66 wt.% MgO, 28 wt.% Al₂O₃, 4 wt.% CaO, 0.4 wt. % SiO₂ and 1.6 wt.% TiO₂. X-ray diffraction analysis revealed periclase and spinel as major phases.

[0094] 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.

WHAT IS CLAIMED IS:

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

a) submitting mining residues or metallurgical wastes to at least one reductive thermal treatment to produce a reduced material;

b) submitting the reduced material to at least one magnetic separation step to produce magnetic fractions of differing magnetic susceptibilities; and

c) recovering the magnetic fractions.

2. The process according to claim 1, further comprising the step of comminuting the reduced material following reductive thermal treatment.

3. The process according to claim 1, 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 reductive thermal treatment.

4. The process according to claim 2, wherein the fractions of differing magnetic susceptibilities comprise at least a fraction consisting of a vanadium rich iron alloy and a fraction consisting of refractory metal oxides.

5. The process according to claim 4, wherein the fraction consisting of the vanadium rich iron alloy has a higher magnetic susceptibility relative to the fraction consisting of the refractory metal oxides.

6. The process according to claim **5**, wherein the vanadium rich iron alloy fraction comprises elements selected from the group consisting of iron, vanadium, chromium, manganese, nickel and cobalt.

7. The process according to claim **5**, wherein the refractory metal oxide fraction comprises elements selected from the group consisting of magnesium, aluminum, calcium, titanium and silicon oxides.

8. The process according to claim **2**, wherein the reductive thermal treatment is performed at a temperature ranging from 500°C to 1,500°C.

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

10. The process according to claim **2**, wherein the magnetic separation is performed using a magnetic flux ranging from 0.01 Tesla to 0.1 Tesla.

11. The process according to claim **3**, wherein the pre-reduction is performed using a reductant selected from the group consisting of a solid reductant, a liquid reductant, a gaseous reductant or mixtures thereof.

12. The process according to claim **1**, wherein the mining residues or metallurgical wastes are by-produced during the beneficiation and upgrading of titania slags.

13. The process according to claim **1**, wherein the mining residues or metallurgical wastes are by-produced during the production of pig iron and steel making.

14. The process according to claim **1**, wherein the mining residues or metallurgical wastes are by-produced during the pyrohydrolysis or spray roasting of spent pickling acids.

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

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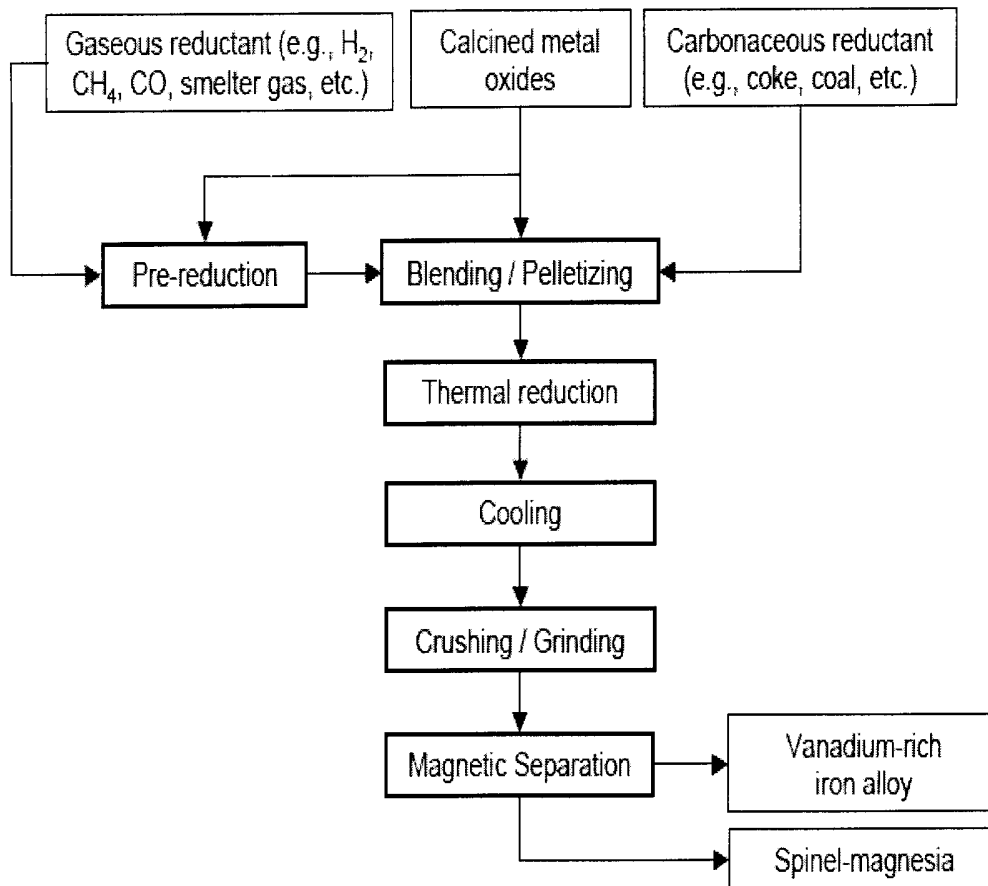


FIG. 1

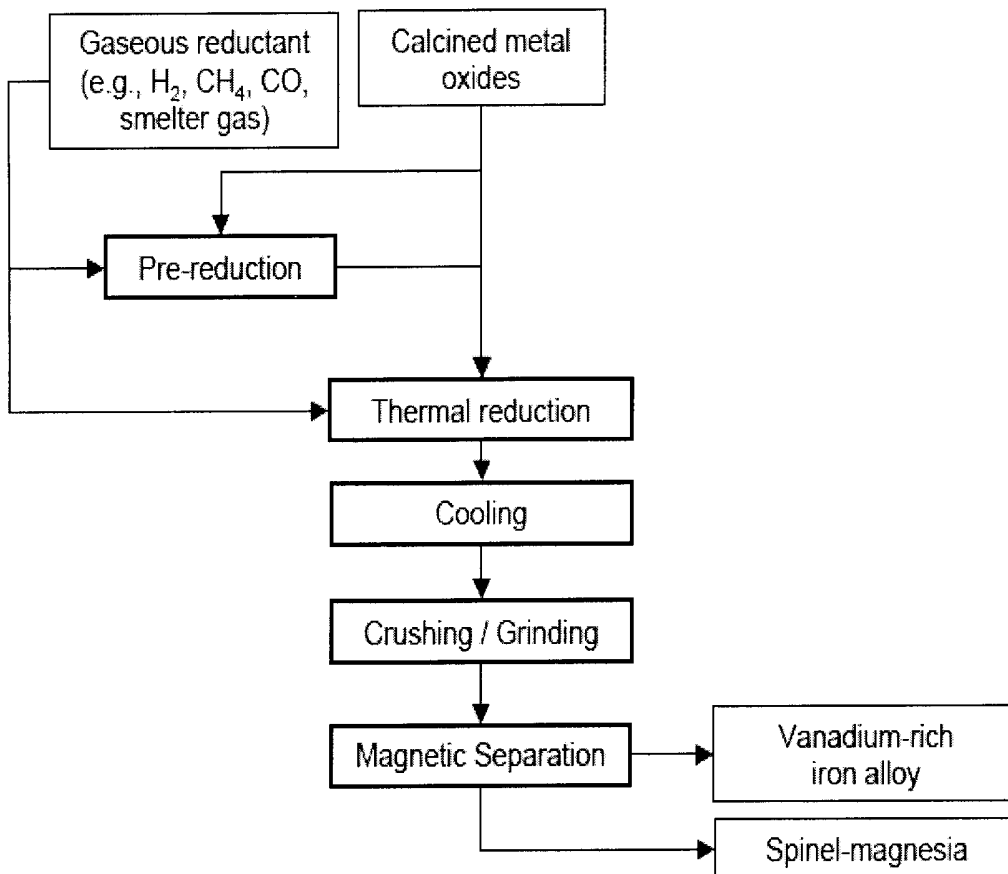


FIG.2

