(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 January 2017 (05.01.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/001081 A1

(51) International Patent Classification:
C22B 9/00 (2006.01) ***C22B 11/02*** (2006.01)

(21) International Application Number:
PCT/EP2016/059154

(22) International Filing Date:
25 April 2016 (25.04.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/186,649 30 June 2015 (30.06.2015) US

(71) Applicants: HERAEUS DEUTSCHLAND GMBH & CO. KG [DE/DE]; Heraeusstr. 12-14, 63450 Hanau (DE). **HERAEUS PRECIOUS METALS NORTH AMERICA LLC.** [US/US]; 15524 Carmenita Road, Santa Fe Springs, US 90670 (US).

(72) Inventors: RITSCHEL, Norbert; 750 Nydeck Road, Robbins, Tennessee 37852 (US). **TAYLOR, Jimmy**; 170 Hamby Road, Sunbright, Tennessee 37872 (US). **ENGLAND, Todd**; 118 White Oak Circle, Sunbright, Tennessee 37872 (US). **PETERS, Brian**; 521 Bob Armes Cr., Wartburg, Tennessee 37887 (US). **STOFFNER, Felix**; Cornelienstr. 40, 63739 Aschaffenburg (DE). **RÖHLICH, Christoph**; Doorner Str. 45c, 63456 Hanau (DE). **VOSS, Steffen**; Dolmenring 14, 63694 Limeshain (DE). **WINKLER, Holger**; Lily-Pringsheim-Weg 17, 64291 Darmstadt (DE).

(74) Agent: HERAEUS IP; Heraeus Holding GmbH, Heraeusstr. 12 - 14, 63450 Hanau (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: PROCESS FOR THE PRODUCTION OF A PGM-ENRICHED ALLOY

(57) Abstract: A process for the production of a PGM-enriched alloy comprising 0 to 60 wt.-% of iron and 20 to 99 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, the process comprising the steps: (1) providing a sulfur-free PGM collector alloy comprising 30 to 95 wt.-% of iron and 2 to 15 wt- % of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, (2) providing a copper- and sulfur-free material capable of forming a slag-like composition when molten, wherein the molten slag-like composition comprises 10 to 30 wt.-% of magnesium oxide and/or calcium oxide and 70 to 90 wt.-% of silicon dioxide, (3) melting the PGM collector alloy and the material capable of forming a slag-like composition when molten in a weight ratio of 1 : 0.75 to 5 within a converter until a multi- or two-phase system of a lower high-density molten mass comprising the molten PGM collector alloy and one or more upper low-density molten masses comprising the molten slag-like composition has formed, (4) contacting an oxidizing gas comprising 0 to 80 vol.-% of inert gas and 20 to 100 vol.-% of oxygen with the lower high-density molten mass obtained in step (3) until it has been converted into a lower high-density molten mass of the PGM-enriched alloy, (5) separating an upper low-density molten slag formed in the course of step (4) from the lower high-density molten mass of the PGM-enriched alloy making use of the difference in density, (6) letting the molten masses separated from one another cool down and solidify, and (7) collecting the solidified PGM-enriched alloy.

WO 2017/001081 A1

Process for the Production of a PGM-enriched alloy

The invention relates to a pyrometallurgical converting process for the production of a PGM-enriched alloy and to the PGM-enriched alloy itself.

The abbreviation “PGM” used herein means platinum group metal.

In general, the enrichment of PGMs by means of pyrometallurgical converting is well-known, see, for example, S.D. MCCULLOUGH, Pyrometallurgical iron removal from a PGM-containing alloy, Third International Platinum Conference ‘Platinum in Transformation’, The Southern African Institute of Mining and Metallurgy, 2008, pages 1-8.

The invention is a pyrometallurgical converting process improved in terms of yielding a PGM-enriched alloy having a considerable high PGM level and exhibiting a remarkably low PGM loss into slag formed as by-product of the pyrometallurgical converting process.

The process of the invention is a process for the production of a PGM-enriched alloy comprising 0 to 60 wt.-% (weight-%) of iron and 20 to 99 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, the process comprising the steps:

(1) providing a sulfur-free PGM collector alloy comprising 30 to 95 wt.-% of iron and 2 to 15 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium,

(2) providing a copper- and sulfur-free material capable of forming a slag-like composition when molten, wherein the molten slag-like composition comprises 10 to 30 wt.-% of magnesium oxide and/or calcium oxide and 70 to 90 wt.-% of silicon dioxide,

(3) melting the PGM collector alloy and the material capable of forming a slag-like composition when molten in a weight ratio of 1 : 0.75 to 5 within a converter until a multi- or two-phase system of a lower high-density molten mass comprising the molten PGM collector alloy and one or more upper low-density molten masses comprising the molten slag-like composition has formed,

(4) contacting an oxidizing gas comprising 0 to 80 vol.-% (volume-%) of inert gas and 20 to 100 vol.-% of oxygen with the lower high-density molten mass obtained in step (3) until it has been

converted into a lower high-density molten mass of the PGM-enriched alloy (i.e. a lower high-density molten mass of the composition of the PGM-enriched alloy),

(5) separating an upper low-density molten slag formed in the course of step (4) from the lower high-density molten mass of the PGM-enriched alloy making use of the difference in density,

(6) letting the molten masses separated from one another cool down and solidify, and

(7) collecting the solidified PGM-enriched alloy.

“0 wt.-%” appears several times in the description and the claims; it means that the respective component is not present or, if it is present, at best present in a proportion of no more than at a technically inevitable impurity level.

The process of the invention is a process for the production of a PGM-enriched alloy comprising 0 to 60 wt.-% of iron and 20 to 99 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium. It is preferred that the PGM-enriched alloy produced by the process of the invention comprises 0 to 45 wt.-% of iron and 30 to 99 wt.-% of one or more of said PGMs, in particular 0 to 20 wt.-% of iron and 40 to 90 wt.-% of one or more of said PGMs. The PGM-enriched alloy made by the process of the invention may also comprise 0 to 60 wt.-% of nickel and 0 to 5 wt.-% of copper. Examples of other elements (elements other than iron, nickel, copper, platinum, palladium and rhodium) which may be comprised by the PGM-enriched alloy made by the process of the invention include, in particular, silver, gold, aluminum, calcium and silicon. The PGM-enriched alloy made by the process of the invention may comprise one or more of said other elements in a total proportion of up to 10 wt.-%. Hence, the PGM-enriched alloy made by the process of the invention may comprise or consist of:

0 to 60 wt.-%, preferably 0 to 45 wt.-%, in particular 0 to 20 wt.-% of iron,

20 to 99 wt.-%, preferably 30 to 99 wt.-%, in particular 40 to 90 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium,

0 to 60 wt.-% of nickel,

0 to 5 wt.-% of copper, and

0 to 10 wt.-%, preferably 0 to 6 wt.-%, in particular 0 to 3 wt.-% of one or more other elements, in particular, one or more other elements selected from the group consisting of silver, gold, aluminum, calcium and silicon.

In an embodiment, the PGM-enriched alloy made by the process of the invention comprises or consists of 0 to 20 wt.-% of iron, 40 to 90 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, 0 to 60 wt.-% of nickel, 0 to 5 wt.-% of copper and 0 to 3 wt.-% of one or more other elements, in particular, one or more other elements selected from the group consisting of silver, gold, aluminum, calcium and silicon.

In step (1) of the process of the invention a sulfur-free PGM collector alloy (hereinafter also called “PGM collector alloy” for short) is provided.

The term “sulfur-free” used herein in the context of step (1) of the process of the invention means that the PGM collector alloy may comprise sulfur in a proportion of no more than at a technically inevitable impurity level of, for example, less than 1000 wt.-ppm.

PGM collector alloys are well-known to the person skilled in the art; they may typically be formed during pyrometallurgic recycling of appropriate PGM containing waste material like, for example, PGM containing waste catalysts, for example, used automotive exhaust catalysts. In the course of such pyrometallurgic recycling the PGMs are separated by smelting the PGM containing waste material, for example, ceramic supports having a PGM containing washcoat (like used automotive exhaust catalysts) together with a collector metal like, for example, iron in an oven, a so-called smelter. The PGMs form a PGM collector alloy with the collector metal, which is separated from slag formed as by-product during smelting.

The PGM collector alloy provided in step (1) comprises 30 to 95 wt.-% of iron and 2 to 15 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium. In an embodiment, the PGM collector alloy may comprise 40 to 70 wt.-% of iron, 0 to 20 wt.-% of nickel and 5 to 15 wt.-% of one or more of said PGMs. It is preferred that the PGM collector alloy comprises no more than 4 wt.-%, in particular ≤ 1 wt.-% of copper. Examples of other elements (elements other than iron, nickel, copper, platinum, palladium and rhodium) which may be comprised by the PGM collector alloy include silver, gold, aluminum, calcium, silicon, phosphorus, titanium, chromium, manganese, molybdenum and vanadium. The PGM collector alloy may comprise one or more of said other elements in a total proportion of up to 30 wt.-%. Hence, the PGM collector alloy may comprise or consist of:

30 to 95 wt.-%, in particular 40 to 70 wt.-% of iron,

0 to 20 wt.-%, in particular 0 to 15 wt.-% of nickel,

2 to 15 wt.-%, in particular 5 to 15 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium,

0 to 4 wt.-%, in particular 0 to 1 wt.-% of copper, and

0 to 30 wt.-%, in particular 0 to 20 wt.-% of one or more other elements, in particular, one or more other elements selected from the group consisting of silver, gold, aluminum, calcium, silicon, phosphorus, titanium, chromium, manganese, molybdenum and vanadium.

In an embodiment, the PGM collector alloy comprises or consists of 40 to 70 wt.-% of iron, 0 to 15 wt.-% of nickel, 5 to 15 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, 0 to 1 wt.-% copper, 0 to 20 wt.-% of one or more other elements, in particular, one or more other elements selected from the group consisting of silver, gold, aluminum, calcium, silicon, phosphorus, titanium, chromium, manganese, molybdenum and vanadium.

In step (2) of the process of the invention a copper- and sulfur-free material capable of forming a slag-like composition when molten (hereinafter also called “material capable of forming a slag-like composition when molten” for short) is provided.

The term “copper- and sulfur-free” used herein in the context of step (2) of the process of the invention means that the material capable of forming a slag-like composition when molten may comprise copper in a proportion of no more than at a technically inevitable impurity level of, for example, less than 1000 wt.-ppm and sulfur in a proportion of no more than at a technically inevitable impurity level of, for example, less than 1000 wt.-ppm.

The term “material capable of forming a slag-like composition when molten” used herein shall illustrate that the molten material looks and behaves like a slag. It shall at the same time express that it is not to be confused with the slag formed as by-product of the process of the invention, i.e. the slag obtained after conclusion of step (4). Moreover, the material capable of forming a slag-like composition when molten is not necessarily identical in composition with the one or more upper low-density molten masses formed in step (3), although it forms at least a predominant part of the latter.

The material capable of forming a slag-like composition when molten has a composition such that the molten slag-like composition itself comprises or consists of: 10 to 30 wt.-%, in particular 15 to 25 wt.-%, even more particular 20 to 25 wt.-% of magnesium oxide and/or calcium oxide,
70 to 90 wt.-%, in particular 75 to 85 wt.-%, even more particular 75 to 80 of silicon dioxide,
0 to 20 wt.-%, in particular 0 wt.-% of iron oxide (in particular FeO),
0 to 20 wt.-%, in particular 0 to 10 wt.-% of sodium oxide,
0 to 20 wt.-%, in particular 0 to 10 wt.-% of boron oxide, and
0 to 2 wt.-%, in particular 0 wt.-% of aluminum oxide.

In an embodiment, the material capable of forming a slag-like composition when molten has a composition such that the molten slag-like composition itself comprises or consists of 20 to 25 wt.-% of magnesium oxide and/or calcium oxide, 75 to 80 wt.-% of silicon dioxide, 0 wt.-% of iron oxide, 0 to 10 wt.-% of sodium oxide, 0 to 10 wt.-% of boron oxide and 0 wt.-% of aluminum oxide.

The material capable of forming a slag-like composition when molten and, as a consequence thereof, also the molten slag-like composition itself does not comprise PGMs with the exception of technically inevitable impurities. However, if the latter is present its proportion should be low; preferably such proportion does not exceed, for example, 10 wt.-ppm in the material capable of forming a slag-like composition when molten.

The material capable of forming a slag-like composition when molten itself is a combination of substances and may comprise the afore mentioned oxides or only said oxides, however, this is not necessarily the case. It may instead or additionally comprise compounds capable of forming such oxides or oxide compositions when heated during formation of the one or more upper low-density molten masses. To name just a few examples of such type of compounds: carbonates are examples of compounds which may split off carbon dioxide and form the corresponding oxides when heated and melted during formation of the one or more upper low-density molten masses; silicates are examples of compounds which may form the corresponding oxides and silicon dioxide when heated and melted during formation of the one or more upper low-density molten masses; borates are examples of compounds which may form the corresponding oxides and boron oxide when heated and melted during formation of the one or more upper low-density molten masses.

In step (3) of the process of the invention the PGM collector alloy and the material capable of forming a slag-like composition when molten are melted in a weight ratio of 1 : 0.75 to 5, preferably 1 : 0.75 to 3, even more preferably 1 : 1 to 3 within a converter until a multi-phase system of a lower high-density molten mass comprising the molten PGM collector alloy and two or more upper low-density molten masses jointly comprising the molten slag-like composition has formed or, in an embodiment, until a two-phase system of a lower high-density molten mass comprising the molten PGM collector alloy and an upper low-density molten mass comprising the molten slag-like composition has formed.

The converter is a conventional pyrometallurgical converter vessel or crucible furnace which allows for melting the PGM collector alloy and the material capable of forming a slag-like composition when molten. The converter has one or more openings at its top and it may have a cylinder- or pear-like shape, for example. Its construction may be such that it allows for a rotating and/or rocking movement to allow support of mixing of its contents. Preferably it is tiltable to allow for pouring out molten content thus enabling performing step (5) of the process of the invention. Its inner which has contact with the multi- or two-phase system of the lower high-density molten mass and the one or more upper low-density molten masses is of a heat-resistant material as is conventional for pyrometallurgical converter vessels, i.e. a material which withstands the high temperatures prevailing in process steps (3) and (4) and which is essentially inert towards the components of said multi- or two-phase system. Examples of useful heat-resistant materials include silica bricks, fireclay bricks, chrome-corundum bricks, zircon mullite bricks, zircon silicate bricks, magnesia bricks and calcium aluminate bricks.

In the course of step (3), first of all, the PGM collector alloy and the material capable of forming a slag-like composition when molten are introduced into the converter, either as premix or as separate components. The process of the invention is a batch process and it is preferred not to introduce the entire batch all at once and then to heat and melt the contents of the converter, but to introduce the materials to be melted portionwise and adapted to the melting speed. Once the entire batch has melted, said multi- or two-phase system of a lower high-density molten mass and the one or more upper low-density molten masses is obtained.

Heating of the converter contents in order to melt the latter and thus form the multi- or two-phase system means raising the temperature of the converter contents to, for example, 1200 to 1850 °C, preferably 1500 to 1800 °C. Such heating may be performed by various means either alone or in combination, i.e. for example plasma heating, indirect electrical heating, arc heating, inductive heating, indirect heating with burners, direct heating with one or more gas burners from the above and any combination of said heating methods. Direct heating with gas burners capable of producing said high temperatures in the range of 1200 to 1850 °C is a preferred method. Examples of useful gas burners include gas burners run with hydrogen or a hydrocarbon-based fuel gas and oxygen or nitrous oxide as oxidant.

After conclusion of step (3), i.e. once the multi- or two-phase system has formed, step (4) of the process of the invention is performed. In step (4) an oxidizing gas comprising or consisting of 0 to 80 vol.-% of inert gas and 20 to 100 vol.-% of oxygen, preferably 0 to 50 vol.-% of inert gas and 50 to 100 vol.-% of oxygen, in particular 0 vol.-% inert gas and 100 vol.-% of oxygen (i.e. oxygen gas) is contacted with the lower high-density molten mass obtained in step (3) until the latter has been converted into a lower high-density molten mass of the PGM-enriched alloy, i.e. the PGM-enriched alloy, has formed. Any gas inert towards the lower high-density molten mass can be taken as the inert gas, in particular argon and/or nitrogen. In preferred embodiments, contact between the oxygen or oxygen containing oxidizing gas and the lower high-density molten mass can be made by passing or bubbling the gas through the lower high-density molten mass from the bottom of the converter and/or by means of a gas lance the exhaust of which being immersed into the lower high-density molten mass. The duration of the contact with the oxidizing gas or, in other words, the amount of oxidizing gas employed depends on when the PGM-enriched alloy of the desired composition has formed. In still other words, the contact with the oxidizing gas is maintained for such period of time, until a PGM-enriched alloy with a desired composition according to any of the afore disclosed embodiments has formed; this will typically take 1 to 5 hours or 2 to 4 hours, for example. The development of the composition of the lower high-density molten mass during performance of step (4) until the PGM-enriched alloy of the desired composition has formed, can be tracked by standard analytical techniques, for example, XRF (X-ray fluorescence) analysis. As by-product an upper low-density molten slag is formed in the course of step (4).

The contact with the oxidizing gas leads to an exothermic oxidation reaction in the course of which nonprecious elements or metals are converted into oxides and absorbed by the one or more upper low-density molten masses. The oxidation process of step (4) results in depletion of elements or metals other than the PGMs, in particular in depletion of iron and, if present, other nonprecious elements or metals within the lower high-density molten mass or, if taking the reverse view, in PGM enrichment within the lower high-density molten mass.

After conclusion of step (4), i.e. once the PGM-enriched alloy of the desired composition has formed, step (5) of the process of the invention is performed. In said step (5) the upper low-density molten slag formed in step (4) is separated from the lower high-density molten mass of the PGM-enriched alloy making use of the difference in density. To this end, the content of the converter is carefully poured out making use of the well-known decantation principle. Once the upper low-density molten slag is decanted the lower high-density molten mass of the PGM-enriched alloy is poured into suitable containers.

Steps (3) to (5) of the process of the invention constitute a sequence of steps, in particular in direct succession. This needs to be understood in such sense that no further steps or at least no further fundamental steps are required or performed between or during said steps (3) to (5). Examples of optional non-fundamental steps are (i) the removal of part of upper low-density molten mass in the course of step (4) or (ii) addition of PGM collector alloy and/or material capable of forming a slag-like composition when molten in the course of step (4).

After conclusion of step (5) subsequent step (6) is performed, in which the separated molten masses are allowed to cool down and solidify.

After solidification the solidified PGM-enriched alloy is collected in step (7). It may then be subject to further conventional refinement, for example, electrometallurgical and/or hydrometallurgical refinement in order to finally obtain the individual PGMs either as metal or as PGM compound or as a solution of the latter.

It is the advantage of the process of the invention that the PGM-enriched alloy collected in step (7) is distinguished by a relatively high PGM content. This relatively high PGM content means less effort and less consumption of chemicals with a view to said further refinement processes. It is a further remarkable advantage of the process of the invention that the slag formed as by-product during step (4) comprises a very low PGM content of less than 50 wt.-ppm. It is not finally understood why, but it is believed that the 1 : 0.75 to 5 or 1 : 1 to 3 weight ratio combination of the specifically composed PGM collector alloy provided in step (1) and the specifically composed material capable of forming a slag-like composition when molten provided in step (2) is key in particular with regard to the remarkably low loss of PGMs into the slag formed as by-product during step (4) of the process of the invention.

Examples

Example 1:

A premix of 500 kg of a sulfur-free PGM collector alloy comprising 49 wt.-% of iron, 13.1 wt.-% of nickel, 8.1 wt.-% of silicon, 4.6 wt.-% of palladium, 3.2 wt.-% of chromium, 2.5 wt.-% of titanium, 2.2 wt.-% of platinum, 1.3 wt.-% of manganese, 0.6 wt.-% of rhodium and 0.4 wt.-% of copper, 120 kg of calcium oxide, 450 kg of silicon dioxide, 15 kg of sodium carbonate and 15 kg of borax was portionwise introduced into an already 1500°C hot cylindrical natural gas-heated furnace and further heated to 1700 °C. After a melting time of 10 hours a two-phase system of a lower high-density molten mass comprising the PGM collector alloy and an upper low-density molten mass comprising a slag-like composition was formed. Oxygen was introduced into the lower high-density molten mass via a ceramic pipe with an oxygen flow of 900 l/min. After 2.5 hours the oxygen introduction was stopped. The upper low-density molten mass was poured into cast iron slag pots in order to cool down and solidify. The lower high-density molten mass was then poured into graphite molds in order to cool down and solidify. After solidification and cooling down to ambient temperature both materials were analyzed by XRF.

Examples 2 and 3:

Example 1 was repeated with the difference that the oxygen introduction took 2.75 hours (Example 2) or 3 hours (Example 3).

The results of the XRF analysis are compiled in Tables 1 and 2. All values are in wt.-%, except the values for the PGM content in the slag which are in wt.-ppm:

Element	Example 1	Example 2	Example 3
Fe	19	12	12
Ni	52	55	49
Cu	2	2	2
Pt	9	11	10
Pd	16	17	24
Rh	2	3	3

Table 1: Composition of the solidified lower high-density mass (PGM enriched alloy)

Element	Example 1	Example 2	Example 3
PGM	48	49	40
Fe	28	30	33
Ni	1	1	2

Table 2: Composition of the solidified upper low-density mass (slag)

CLAIMS

1. A process for the production of a PGM-enriched alloy comprising 0 to 60 wt.-% of iron and 20 to 99 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium, the process comprising the steps:

(1) providing a sulfur-free PGM collector alloy comprising 30 to 95 wt.-% of iron and 2 to 15 wt.-% of one or more PGMs selected from the group consisting of platinum, palladium and rhodium,
(2) providing a copper- and sulfur-free material capable of forming a slag-like composition when molten, wherein the molten slag-like composition comprises 10 to 30 wt.-% of magnesium oxide and/or calcium oxide and 70 to 90 wt.-% of silicon dioxide,
(3) melting the PGM collector alloy and the material capable of forming a slag-like composition when molten in a weight ratio of 1 : 0.75 to 5 within a converter until a multi- or two-phase system of a lower high-density molten mass comprising the molten PGM collector alloy and one or more upper low-density molten masses comprising the molten slag-like composition has formed,
(4) contacting an oxidizing gas comprising 0 to 80 vol.-% of inert gas and 20 to 100 vol.-% of oxygen with the lower high-density molten mass obtained in step (3) until it has been converted into a lower high-density molten mass of the PGM-enriched alloy,
(5) separating an upper low-density molten slag formed in the course of step (4) from the lower high-density molten mass of the PGM-enriched alloy making use of the difference in density,
(6) letting the molten masses separated from one another cool down and solidify, and
(7) collecting the solidified PGM-enriched alloy.

2. The process of claim 1, wherein the PGM-enriched alloy comprises or consists of:
0 to 45 wt.-% of iron,
30 to 99 wt.-% of the one or more PGMs,
0 to 60 wt.-% of nickel,
0 to 5 wt.-% of copper, and
0 to 10 wt.-% one or more other elements.

3. The process of claim 1, wherein the PGM-enriched alloy comprises or consists of:
0 to 20 wt.-% of iron,
40 to 90 wt.-% of the one or more PGMs,
0 to 60 wt.-% of nickel,
0 to 5 wt.-% of copper, and
0 to 3 wt.-% of one or more other elements.

4. The process of claim 2 or 3, wherein the one or more other elements are selected from the group consisting of silver, gold, aluminum, calcium and silicon.

5. The process of any one of the preceding claims, wherein the PGM collector alloy provided in step (1) comprises 40 to 70 wt.-% of iron, 0 to 20 wt.-% of nickel and 5 to 15 wt.-% of the one or more PGMs.

6. The process of any one of the preceding claims, wherein the PGM collector alloy comprises no more than 4 wt.-% of copper.

7. The process of any one of claims 1 to 4, wherein the PGM collector alloy comprises or consists of:
30 to 95 wt.-% of iron,
0 to 20 wt.-% of nickel,
2 to 15 wt.-% of the one or more PGMs,
0 to 4 wt.-% of copper, and
0 to 30 wt.-% one or more other elements.

8. The process of any one of claims 1 to 4, wherein the PGM collector alloy comprises or consists of:
40 to 70 wt.-% of iron,
0 to 15 wt.-% of nickel,
5 to 15 wt.-% of the one or more PGMs
0 to 1 wt.-% copper,
0 to 20 wt.-% of one or more other elements.

9. The process of claim 7 or 8, wherein the one or more other elements are selected from the group consisting of silver, gold, aluminum, calcium, silicon, phosphorus, titanium, chromium, manganese, molybdenum and vanadium.

10. The process of any one of the preceding claims, wherein the molten slag-like composition comprises or consists of:
10 to 30 wt.-% of magnesium oxide and/or calcium oxide,
70 to 90 wt.-% of silicon dioxide,
0 to 20 wt.-% of iron oxide,
0 to 20 wt.-% of sodium oxide,
0 to 20 wt.-% of boron oxide, and
0 to 2 wt.-% of aluminum oxide.

11. The process of any one of claims 1 to 9, wherein the molten slag-like composition comprises or consists of:
20 to 25 wt.-% of magnesium oxide and/or calcium oxide,
75 to 80 wt.-% of silicon dioxide,
0 wt.-% of iron oxide,
0 to 10 wt.-% of sodium oxide,
0 to 10 wt.-% of boron oxide, and
0 wt.-% of aluminum oxide.

12. The process of any one of the preceding claims, wherein the PGM collector alloy and the material capable of forming a slag-like composition when molten are melted in a weight ratio of 1 : 0.75 to 3 or 1 : 1 to 3.

13. The process of any one of the preceding claims, wherein the temperature of the converter contents is raised to 1200 to 1850 °C.

14. The process of any one of the preceding claims, wherein the oxidizing gas is oxygen.

15. The process of any one of the preceding claims, wherein the contact between the oxidizing gas and the lower high-density molten mass is made by passing or bubbling the gas through the lower high-density molten mass from the bottom of the converter and/or by means of a gas lance the exhaust of which being immersed into the lower high-density molten mass.

16. The process of any one of the preceding claims, wherein the contacting with the oxidizing gas takes 1 to 5 hours.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059154

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B9/00 C22B11/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	S.D. Mccullough ET AL: "PYROMETALLURGICAL IRON REMOVAL FROM A PGM-CONTAINING ALLOY 169", , 1 January 2008 (2008-01-01), pages 169-176, XP055282629, Retrieved from the Internet: URL:http://pbzn.org/Pt2008/Papers/169-176_McCullough.pdf [retrieved on 2016-06-22] cited in the application the whole document -----	1-16
A	GB 2 086 941 A (ENGELHARD CORP) 19 May 1982 (1982-05-19) the whole document ----- -/--	1-16

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 23 June 2016	Date of mailing of the international search report 04/07/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Swiatek, Ryszard

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059154

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 428 768 A (DAY JOSEPH G [GB]) 31 January 1984 (1984-01-31) the whole document -----	1-16
A	EP 0 512 959 A2 (TANAKA PRECIOUS METAL IND [JP]; DOWA MINING CO [JP]; KOSAKA SMELTING &) 11 November 1992 (1992-11-11) the whole document -----	1-16
A	EP 2 666 876 A1 (DOWA METALS & MINING CO LTD [JP]) 27 November 2013 (2013-11-27) the whole document -----	1-16

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/059154

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2086941 A	19-05-1982	FR 2493342 A1	07-05-1982
		GB 2086941 A	19-05-1982
		GB 2087056 A	19-05-1982
US 4428768 A	31-01-1984	BE 886894 A1	16-04-1981
		CA 1162054 A	14-02-1984
		DE 3047194 A1	17-09-1981
		FR 2472617 A1	03-07-1981
		JP S6366885 B2	22-12-1988
		JP S56112427 A	04-09-1981
		US 4428768 A	31-01-1984
		ZA 8007646 A	24-02-1982
EP 0512959 A2	11-11-1992	CA 2065601 A1	11-10-1992
		DE 69220617 D1	07-08-1997
		DE 69220617 T2	16-10-1997
		EP 0512959 A2	11-11-1992
		JP 3222894 B2	29-10-2001
		JP H04317423 A	09-11-1992
		US 5252305 A	12-10-1993
EP 2666876 A1	27-11-2013	CA 2825122 A1	26-07-2012
		CN 103328662 A	25-09-2013
		EP 2666876 A1	27-11-2013
		JP 5713697 B2	07-05-2015
		JP 2012149298 A	09-08-2012
		KR 20140005240 A	14-01-2014
		US 2014053687 A1	27-02-2014
		WO 2012099009 A1	26-07-2012