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(54) **Title**: LITHIUM-RICH METALLURGICAL SLAG

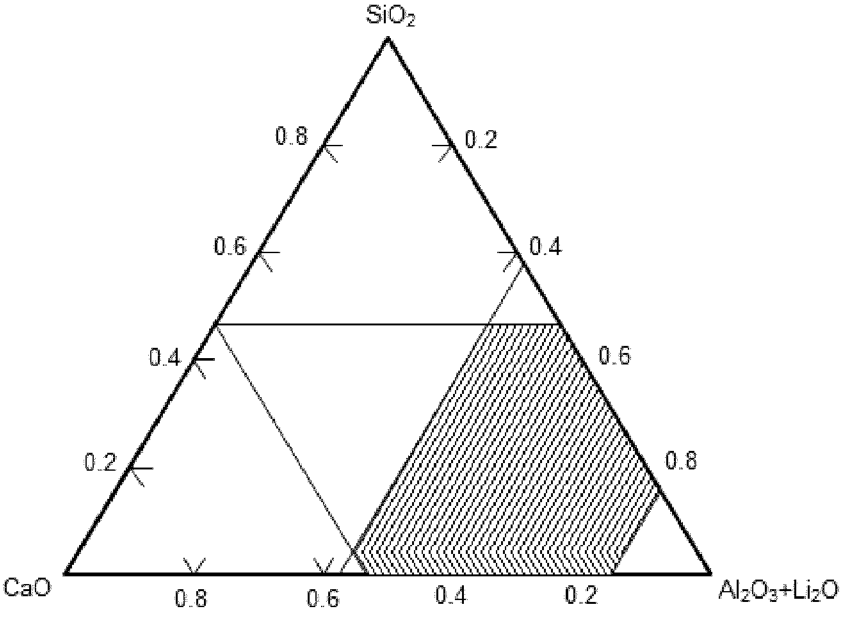

Fig. 1

(57) **Abstract**: The present invention concerns a slag composition having a high lithium content, suitable as additive in the manufacture of end-user products, or for the economic recovery of the contained lithium. The lithium concentration indeed compares favorably with that of spodumene, the classic mineral mined for lithium production. This slag is characterized by a composition according to : $3\% < Li_2O < 20\%$; $1\% < MnO < 7\%$; $38\% < Al_2O_3 < 65\%$; $CaO < 55\%$; and, $SiO_2 < 45\%$.

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Lithium-rich metallurgical slag

The present invention concerns a slag composition having a high lithium content, suitable as additive in the manufacture of end-user products, or for the economic recovery of the contained lithium.

Lithium is normally sourced from ore deposits or from salt brines. For the reasons detailed below, lithium valuation and recovery from secondary materials has however become an important economic and environmental issue.

The lithium content (expressed as Li_2O) of commercial ore deposits is typically below 3% (all % expressed by weight). The ore can be concentrated to 4 to 8% using common mining techniques such as milling, classification and flotation. The mineral concentrates can be used directly in end products or for the preparation of pure compounds such as lithium carbonates or hydroxides. Lithium extracted from salt brines is mainly used for the production of pure lithium compounds.

Lithium is found in more than 100 different minerals, but it is in practice extracted only from spodumene ($Li_2O.Al_2O_3.4SiO_2$), lepidolite ($KLi_2Al(Al,Si)_3O_{10}(F,OH)_2$), petalite ($LiAlSi_4O_{10}$), amblygonite ($(Li,Na)AlPO_4(F,OH)$), and eucryptite ($LiAlSiO_4$).

For some applications, both mineral concentrates and pure compounds are needed, such as in glass, ceramics, and glass-ceramic manufacturing. For other applications like greases, aluminum smelting, and rechargeable batteries, only pure compounds are needed. Lithium, furthermore, goes in its metallic form in lithium primary batteries, and in specific pharmaceuticals and catalysts.

The demand for pure lithium compounds in rechargeable batteries is expected to exceed that of all other applications in the near future. Recycling lithium-bearing batteries is consequently a major topic, the economic driving force being further boosted if the cobalt and nickel contained in such batteries can be valuated alongside with the lithium. Pyrometallurgy processes lend themselves well to reach this combined objective.

In a known pyrometallurgy process using a molten bath furnace for the recycling of e.g. lithium-bearing batteries, the addition of fluxing compounds leads to the formation of a slag wherein the more easily oxidized elements such as aluminum, silicon and lithium are collected; the less easily oxidized elements such as copper, nickel, and cobalt are collected in a separate alloy phase.

When processing lithium batteries in a molten bath furnace, Al_2O_3 is an important yet unavoidable slag component: metallic aluminum is indeed typically present in the electrodes or casing and will oxidize despite the strong reducing conditions maintained to form the alloy. Classically, CaO and SiO_2 are added as fluxing compounds to bring the melting point of the slag down to a reasonable working temperature. The obtained slag is of low economic value because of the dilution of the lithium by the fluxing agents. It may moreover contain significant amounts of heavy metals, precluding its re-use in some applications.

It has now been found that high concentration of Li_2O combined with MnO can reduce the viscosity of a slag containing high amounts of Al_2O_3. As a result, less CaO and SiO_2 is needed as fluxing agents, thus avoiding the lithium dilution effect. Yet, by respecting specific bounds of compositions, practical working conditions of melting point and viscosity are reached below 1700°C, or even below 1600°C. The latter temperature limit is advantageous in view of the lower energy demands and of the increased longevity of the furnace lining.

More specifically, a suitable Li_2O bearing metallurgical slag should comprise:
$3\% < Li_2O < 20\%$;
$1\% < MnO < 7\%$;
$38\% < Al_2O_3 < 65\%$;
$CaO < 55\%$; and,
$SiO_2 < 45\%$.

Figure 1 illustrates the above-defined domain as a hatched area on a CaO – SiO_2 – (83% Al_2O_3+17% Li_2O) phase diagram. It should be noted that this representation is approximate and indicative only: it is only valid for a fixed albeit typical Al_2O_3 to Li_2O ratio of 83 to 17, and it does not account for other compounds such as MnO or FeO.

The lower limit on the Li_2O of 3%, together with the upper limits on fluxing agents CaO and SiO_2 of respectively 55% and 45%, define a domain where the valorization of lithium remains economical, without facing too high a penalty due to dilution.

The upper limit on the Al_2O_3 content, together with the lower bound on the sum of CaO and SiO_2 ensure that the slag melting point remains below 1700°C. By limiting Al_2O_3 to 55%, a further decrease of temperature is possible, down to 1600°C or less.

The slag will consist essentially of Al_2O_3, SiO_2, CaO, Li_2O, and MnO, these 5 compounds forming at least 73% of the total composition. Other typical compounds that may be present are FeO and MgO. In a preferred embodiment, the above-mentioned essential compounds should represent more than 80% of the total slag composition.

The Li_2O concentration is preferably higher than 5%, more preferably higher than 10%. This ensures a better recovery yield of the lithium as e.g. carbonate or hydroxide when processing the slag to obtain pure lithium compounds. Suitable processes for this could be any one of the known acid or alkaline leaching processes similar to those used for lithium recovery from spodumene.

The upper limit for Li_2O in the slag is a practical one, as its viscosity becomes impractical when a concentration of more than 20% is reached.

The upper limit on SiO_2, when combined with a minimum amount of MnO, helps in keeping the viscosity of the slag sufficiently low, even at temperatures close to the melting point. A low viscosity is important to allow for the fast and complete settling of the metallic alloy phase. A deficient decantation would indeed result in alloy droplets remaining dispersed in the slag. This would jeopardize the cobalt yields.

MnO is also beneficial as an additive in the manufacture of glass, ceramics and glass-ceramics. MnO is indeed often added to obtain a brown to purple color. MnO is also used in mold powders, which provide lubrication and control the heat transfer in e.g. steel slab casting.

A proper level of reduction is needed during smelting to collect the cobalt and nickel in an alloy phase. A lesser level of reduction would limit the re-use of the slag to those rare application where cobalt oxide is actually welcome, such as for the manufacture of blue glass. More generic reuse could however be precluded.

Indeed, the current European REACH regulation addresses the production and use of chemical substances and their potential impact on human health (cf. Annex VI of the CLP Regulation (EC) No 1272/2008). Cobalt oxide, as well as cobalt metal, is hereby taken into account for the determination of the substances' classification. Both cobalt-bearing species contribute significantly, but other typical slag impurities also have to be accounted for. In view of a favorable classification, a total cobalt content in the slag of less than 1% is preferred, less than 0.5% being more preferred.

According to a preferred embodiment, a SiO_2 concentration lower than 25%, or more preferably lower than 15% is chosen. The specific benefits of reducing the SiO_2, thus selecting working conditions in the lower-left part of the shaded area in Figure 1 are:
- SiO_2 tends to increase the viscosity of the slag, which is undesired;
- SiO_2 interferes with some of the lithium refining steps.

According to a preferred embodiment, a CaO concentration lower than 25%, or more preferably lower than 15% is chosen. The specific benefits of selecting working conditions in the upper-right part of the hatched area in Figure 1 are:
- A more concentrated lithium slag is obtained, as the lithium is not diluted by CaO; more Li_2O means that even less CaO is needed to guarantee a low viscosity, as it is assumed that Li_2O may substitute CaO with respect to this effect;
- Because calcium is usually added as limestone, which contains carbonates, an appreciable amount of energy is required for its conversion to CaO, thereby releasing CO_2, which is undesired;
- Slag depleted in CaO can be used in applications where calcium is not well tolerated, such as in glass-ceramics manufacturing;
- A low CaO content is also desirable when the slag is processed for the recovery of lithium as pure compounds. Calcium indeed interferes with some of the purification steps.

In another embodiment of the invention, a pyrometallurgy process for smelting lithium-bearing batteries, their components or their scraps is defined, thereby producing a metal-bearing alloy, and a Li_2O bearing metallurgical slag according to the above-mentioned characteristics.

The different embodiments are illustrated with the following example.

Use is made of an apparatus comprising a bath smelter equipped with a lance for blowing gasses directly into the slag layer residing on top of the molten metal alloy. A so-called starting bath of molten slag is provided, such as from a previous operation performed in similar conditions.

Spent rechargeable lithium-ion batteries are fed to the furnace at a rate of 100kg/h while limestone ($CaCO_3$) and sand (SiO_2) are simultaneously added at rates of 10kg/h and 5.5kg/h respectively. About 38Nm^3 O_2 per ton batteries is supplied through the lance to provide heat to the furnace. This amount is chosen so as to guarantee strongly reducing conditions, i.e. leading to the formation of an alloy collecting copper, nickel, iron, and cobalt, each with yields of preferably more than 95% versus total elemental input.

In this particular case, the process appears to be autogenous, as no additional fuel is needed. This is due to the relatively high amounts of reducing agents such as metallic aluminum (about 6%) and carbon (about 20 to 25%) in the spent batteries treated. A bath temperature between 1400°C and 1700°C is achieved, which is suitable to maintain both the slag and the alloy sufficiently fluid for easy tapping and handling. The produced alloy and slag are then tapped, either periodically or continuously.

Table 1 shows the amounts and analyses of the input and output phases of the process, on an hourly basis. The figures between parentheses correspond to the elemental concentrations expressed as weight % of the main oxidized species assumed to prevail in the slag. Significantly more than 50% of the lithium reports to the slag, while a minor fraction escapes with the fumes. The slag is fluid and is free of metallic droplets.

Table 2 illustrates other slag compositions that are obtained using a similar process. These slags correspond to the above-mentioned suitable Li_2O bearing metallurgical slag, and/or according to said first or second preferred embodiments.

Table 1: Input and output phases of the process on an hourly basis

Input	**Mass (kg)**	**Composition (%)**								
		Cu	Ni	Fe	Co	Mn (MnO)	Al (Al_2O_3)	Si (SiO_2)	Li (Li_2O)	$CaCO_3$ (CaO)
Batteries	100	10	4.0	14	10	2.0	6.0		1.5	
Sand	5.5							(100)		
Limestone	10									100
Output										
Alloy	40	25	10	35	25	4.0				
Slag 1	26	0.08	0.05	0.17	0.1	(2.1)	(44.4)	(21.8)	(8.4)	(22)

Table 2: Composition of other slags produced

	Composition (%)								
	Cu	Ni	Fe	Co	MnO	Al_2O_3	SiO_2	Li_2O	CaO
Slag 2	0.60	0.20	1.60	0.90	2.6	44.2	30.0	9.0	11.4
Slag 3	0.10	0.06	0.40	0.25	1.3	48.0	36.4	11.6	2.5
Slag 4	0.30	0.10	1.00	0.20	3.9	39.1	25.7	8.1	8.0
Slag 5	0.18	0.07	0.46	0.35	2.5	47.6	21.1	9.0	16.6
Slag 6	0.09	0.02	0.36	0.21	1.2	48.4	18.9	9.8	22.8

The described metallurgical slags are suitable as such with respect to the smelting process itself: they allow for the desired separation between more easily oxidized metals such as lithium, and less easily oxidized metals such as cobalt and nickel. The Li_2O content of the slag may reach concentrations well above those found in minerals, making the slag an economical source for lithium recovery. The process also allows for the recovery of other valuable metals, in particular cobalt and nickel, which are concentrated in metallic form in the alloy.

Claims

1. A Li_2O bearing metallurgical slag comprising Al_2O_3, SiO_2, CaO, and MnO, characterized by a by-weight composition according to:
$3\% < Li_2O < 20\%$;
$1\% < MnO < 7\%$;
$38\% < Al_2O_3 < 65\%$;
$CaO < 55\%$; and,
$SiO_2 < 45\%$.

2. A Li_2O bearing metallurgical slag according to claim 1, characterized in that the Li_2O concentration is higher than 5%, more preferably higher than 10%.

3. A Li_2O bearing metallurgical slag according to claims 1 or 2, characterized in that the SiO_2 concentration is lower than 25% or more preferably lower than 15%.

4. A Li_2O bearing metallurgical slag according to claims 1 or 2, characterized in that the CaO concentration is lower than 25%, more preferably lower than 15%.

5. A Li_2O bearing metallurgical slag according to any one of claims of 1 to 4, characterized in that the sum of the Al_2O_3, SiO_2, CaO, MnO, and Li_2O concentrations is higher than 80%.

6. Use of the Li_2O bearing metallurgical slag according to any one of 1 to 4, in a smelting process, wherein lithium-bearing batteries, their components or their scraps are fed to the process, so as to produce a metal-bearing alloy, and said lithium bearing metallurgical slag.

7. Use according to claim 6 of the Li_2O bearing metallurgical slag in a smelting process, wherein the total cobalt in the slag is lower than 0.5%.

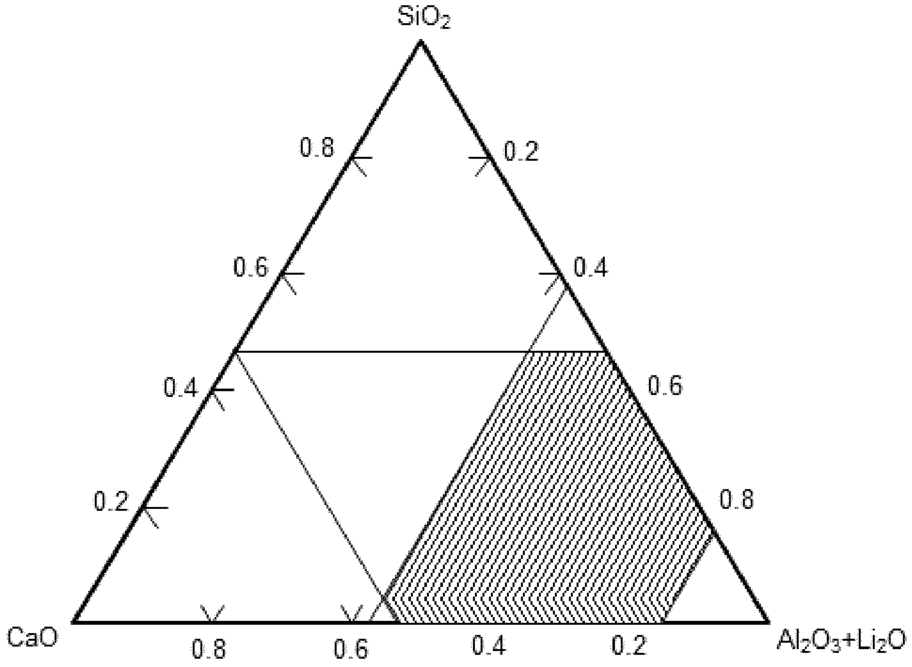

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/050097

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B7/04 C22B26/12
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, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ELWERT T ET AL: "Phase composition of high lithium slags from the recycling of lithium ion batteries", WORLD OF METALLURGY - ERZMETALL, GDMB - MEDIENVERLAG, CLAUSTHAL-ZELLERFELD, DE, vol. 65, no. 3, 1 May 2012 (2012-05-01), pages 163-171, XP009185147, ISSN: 1613-2394 the whole document -----	1-7
A	WO 2011/141297 A1 (UMICORE NV [BE]; YAZICIOGLY BEGUM [BE]; TYTGAT JAN [BE]) 17 November 2011 (2011-11-17) the whole document -----	1-7

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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"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 15 February 2017	Date of mailing of the international search report 22/02/2017
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 Juhart, Matjaz

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/050097

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011141297 A1	17-11-2011	NONE	