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- (54) Benævnelse: **LITHIUMRIG METALLURGISK SLAGGE**
- (56) Fremdragne publikationer:
WO-A1-2011/141297
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

DESCRIPTION

[0001] 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.

[0002] 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.

[0003] 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.

[0004] Lithium is found in more than 100 different minerals, but it is in practice extracted only from spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), lepidolite ($\text{KLi}_2\text{Al}(\text{Al},\text{Si})_3\text{O}_{10}(\text{F},\text{OH})_2$), petalite ($\text{LiAlSi}_4\text{O}_{10}$), amblygonite ($\text{Li},\text{Na}\text{AlPO}_4(\text{F},\text{OH})$), and eucryptite (LiAlSiO_4).

[0005] 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.

[0006] 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 valued alongside with the lithium. Pyrometallurgy processes lend themselves well to reach this combined objective.

[0007] 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.

[0008] 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 SiO₂ 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.

[0009] It has to be noted that Elwert et al. (World of Metallurgy - Erzmetall vol.65, no.3, 2012, pages 163-171) investigate the phase composition and structure of some lithium containing slags originating from a pyro-metallurgical process for battery recycling.

[0010] In another document, WO 2011/141297 A1, a lithium-bearing metallurgical slag is presented as aggregate in concrete. This slag does not contain MnO.

[0011] It has now been found that high concentration of Li₂O combined with MnO can reduce the viscosity of a slag containing high amounts of Al₂O₃. As a result, less CaO and SiO₂ 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.

[0012] More specifically, a suitable Li₂O bearing metallurgical slag should comprise:

3% < Li₂O < 20%;

1% < MnO < 7%;

38% < < 65%;

CaO < 55%;

SiO₂ < 45%; and,

Li₂O + Al₂O₃ + SiO₂ + CaO + MnO ≥ 73%.

[0013] Figure 1 illustrates the above-defined domain as a hatched area on a CaO - SiO₂ - (83% Al₂O₃+17% Li₂O) phase diagram. It should be noted that this representation is approximate and indicative only: it is only valid for a fixed albeit typical to Li₂O ratio of 83 to 17, and it does not account for other compounds such as MnO or FeO.

[0014] 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.

[0015] 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 cobaltbearing 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] The different embodiments are illustrated with the following example.

[0020] 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.

[0021] 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 $38\text{Nm}^3 \text{O}_2$ 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.

[0022] 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.

[0023] 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.

[0024] 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		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	

	Composition (%)								
	Cu	Ni	Fe	Co	MnO		SiO ₂	Li ₂ O	CaO
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

[0025] 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 Li₂O 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.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- [WO2011141297A1](#) **[0010]**

Non-patent literature cited in the description

- **ELWERT et al.** World of Metallurgy - Erzmetall, 2012, vol. 65, 3163-171 **[0009]**

PATENTKRAV

1. Li_2O -holdig metallurgisk slagge, der omfatter Al_2O_3 , SiO_2 , CaO og MnO ,
kendetegnet ved en sammensætning efter vægt ifølge:

$\text{Co} < 1 \%$;

5 $3 \% < \text{Li}_2\text{O} < 20 \%$;

$1 \% < \text{MnO} < 7 \%$;

$38 \% < \text{Al}_2\text{O}_3 < 65 \%$;

$\text{CaO} < 55 \%$;

$\text{SiO}_2 < 45 \%$; og

10 $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CaO} + \text{MnO} \geq 73 \%$.

2. Li_2O -holdig metallurgisk slagge ifølge krav 1, **kendetegnet ved, at**
 Li_2O -koncentrationen er højere end 5 %, mere fortrinsvis højere end 10 %.

3. Li_2O -holdig metallurgisk slagge ifølge kravene 1 eller 2, **kendetegnet**
ved, at SiO_2 -koncentrationen er lavere end 25 % eller mere fortrinsvis lavere
15 end 15 %.

4. Li_2O -holdig metallurgisk slagge ifølge kravene 1 eller 2, **kendetegnet**
ved, at CaO -koncentrationen er lavere end 25 %, mere fortrinsvis lavere end
15 %.

5. Li_2O -holdig metallurgisk slagge ifølge et hvilket som helst af kravene af
20 1 til 4, **kendetegnet ved, at** summen af Al_2O_3 -, SiO_2 -, CaO -, MnO - og Li_2O -
koncentrationerne er højere end 80 %.

6. Anvendelse af den Li_2O -holdige metallurgiske slagge ifølge et hvilket
som helst af 1 til 4 i en smelteproces, hvor lithiumholdige batterier, komponenter
deraf eller affald deraf tilføres processen med henblik på at fremstille en
25 metalholdig legering og den lithiumholdige metallurgiske slagge.

7. Anvendelse ifølge krav 6 af den Li_2O -holdige metallurgiske slagge i en smelteproces, hvor det samlede cobaltindhold i slaggen er lavere end 0,5 %.

DRAWINGS

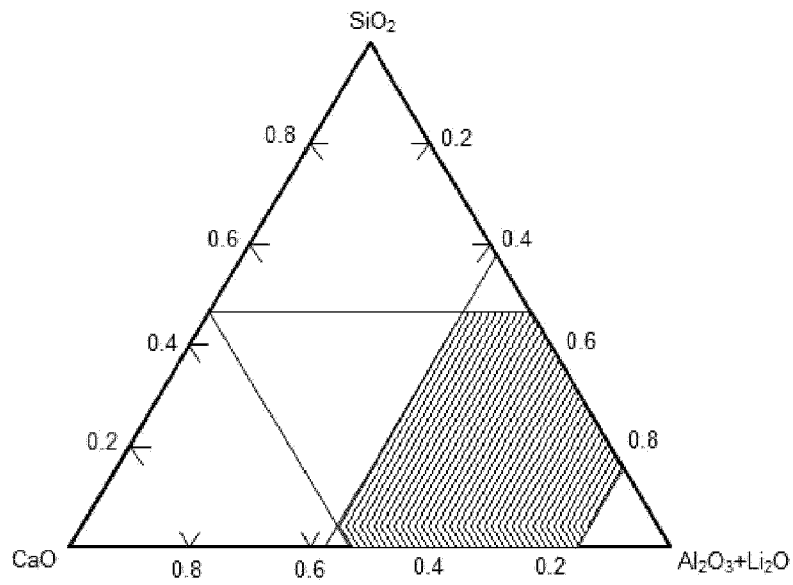


Fig. 1