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THE FUNDAMENTAL ASPECTS OF FERRO-ALLOY PRODUCTION FROM SPENT LITHIUM-ION BATTERIES BY REDUCTION USING CALCIUM-ALUMINATE SLAGS

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Abstract: The production of ferro-alloys from waste Li-ion batteries has been examined thermosdynamically and experimentally. It was found that Co and Ni can be reduced even with relatively low p_{CO}/p_{CO2} ratios in the gas phase, while the reduction of Mn or Fe requires strongly reducing conditions and higher temperatures. Even the reduction and selective recovery of Li are thermodynamically possible due to the possible evaporation. The optimum slag compositions were evaluated theoretically, followed by an experimental investigation. Ferrocobalt, ferrocobalt-nickel and ferrocobalt-nickel-manganese were produced using calcium-magnesium-ferrite type slags. Furthermore, secondary Al dross – containing Al – was also tested both as a reducing and a slag-forming agent for the production of ferrocobalt and ferromanganese affiné.

Keywords: Li-ion battery, recycling, ferroalloys, slag

INTRODUCTION

In the past decade, Li-ion batteries have been employed mainly in portable devices; however, the abrupt spreading of electromobility and grid energy storage systems greatly enhanced their production [1] [2] and the scale of their application. These secondary batteries can be categorized by their active cathode materials. Portable devices mostly use $LiCoO_2$ (LCO) type cathode chemistry, while the automotive sector mainly applies Ni-rich chemistries such as the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811) or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) materials [3] [3] [4] [5] [6] [7]. Formerly conventional compositions like the $LiMnO_2$ (LMO) or $LiFePO_4$ (LFP) are of less importance, although, the latter can be revived by a suspected massive Chinese interest. Increased consumption will undoubtedly lead to an increased flux of waste materials, too. Due to the metallic values (Al, Cu, Co, Ni, Mn and Li) and environmental concerns, the spent batteries and the production wastes need to be recycled. This process usually begins with a physical preparation where the batteries are shredded, and the material is classified by type and particle size to enrich the metallic and oxidic portions in different fractions. The finest fraction (usually <0.1 mm) is called the black mass, consisting of graphite from the anode and the oxides from the cathode (referred to as the active cathode material). In case of the modern NMC and the popular LCO batteries, the high Ni and Co contents make this material highly valuable. The concentration of the valuable transition metals can reach ~40%. Nevertheless, the usual ~4% Li content is also of concern. The price for battery grade $LiOH.H_2O$ (16% Li) is 80,000 $/t, while for Co and Ni metal, it is ~60,000 $/t and ~30,000 $/t, respectively. The utilization of

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black mass can be versatile, depending on the desired end product. Pyrometallurgical recycling by Ni-Co-Cu smelters can produce a Ni-Co-Cu alloy, while Li and Mn are transferred into the slag phase. Hydro-electrometallurgy can produce pure metal compounds or metals [8] [9] [10] [11] [12]. Another option, however, is the production of ferroalloys, as both Co and Ni are important alloying elements of steel. Like most elements, these are introduced into the melt in the forms of ferroalloys such as ferrocobalt, ferronickel or mixed ferrocobalt-nickel. Since there are no abundant sources of oxidic Ni or Co raw materials [13], ferroalloy-producing companies must often buy expensive Co and Ni produced by electrolytic reduction to be smelted in electric arc furnaces with steel scrap or iron ore into the desired ferroalloy. A new approach could be the utilization of black mass for the production of these alloys. Since the black mass contains ~50% graphite, the reducing agent is mostly present in the raw material. Moreover, at high temperatures (1500–1600 °C), Li can be selectively volatilised and recovered in the electric arc flue dust as Li_2CO_3. However, such smelting operations require precisely optimized slag for smooth quality production. This article is focused on the fundamental aspects of ferroalloy production from the black mass of spent LCO and NMC 811 batteries using different types of slags.

1. EXPERIMENTAL PROCEDURE AND MATERIALS

The devices containing the spent Li–ion batteries of the LCO type were donated to our institute by Finastra Hungary Kft. The NMC811 cathode material – also used for the experiments – was purchased from the market. The batteries were dismantled and opened manually, followed by calcination at 500 °C for 2 hours to remove the organic and fluoride-bearing materials via evaporation. The obtained calcine was ground in a knife mill, followed by sieving. The <100 μm fractions were used in the experiments. The purchased NMC powder cathode material was treated in the same way, omitting the grinding step, which was unnecessary in this case. The carbothermal reduction was conducted in clay-graphite crucibles in a Nabertherm LHT02/16 laboratory furnace of resistance heating. The black mass was mixed with the slag-forming agents (in a ratio of 20%), and 99.99% pure graphite. For selected samples, mild steel chips were also added. The mixed material was then kept at 1500 °C for 2 hours. After the reduction procedure, the produced metal and the slag phases were tapped separately. The slag was crushed in a mortar with a pestle. The metal concentration (entrapped in metallic form) was determined by reacting the fine powder with 3 M H_2SO_4 at 55 °C, during which the volume of evolved H_2 was measured. The obtained alloys were dissolved in hot aqua regia. The solutions were analyzed by atomic absorption spectrometry (AAS) with a Varian SpectrAA 330 instrument to serve as the basis for determining the concentrations of the main elements in the produced alloys. Thermodynamic calculations were carried out using HSC Chemistry 9. The procedure and the equipment used for the carbothermal reduction are shown in *Figure 1.*

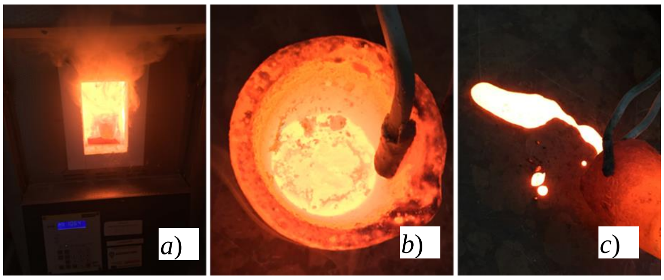

Figure 1

The carbothermal reduction equipment (a), the melt surface (b) and the tapping (c)

2. THERMODYNAMIC AND KINETIC CONSIDERATIONS

Theoretically, carbothermal reduction can be used to reduce any metal from its oxides. The reducing power of the system can be conveniently controlled – through the Boudouard reaction – by the temperature, the amount of added carbon, the gas permeability and the height of the charge. The reducing agent is effectively CO. This is practically formed by the oxidation of C at high temperatures. According to the thermodynamic equilibrium, CO_2 reacts with C, stabilizing CO at temperatures higher than ~800 °C, as shown in *Figure 2*. This reaction provides the foundation for carbothermal reduction. As the freshly produced CO reduces the metal oxides, CO_2 is formed, which is a potent oxidizing agent. However, at high temperatures, the Boudouard-reaction can regenerate CO ensuring its dominance in the gas phase.

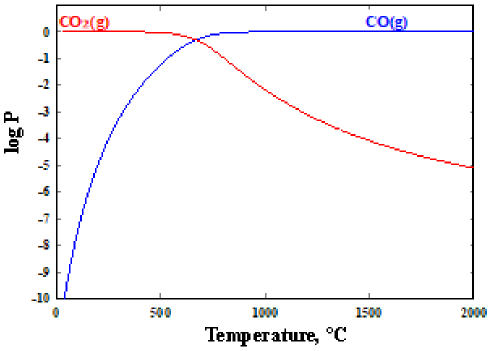

Figure 2

The partial pressures of the CO_2 and CO components in equilibrium with elemental C at different temperatures

For the reduction of the oxides of less reactive metals, such as Ni and Co, the required p_{CO}/p_{CO2} ratios are not extremely high. Thermodynamically – as seen in *Figure 3* – the increase in the partial pressure of CO results in a higher thermodynamic driving force for the reduction, which entails a decrease in selectivity. However, the reduction of Mn would only be possible by applying very aggressive reducing conditions. However, the production of a Mn-free ferroalloy is also reasonable, and ferromanganese production can still be possible by recycling the residual slag to the conventional industrial technology.

Lithium is a highly reactive alkali metal whose oxide has remarkably high thermodynamic stability:

$$4Li + O_{2(g)} = 2Li_2O, \log K_{1273} = 35 \quad (1)$$

The reduction is still possible if the actual activity index can be set lower than the equilibrium constant marked in *Equation (1)*. This can be facilitated by the relatively low 1,342 °C boiling point of lithium. Even at lower temperatures, the vapour pressure can be significantly high to yield an appreciable amount of gaseous Li. The gaseous product immediately leaves the reaction front; thus, a carbothermal reduction is possible, as seen in *Figure 4*.

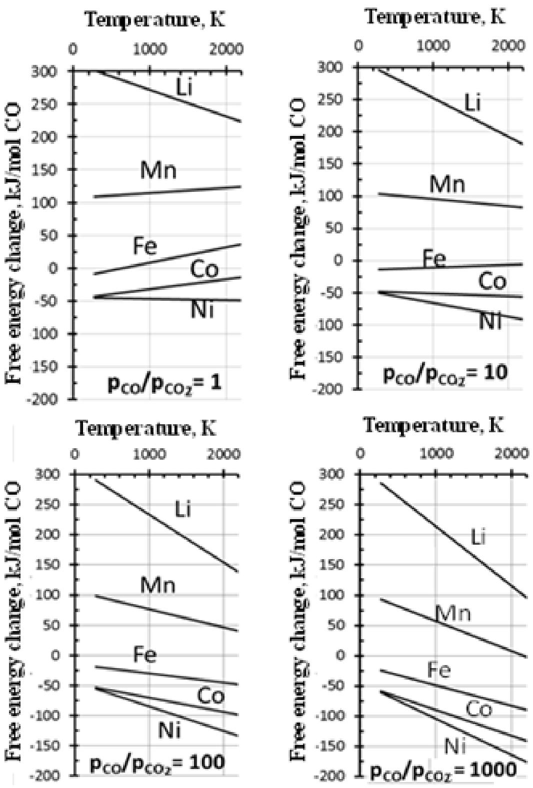

Figure 3
The Gibbs free energy change accompanying the carbothermal reduction of Fe, Mn, Li, Co and Ni oxides

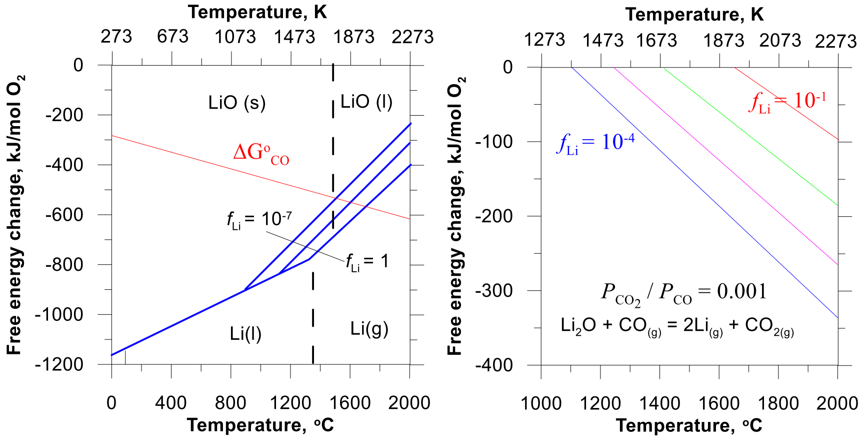

Figure 4
The fundamental thermodynamic conditions of Li reduction

The thermodynamic driving force of the reduction greatly depends on the fugacity of the Li vapour above the reaction front. Evaporation is accompanied by heat consumption and, thus, a possible drop in the local temperature. Cooling reduces the efficiencies of the reduction and also of the Boudouard reaction, while the drop in pressure increases it. Moreover, cooling encourages the re-oxidation of Li, forming Li_2O. This usually happens when the gas phase has left the hot reduction zone. However, Li_2O is unstable in a CO_2-rich atmosphere; therefore, it reacts further to form Li_2CO_3, which condenses in the flue dust. If the carryover from carbon and the transition metal oxides are low, a relatively pure Li_2CO_3 can be recovered. If the C content is insufficient to provide the required dominance of CO in the gas phase, the re-oxidation of Co and Ni may also occur, as seen in *Figure 5*.

However, if excess C is added, Ni and Co can be kept in the elemental state and – at higher temperatures – even Mn can be reduced and the reduction of Fe can also be ensured. However, directly reduced iron (DRI) or scrap steel is relatively cheap, and can be added as the iron carrier, instead of the required reduction of the contained FeO. Moreover, after a molten slag is formed, the addition of metallic Fe can result in the reduction of Ni^{2+} and Co^{2+} ions from the slag phase. These processes, however, require precise slag compositions. In the past century, non-ferrous metallurgy used mainly acidic (SiO_2-based) slags. Acidic slags have low solubility for amphoteric oxides; thus, precipitation tends to occur. This is especially unpleasant if high amounts of Fe must be transferred to the slag. Precipitation increases viscosity, which is even further increased as the Si^{4+} ions arising from the melting of SiO_2 are forming oxo-complex structures of various complexity. Highly acidic slags with low O^{2-} activity are dominated by long-chained polymerized silicate anions. As basicity is increased, complexes of higher coordination begin to form, and – eventually – at an O/Si ratio of 4, the larger complexes are broken up and tetrahedral complex structures become the dominant ionic form [14] [15]. This is beneficial for lower viscosity and, consequently, higher reactivity and less metal entrapment. However, silicate slags are very sensitive to Al_2O_3, as Al^{3+} is also prone to oxy-anion formation.

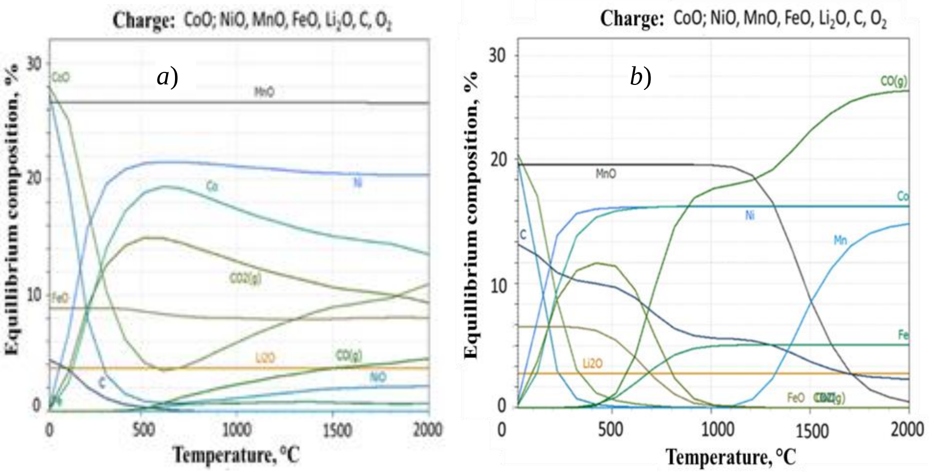

Figure 5

The equilibrium concentrations in the C – CoO-NiO-MnO-FeO-Li_2O-O_2 system as the functions of temperature with lower (a) and higher (b) initial concentrations of C present

In basic slags, these complexes provide no hindrance as they form smaller chains, and their ability to polymerise is much lower. In acidic systems, however, aluminium-oxy complexes are incorporated into the silicate chains, forming a slag with remarkedly high viscosity, which can be schematically illustrated [14], as constructed in *Figure 6*.

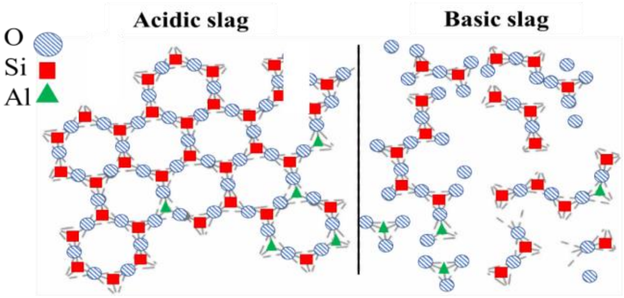

Figure 6
The structures of acidic and basic aluminosilicate slags

Thus, using acidic slags is difficult even in the pyrometallurgical processing of Cu or Ni-Co-Cu concentrates. Modern processes use different slag compositions, and one of the more prominent types is calcium-ferrite-based chemistry. Such systems possess low (0.025–0.04 kg/ms) viscosity and low specific weight (3.1–3.8), while their surface tensions are moderate (0.58–0.6 N/m). The retention of metals in these slags is much lower, while amphoteric oxides are more soluble and no excess foaming occurs. Another possible option is the use of calcium-aluminate slags. These are already implemented in the steel industry as synthetic slags. This is increasingly prominent as the expensive pure alumina additive is increasingly replaced by secondary resources of Al_2O_3. Such a novel additive can be the residual dross from secondary aluminium smelting. These raw materials are currently landfilled in Hungary in 100,000 t/year amounts, a practice likely to be prohibited soon. Some more modern Li-ion batteries, however, may incorporate also Si into their active anode materials, which will have to be taken into account for the pyrometallurgical waste processing if it becomes practical. Although the theoretical study has shown the significance of the major thermodynamic factors, the possible effects of the slag chemistry needs experimental investigation.

Therefore, pyrometallurgical reduction experiments were carried out – after the required mechanical and thermal preparation of the raw material and the addition of the different agents – as described in Section 1. According to the potential advantages of the calcium ferrite and the calcium aluminate systems, two relavant slag compositions were formed for the reduction smelting step. In the first series of experiments, a CaO-MgO-FeO slag system was applied. The black mass was mixed with CaO and MgO, and C45 steel scrap. During the melting in the open crucibles, iron oxides were inevitably formed, which could, however, improve the fluxing of the slag. Since the reducing strength of the system was relatively low, no reduction of the iron oxides could be expected. The results of the carbothermic reduction of the NMC811 cathode material and its mixture with steel chips, applying low and high ratios of the added graphite powder and applying the calcium ferrite type system are shown in successive columns of *Table 1*. The compositions of the reduced products and the recoveries indicate that the valuable oxides of Co and Ni were always efficiently reduced, but a considerable reduction of the oxides of Mn and Fe could only take place at the applied strongest reducing conditions when highr carbon addition was applied besides the steel chips.

Table 1

The characteristics of the carbothermic reduction with calcium ferrite-type slags

Raw material	**A (NMC811)**	**B (NMC811 + steel)**	**C (NMC811 + steel)**
Reducing power	mild	medium	strong
C/oxides, m/m	1.8	1.8	5
Co, %	71.15	34.15	25.14
Ni, %	27.18	19.74	16.61
Mn, %	0.55	0,75	11.15
Fe, %	0.94	44.17	45.74
Cu, %	0.38	0.89	0.67
Al, %	0.13	–	0.125
Co-Ni recovery	97.11	98.57	96.15
Me in slag, %	0.578	0.214	0.011
Evaporated Li, %	31.18	48.57	68.11

In the second run of the reduction smelting experiments, to produce the calcium aluminate slag system, a salt-free secondary aluminium melting dross was applied after grinding and and sieving. Thereby the Al content of this dross was concentrated in the coarse (0.25–1 mm) fraction (yielding ~50% metallic Al) and the fine (<0.25) mm fraction had an almost negligible metal content. When the LCO-type black massmixed with steels chips was smelted, only the Al_2O_3-rich fraction was mixed with ground CaO. On the other hand, the slag residue from the previous smelting of NMC811 + steel mixture with carbon was either mixed with this fraction or with the coarse fraction of the prepared aluminium dross and the ground CaO material. The reducing agents in this case were either carbon or the metallic Al content. The results of the second series of the reduction procedures are shown in *Table 2*.

Table 2

The characteristics of the carbothermic reduction with calcium aluminate slags

Raw material	**LCO black mass + steel**	**Slag residue from B**	**Slag residue from C**
Reducing power	medium	strong	strong
C/oxides, m/m	1	5	–
Al/oxides, m/m	–	–	2
Co, %	72.15	0.087	0.097
Ni, %	0.139	–	–
Mn, %	–	51.12	84.78
Fe, %	27.51	29.18	12.4
Cu, %	0.0124	0.087	–
Al, %	–	0.097	0.215
Co-Ni recovery	98.97	–	–
Me in slag,%	0.124	2.58	1.12
Mn recovery, %	–	57.5	76.15
Evaporated Li, %	49.11	37	69.98

The metal retention in the calcium aluminate slag was slightly lower than with the calcium ferrite system, while the Li evaporation also decreased. It is possible that the solubility of Li_2O is higher in the calcium-aluminate slag because of the higher amphoteric oxide concentration. The reducing power of the metallic Al content in the added coarse fraction of the prepared aluminium dross is remarkable. The recovery of Mn was far higher when the metallic fractions were used as reducing agents. It indicates that the use of secondary Al dross as a slag-forming and reducing agent could be advantageous during the production of different ferroalloys from waste Li-ion batteries. Low-carbon ferromanganese (ferro-manganese affiné) is highly sought after as it – as an alloying material – does not increase the C content of the produced steel. However, the Mn-free ferroalloy products obtained with the mild/medium reducing conditions shown in Table 1 may be of also practical interest, while the Mn-rich residual slag can be used in the commercial ferromanganese production.

CONCLUSIONS

The thermodynamic aspects of reducing the oxides of Co, Ni, Mn, Fe and Li from spent Li–ion batteries were examined. It was found that Co and Ni can be reduced easily even with low p_{CO}/p_{CO2} ratios, while Fe and Mn reduction requires more aggressive conditions, provided by higher temperatures and much higher CO concentrations in the gas phase. The reduction of Li is also possible through selective evaporation. The possible slag systems were evaluated theoretically and experimentally during the carbothermal reduction of the black mass of the LCO battery and the NMC811 cathode material. Using the CaO-MgO-FeO system results in a higher Li evaporation ratio than with the CaO secondary Al system, but more metal is retained in the slag. Moreover, even Mn can be effectively reduced using the Al content of the applied secondary Al dross. Utilizing waste Li-ion batteries for ferro alloy production by carbothermal smelting seems advantageous, especially when secondary Al dross is also utilised both as a slag-forming and as a reducing agent.

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