Thermodynamic analysis and experimental validation of carbothermically producing AlSi-alloy

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1 Introduction

Many technological concepts for an alternative aluminium production process have been developed during the last century, because the still utilized Hall-Héroult process is one of the most energy and CO_2 intensive industrial processes. However no basic approach was able to prevail in industrial scale. The most promising alternative process is still the carbothermic reduction of alumina, which has been investigated by several companies and researchers. The greatest challenges are the extensive aluminium volatilization occurring at high reaction temperatures, the complicated back-reaction and carbide formation mechanisms as well as critical reactor design issues.

To lower the aluminium activity it is helpful to include a "carrier" metal like silicon into the reduction process. Co-reduction of the oxides reduces vaporization of both aluminium and silicon by forming an AlSi master alloy. A successful further development of such a carbothermic reduction process implicates a sustainable improvement in the primary aluminium production with significantly less energy consumption, reduced GHG emissions and lower investment costs.

In previous investigations at IME, RWTH Aachen University, first experiments of creating an AlSi master alloy out of an oxide residue of Al-slag-treatment were conducted. The collaborative research project "ENEXAL" has resumed this idea, but with carbothermic reduction of technical pure raw materials. The present work presents the experimental validation in a small scale Lab-EAF (25 kW) of a previous performed theoretical thermodynamic study with Fact Sage 6.2 software. Different modes of operation, initial system compositions and reducing agents were considered as parameter for the investigation. To prove the quality of the AlSi-alloy chemical analysis were done as well as structure analysis.

The full paper will be published immediately after the conference in World of Metallurgy as peer reviewed paper.

2 Thermodynamic study – Suppressing the activity of liquid aluminium

The idea of utilizing a metal bath to reduce the activity of metallic aluminium has been explored in the work of ROBERT FRANK [1], in which a process for using a tin or copper bath to collect the metallic aluminium was proposed. The dissolved aluminium in the metal bath has significantly lower activity, therefore drastically diminishing the extent of vaporization, oxycarbide formation and back-reactions. However such processes require the continuous processing and recycling of large copper or tin volumes which render the process unattractive for industrial application.

To produce an industrially viable process the use of small amounts of silicon is examined as an alternative route for the direct production of Al-Si master alloys. Al-Si alloys are used in casting application which approximately account for 30% of all Aluminium utilization in 2010 [2]. Aluminium and Silicon are elements with similar chemical behaviour. Silicon oxide reacts with carbon according to

$$SiO_2 + 2C = Si_{(l)} + 2CO_{(g} \tag{1}$$

which according to simple thermodynamic calculations is possible above 1700°C as at that temperature it has a free Gibbs energy potential ΔG^0=-10896 J (using FactSage 6.2 software[3]). Similar to alumina carbothermic reduction the system is complicated by the formation of Silicon carbides (SiC) and silicon vaporization as silicon suboxide (SiO). To model the effect of silicon oxide in the carbothermic reduction of alumina system the following initial molar composition is used in.

$$3\text{-}X\ Al_2O_3 + X\ SiO_2 + 9\text{-}X\ C\text{, with X ranging from 0 to 3} \tag{2}$$

The above composition is stoichiometric in carbon for all values of X. The calculated recovery of Aluminium in the liquid metal phase at thermodynamic equilibrium is presented in Figure 1.

Figure 1: Prediction of molar aluminium recovery rates in liquid metal phase at various temperatures and for different Si:Al molar ratios in the system

The maximum Aluminium recovery[1] is in systems with Si:Al molar ratio between 0.25 and 0.35, or with X ranging from 1 to 1.15, signifying that indeed in such concentration, silicon addition can increase the aluminium metal yield.

3 Experimental Setup

The lab-scale electric arc furnace in IME is operating in single-phase alternating current mode and has a barrel capacity of 6 l. Schematic of the setup is shown in Figure 2. The furnace vessel consists of a steel jacket, which is lined with a ramming mass (type is use-oriented). In the conducted experiments a heat-resistance light-weight concrete is adopted composed of 94 % Al_2O_3. The water cooled bottom electrode consisting of copper is embed into the ramming mass, in which the temperature monitoring is very important in order not to risk partial melting of the electrode.

As top electrode it is possible to use a full graphite electrode or a hollow electrode with 50 mm in diameter. In the conducted experiments a full graphite electrode was used. The top electrode is continuously adjustable by a hydraulic system as well as tiltable for casting. A welding transformer makes secondary voltage of 120-700 A and induced current of 20-70 V available.

Figure 2: Scheme of the setup of IME labscale EAF

A graphite crucible is locked into position above a coke bed to ensure a conductive connection between crucible and copper bottom electrode. Advantages of the graphite crucibles are in addition to

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[1] Molar Aluminium recovery or yield is calculated as moles of aluminium present in the liquid metal phase to total moles of aluminium present in all phases of the system

high temperature stability and prevention of chemical reaction between initial material and refractory material, especially a simple exchangeability.

4 Carbothermic reduction of technical pure alumina with silica

By co-reduction of alumina and silica it is possible to limit the Al_4C_3 formation and to produce an Al-Si master alloy with relatively low vapour pressure, without changing the basic furnace design. First experiments have already shown that the reduction process can be controlled much more properly in the laboratory electric arc furnace contrary to alumina reduction alone. Additionally the physical and chemical properties of the pellets could be improved compared to previous pellets. To increase the purity of the AlSi-alloy technical grade alumina and silica were used as raw material combined with ca. 7 % corn starch as binder and lignite coke and wood charcoal as reducing agent. Aim of the first experiments was to investigate the influence of different Si:Al ratios described in chapter 2, different reducing agends and different modes of operation.

After changing to wood charcoal as reducing agent, a different course of action regarding the feeding, a longer melting time, but a shorter time on temperature we received a visible aluminium looking melting phase with a characteristic melting “skin”.

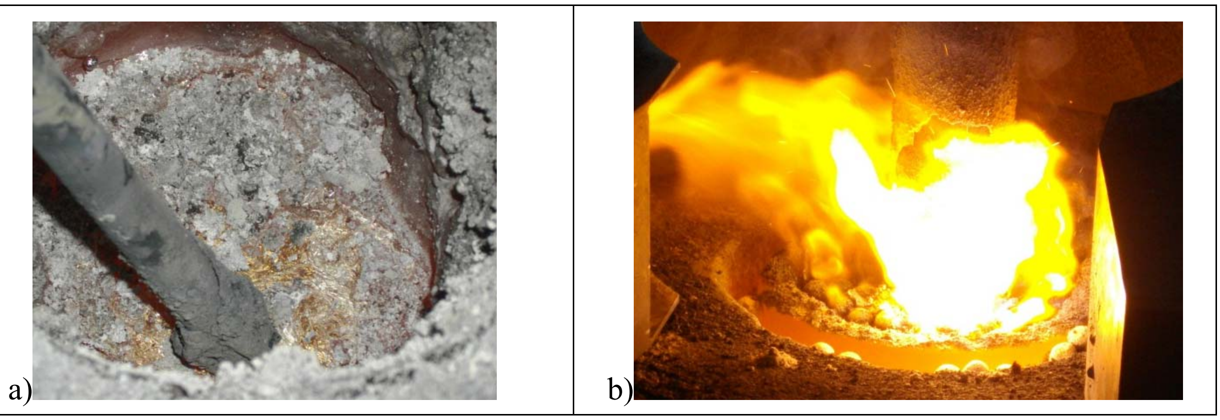

Figure 3: a) Visible aluminium melting “skin” during solidification process; b) more stable pellets during solidification process

Compared to all previous experiments a completely liquid melting pool was always created at the end of the last five experiments. Besides sampling during solidification the crucible was removed from the furnace below a temperature of 1000 °C and cast in a mould. Beneath this temperature the solubility of carbon in liquid aluminium is practically nil [4], so that the melt could be cast without difficulties.

For quality control all smelting products were checked with diverse analysing methods. Overall the expectations to get a more simple process with the implementation of silicon as carrier metal were fully met. After a few initial difficulties the process of carbothermic co-reduction of alumina and silica could be improved successively. The obtained product is an Al-Si alloy with a silicon content in the range of 20-40 wt.-% of acceptable quality. After successful conduction of the experiments in a labscale EAF it is necessary to check the feasibility of the process in a bigger furnace. Furthermore a controlled tapping and solidification process is helpful to refine the AlSi-alloy.

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