



# Thermodynamic analysis and experimental validation of carbothermically produced AlSi-alloy

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The production process of primary aluminium is still consisting of the combination of the Bayer process and the electrolytic Hall-Héroult process developed by the end of the 19<sup>th</sup> century. The process has been and continues to be reliable, but is extraordinary energy-intensive and costly, so several researchers have investigated alternative solutions for its substitution. A basic approach could be the carbothermic reduction of alumina. Previous experiments have stumbled on the high solubility of carbon in liquid aluminium, the chemical stability of alumina, the complex separation of aluminium and its carbides and the high vapour pressures of aluminium and its suboxides at required process temperatures. In order to overcome most of these obstacles in the present work an AlSi-alloy will be produced based on a theoretical thermodynamic study. Silicon is particularly suited as an alloying-metal, because an increased aluminium yield can be reached due to its reduced activity in the melt, thereby hindering volatilization phenomena. Additionally silicon is the main alloying element of aluminium.

**Keywords:** AlSi-alloy, carbothermic reduction, EAF, alumina, silica, Hall-Héroult process

Die Prozessroute der primären Aluminiumherstellung besteht bis heute aus der Kombination des Bayer-Verfahrens und der von Hall und Héroult gegen Ende des 19. Jahrhunderts entwickelten Schmelzflusselektrolyse. Diese äußerst energie- und kostenintensive Herstellungsweise gab seither steten Anlass den konventionellen Produktionsprozess durch ein alternatives Gewinnungsverfahren zu substituieren. Einen alternativen Verfahrensansatz stellt dabei die carbothermische Reduktion von Aluminiumoxid dar. Die bisherigen Versuche Aluminium carbothermisch zu reduzieren sind an der hohen Löslichkeit des Kohlenstoffs in flüssigem Aluminium, der chemischen Stabilität der Verbindung  $\text{Al}_2\text{O}_3$ , der aufwendigen Trennung von Aluminium und Aluminiumkarbid und den hohen



Dampfdrücken von Aluminium und Aluminiumsuboxiden bei den benötigten Prozesstemperaturen gescheitert. In der vorliegenden Untersuchung wird daher eine AlSi-Legierung, anhand vorher durchgeführter thermochemischer Berechnungen, hergestellt. Silizium eignet sich dabei besonders gut als Legierungs-Metall, da ein erhöhtes Metallausbringen während der gemeinsamen Reduktion durch die kinetische Hemmung der Aluminiumkarbidbildung erzielt werden kann, die Verdampfungsverluste von Aluminium und die Rekombination mit  $\text{CO}_{(\text{g})}$  minimiert werden können und es das Hauptlegierungselement von Aluminium ist.

**Schlüsselwörter: AlSi-Legierung, Carbothermische Reduktion, Lichtbogenofen,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , Hall-Héroult Prozess**

**Analyse thermodynamique et validation expérimentale d'alliages Al-Si produits par réduction carbothermique**

**Análisis termodinámico y validación experimental de aleaciones Al-Si, producido por reducción carbotérmica**

## 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  $\text{CO}_2$  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 [1]. The greatest challenges to be faced 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 an alloying-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 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, exploratory experiments for producing an AlSi master alloy from an oxide residue of Al-slag-treatment were conducted [2]. The collaborative research project “ENEXAL” has resumed this idea, but with carbothermic reduction of technical pure raw materials. The present work describes the experimental validation in a small scale Lab-EAF (25 kW) at IME, RWTH Aachen based on recipes predicted through theoretical thermodynamic study performed at the Laboratory of Metallurgy, NTUA. Different modes of operation, initial system compositions and reducing agents were considered as parameters for investigation. The AlSi-alloy was characterized both chemically and morphologically.

## 2 Thermodynamic study – Suppressing the activity of liquid aluminium

A detailed review of the processes developed for carbothermic reduction of alumina and the fundamental thermodynamic setbacks of the system have been published in previous work of the authors [3]. Accordingly, a key issue in achieving high liquid aluminium metal yields at high temperatures is the extensive volatilization of aluminium both as aluminium vapours and as aluminium sub-oxides vapours. The latter species act as a “catalyst” in the system through the comproportionation reaction of aluminium species, ultimately promoting the formation of gaseous over liquid aluminium. To avoid this problem one should either move towards conditions favouring complete gaseous aluminium production or try to diminish the activity of liquid aluminium in order to minimize the extent of the vaporization phenomena.

The idea of utilizing a metal bath to reduce the activity of metallic aluminium has been basically explored in the work of ROBERT FRANK [4], 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 [5]. Aluminium and silicon are elements with similar chemical behaviour.

Simple thermodynamic calculations show that the following reaction is possible at temperatures above 1700 °C with a Gibbs free energy potential  $\Delta G^0_{1700^\circ\text{C}} = -10896 \text{ J}$  (using FactSage 6.2 software[6]).



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:



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 (all calculations using FactSage 6.2 software).

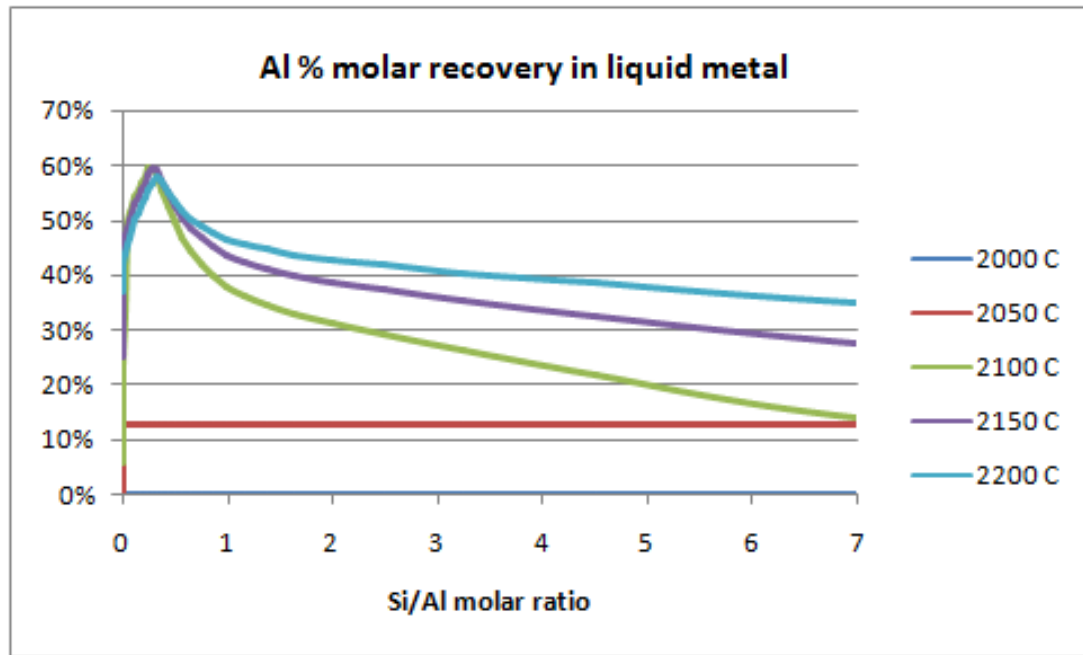


Figure 1: Prediction of molar aluminium recovery rates in liquid metal phase at various temperatures and for different Si:Al molar ratios in the system



The maximum aluminium recovery<sup>1</sup> is reached in systems with Si:Al molar ratio between 0.25 and 0.35 (Figure 3), or with X ranging from 1 to 1.15, signifying that indeed in such concentration, silicon addition can increase the aluminium metal yield.

The weight percentage of silicon in the liquid metal phase is presented in figure 2.

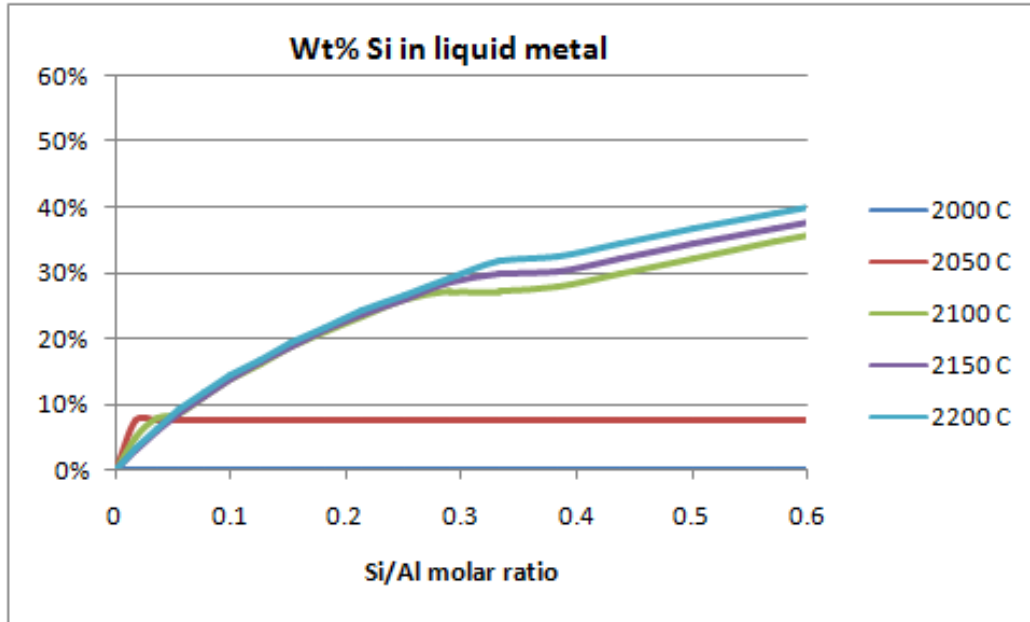


Figure 2: Prediction of Si wt-% in liquid metal phase at various temperatures and for different Si:Al molar ratios in the system.

As expected the increase of the Si:Al molar ratio increases the presence of silicon in the metal alloy phase, and therefore it is best to maintain the ratio at its minimum, that is 0.25 or  $X=1.0$ .

The effect of varying carbon in the system is examined in figure 3, where it is seen that for the Al:Si molar ratio region of interest, carbon in the system must be at least at stoichiometric ratio. As in the case of the simple carbothermic reduction of alumina described in [3], the carbon excess does not influence the system because it has reached a state of thermodynamic equilibrium.

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<sup>1</sup> 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

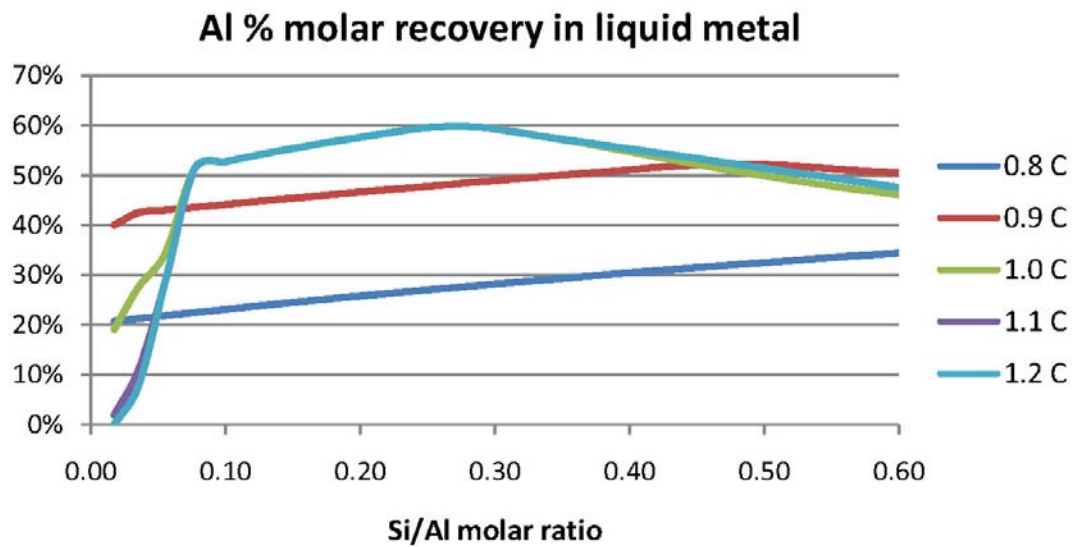


Figure 3: Prediction of molar aluminium recovery rates in liquid metal phase at various initial carbon and for different Si:Al molar ratios in the system at 2100 °C. 1.0 C stands for stoichiometric carbon ratio.

The above study concludes that thermodynamically the best system for maximizing the aluminium recovery in the liquid metal phase is represented by an initial feed of  $2 \text{ Al}_2\text{O}_3 + 1 \text{ SiO}_2 + 8 \text{ C}$  at temperatures above 2050 °C. The calculated molar speciation of the system at thermodynamic equilibrium is presented in figure 4, the composition of the produced metal alloy in figure 5 and the molar distribution of aluminium species is given in figure 6.

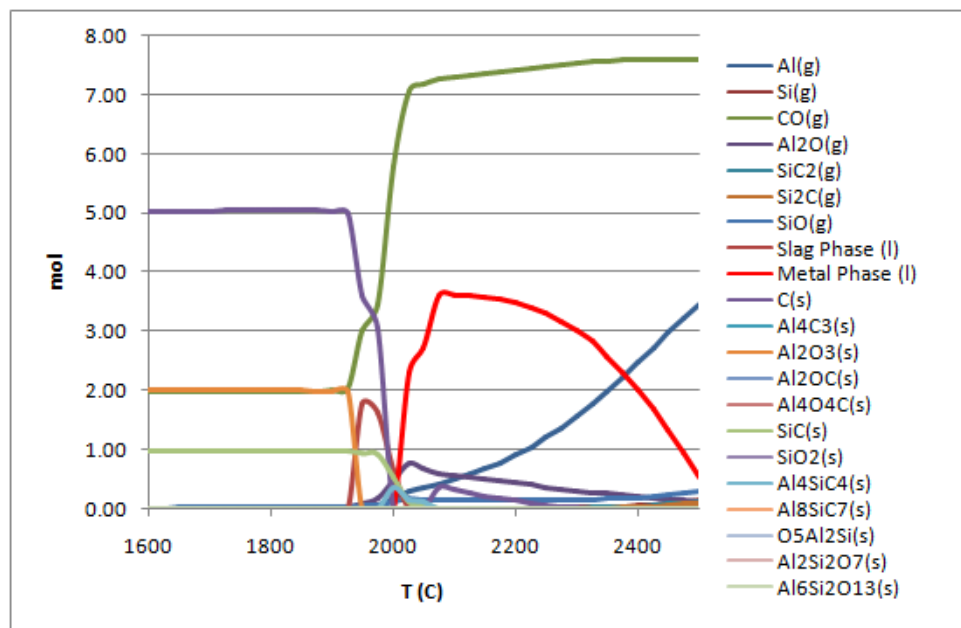




Figure 4: Prediction of molar speciation for the system  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$

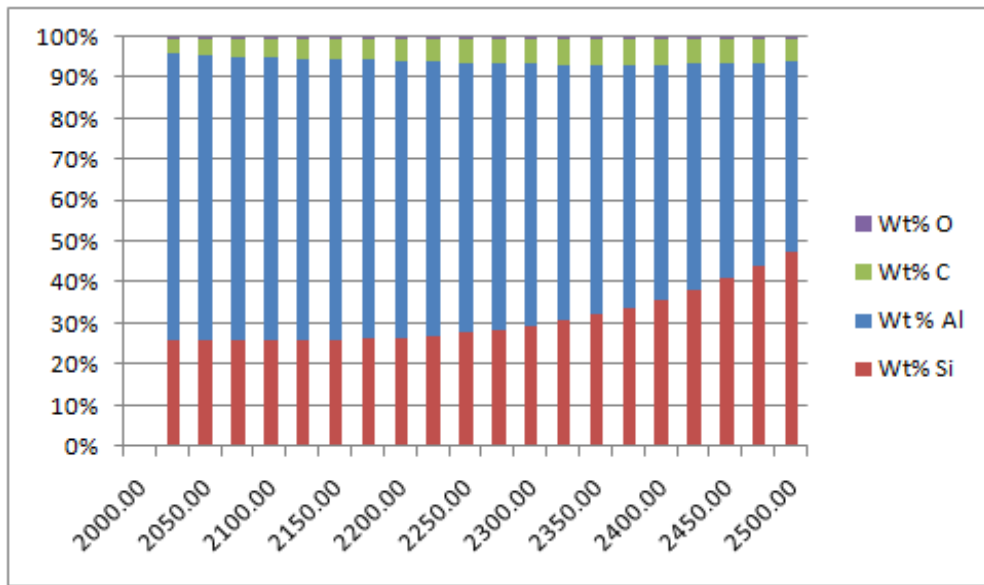


Figure 5: Prediction of elemental weight distribution in the liquid metal alloy phase of the system  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$

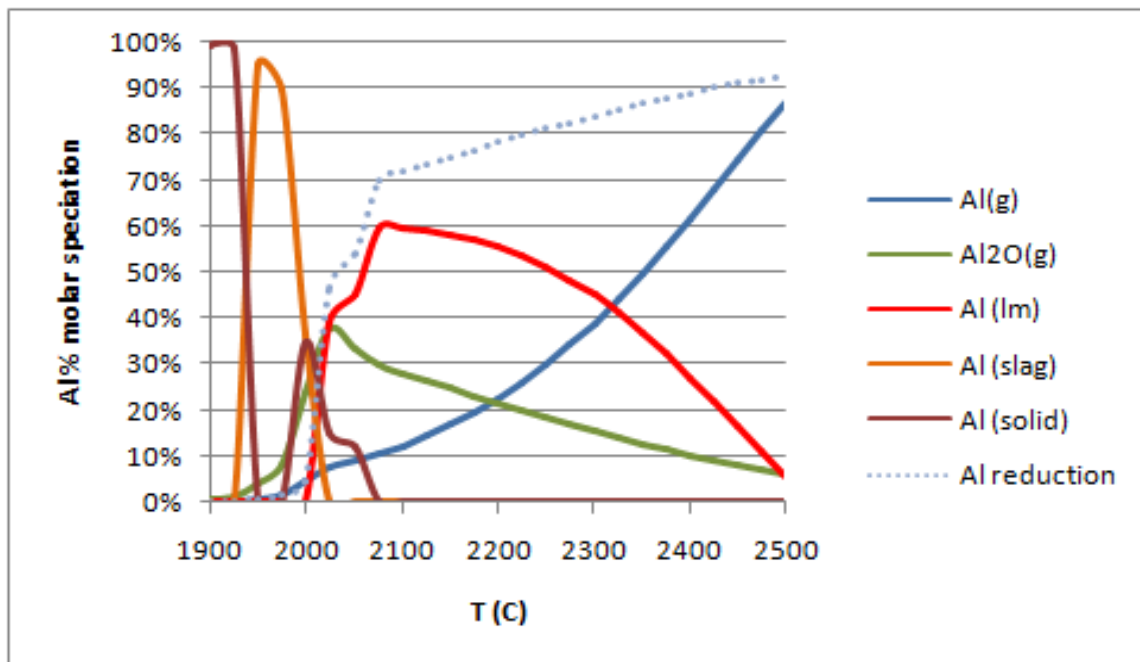


Figure 6: Prediction of aluminium species molar distribution at equilibrium for the system  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$ . Al(solid) includes  $\text{Al}_2\text{O}_3$ , Al-carbides and solid oxycarbides and various solid aluminosilicates, Al(slag) is the oxycarbide slag phase, and Al(lm) is the aluminium in the liquid metal phase.



To better comprehend the effect of  $\text{SiO}_2$  in the system a comparison between the  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$  and the  $\text{Al}_2\text{O}_3 + 3 \text{C}$  systems is presented in figures 7 and 8.

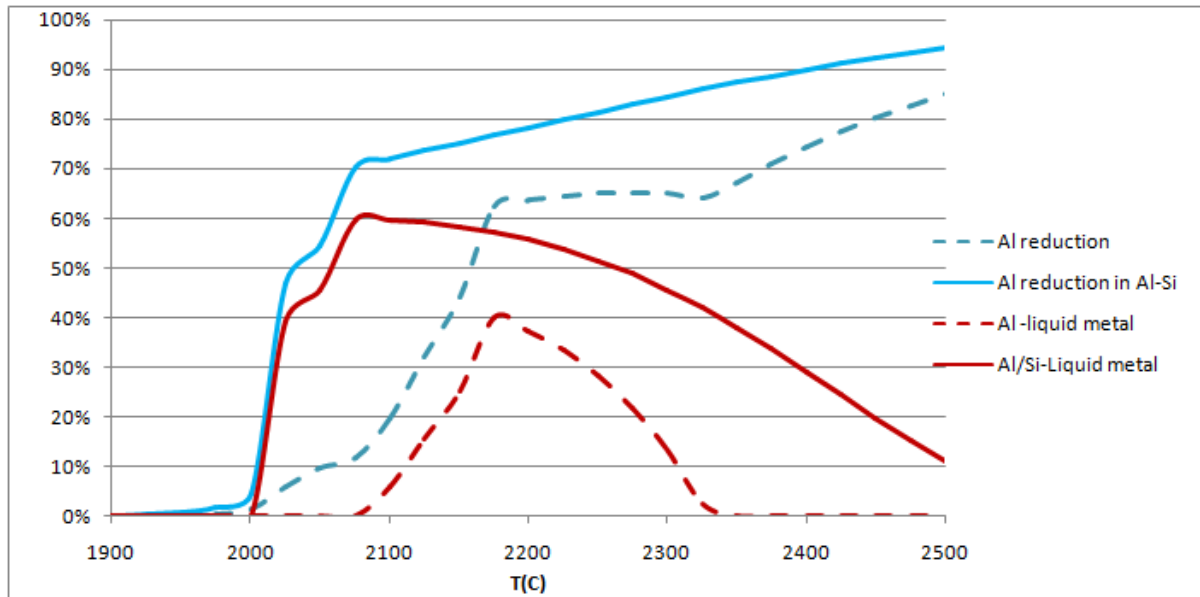


Figure 7: Prediction of aluminium overall reduction rate and aluminium liquid metal recovery rates for the system  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$  (solid lines) and the system  $\text{Al}_2\text{O}_3 + 3 \text{C}$  (dashed lines).

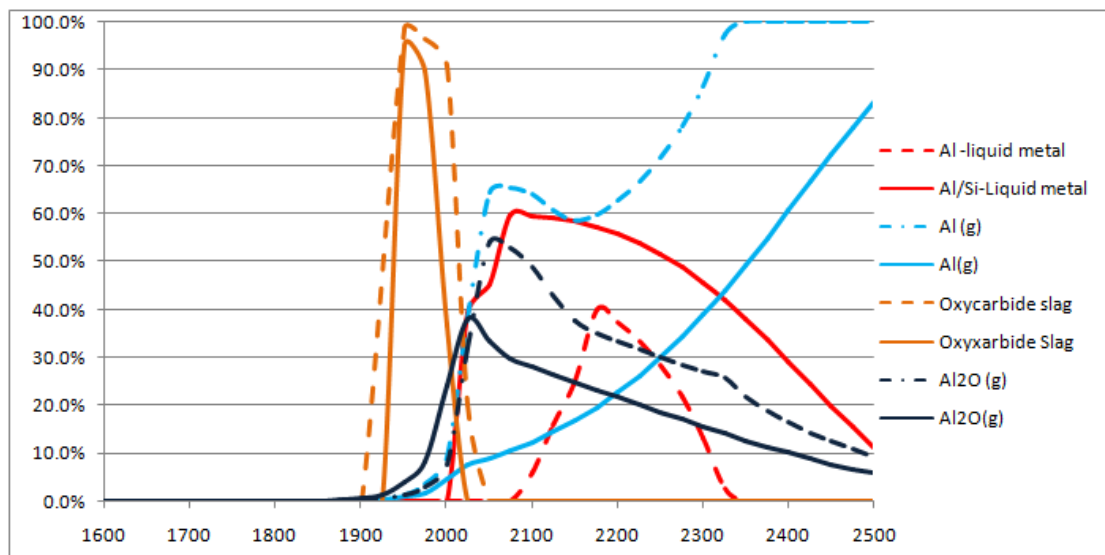


Figure 8: Prediction of aluminium species molar distribution at equilibrium for the system  $2 \text{Al}_2\text{O}_3 + 1 \text{SiO}_2 + 8 \text{C}$  (solid lines) and the system  $\text{Al}_2\text{O}_3 + 3 \text{C}$  (dashed lines). Solid species present below 2000 °C have been omitted from the figure.





As seen in figure 7 the aluminium content in the liquid metal phase and the overall aluminium reduction yield are both “enlarged” achieving higher percentages as well as larger temperature ranges. The maximum aluminium recovery in the liquid metal phase in the case of the Al-Si system can be expected to 60 % at 2100 °C while in the alumina system it is 40 % at 2200 °C. In figure 8 it is clearly seen that the presence of SiO<sub>2</sub> in the system substantially reduces the production of aluminium vapours and of alumina sub-oxide vapours. Therefore thermodynamically it is feasible to achieve the direct production of Al-Si master alloy from the carbothermic co-reduction of alumina and silica.

### 3 Carbothermic reduction of technical pure alumina with silica

The main target of the experimental work was to verify the thermodynamic predictions and to provide a proof-of concept for the carbothermic production of Al-Si alloy. The latter should have the required purity and Al/Si ratio to be used directly as “universal” Al-Si casting alloy or master alloy for eutectic, near-eutectic or hypereutectic alloys instead of using primary aluminium alloyed with silicon metal. Such a process could substitute part of the Hall-Héroult primary aluminium by carbothermic production. Al-Si alloys approximately account for 30 % of all aluminium utilization [5].

#### 3.1 Experimental Setup

The lab-scale electric arc furnace at IME is operating in single-phase alternating current mode and has a barrel capacity of 6 l. A schematic of the setup is shown in Figure 9. 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<sub>2</sub>O<sub>3</sub>. The water cooled bottom electrode consisting of copper is embedded into the ramming mass. There the temperature monitoring is very important in order not to risk partial melting of the electrode.

As top electrode a full graphite electrode or a hollow electrode with 50 mm in diameter can be used. In the conducted experiments a full graphite electrode was chosen. The top electrode is continuously adjustable by a hydraulic system, while the bowl of the furnace is tiltable for casting. A welding transformer generates a secondary voltage of 20-70 V and an induced current of 120-700 A available.

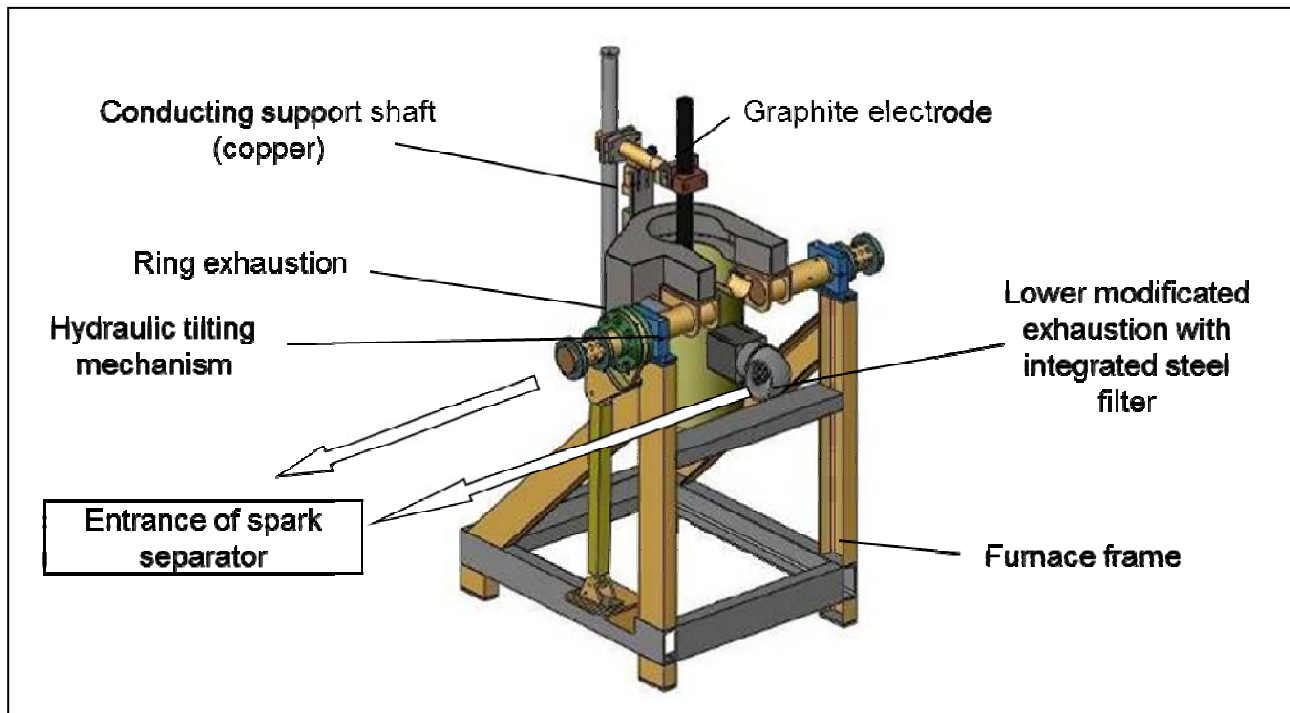


Figure 9: Scheme of the setup of IME lab-scale EAF

A graphite crucible is locked into position above a coke bed to ensure a conductive connection between crucible and copper bottom electrode. Advantage of the graphite crucibles is in addition to high temperature stability and prevention of chemical reaction between initial material and refractory material, especially a simple exchangeability. The geometric dimensions of the reaction chamber are constituted in Figure 10. To avoid the crucible dropping out of the furnace the air gap to the refractory material is filled up with fine-grained coke.

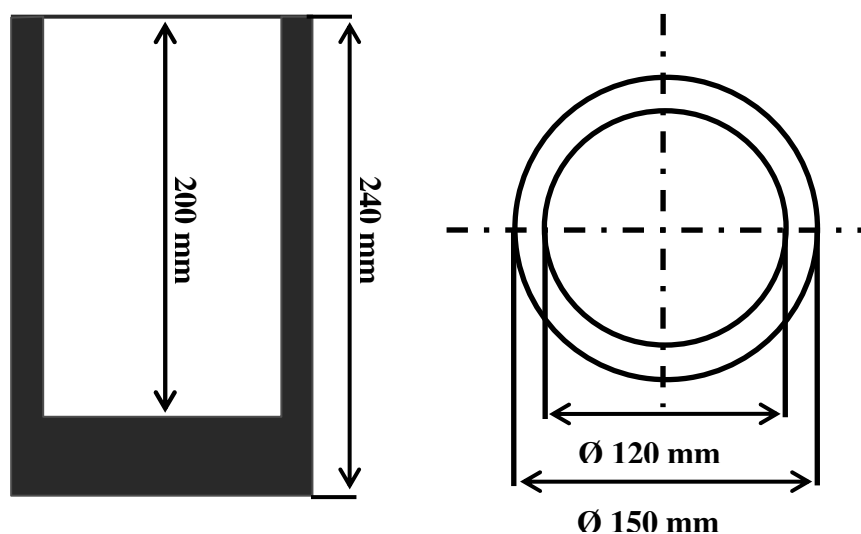


Figure 10: Geometric dimensions of the graphite crucible



The process gas is captured via ring exhaustion at the top and cleaned by a spark separator and following bag filter.

### 3.2 Experimental Process

By co-reduction of alumina and silica it is aimed to limit the  $\text{Al}_4\text{C}_3$  formation and to produce an Al-Si master alloy with relatively low vapour pressure, without changing the basic furnace design described in the section above. First experiments [2] have already shown that the reduction process can be controlled much more properly in the laboratory electric arc furnace contrary to alumina reduction alone.

The feeding material for the current experiments is consisting of lignite coke or wood charcoal used as reducing agents, technical grade alumina from ALSA plant in Greece and silica sand. In order to achieve a good gas permeability of the charged material, the initial mixed material has to be pelletized (Figure 11) due to its small grain size. Furthermore the powdered material would cause high material losses in terms of discharged particles through the exhaust stream. Besides different types and content of binding agents (corn starch & molasses), a valuation of suitability of the pellets was carried out by optical durability and measurement of the compressive strength after drying at temperatures up to 160 °C for several times (2 h, 4 h and 24 h) compared to cold curing at room temperature. Best results were achieved for 7 – 10 % corn starch as binding agent and drying at 160 °C for 24 h.



Figure 11: Pelletizing: a) pelletizer at IME; b) dry pellets

After examination and determination of some main relevant parameters (properties of the pellets, stoichiometric carbon content, content of binding agent) the chemical composition of the initial material (Si:Al ratio, reducing agent) combined with the optimal utilisation of the furnace practice had to be investigated and improved to produce an Al-Si alloy in accordance to the objectives. In addition to different alumina to silica ratios, based on preliminary thermochemical calculations of NTUA, the range of a Si/Al ratio of 0.25 to 0.35 was investigated more in detail.

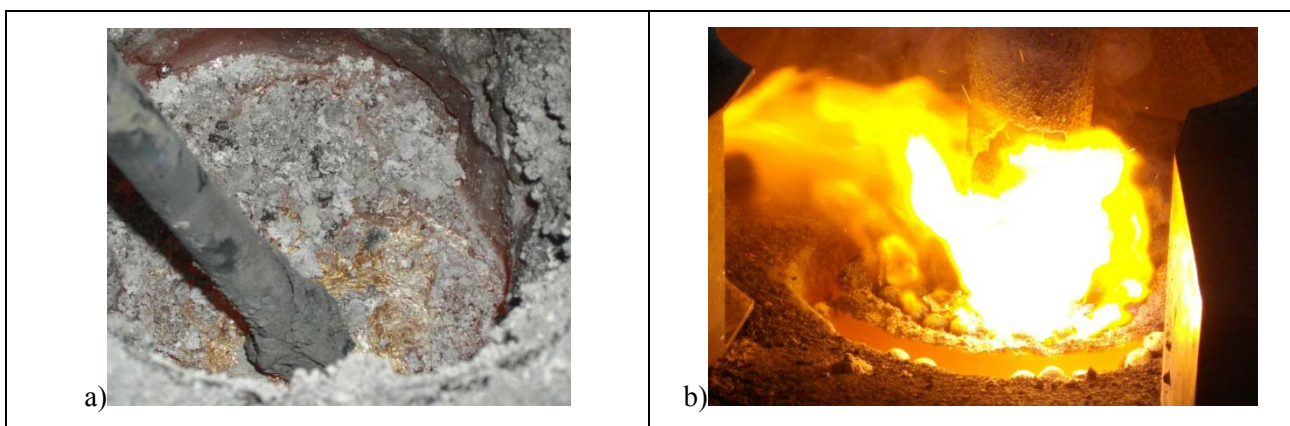


Figure 12: a) Visible aluminium melting “skin” during solidification process; b) more stable pellets during the experiment

Experiments were conducted both within the limits of equation 3 & 4 and a few outside the limits. In previous experiments [2] and at the first experiments with technical pure raw materials, lignite coke as reducing agent and a comparatively straight feeding frequency (ca. 30 min for 7 kg) until filling the graphite crucible up to the crucible edge, and a “time at temperature” of 40 min were chosen as parameter for operational mode. This procedure however was not able to produce a high enough temperature during the feeding of the material in order to produce a fully liquid bath and the furnace had to operate in open arc mode during the second heating phase (time at temperature).

To increase the melt temperature above 2000 °C in the labscale EAF with the aforementioned dimensions the feeding phase was prolonged (up to 1 h) and the time at temperature reduced (20 min). New pellets with wood charcoal as reducing agent were used. After 20 minutes time at temperature and a fully liquid crucible the electrode was retracted and the melt was left to solidify. The temperature of the melt was measured during solidification with an optical pyrometer.



Besides sampling during solidification with a sampling spoon (typical sample in Figure 13a) 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 [7], so that the melt could be cast without any difficulties.

For quality control all smelting products were checked with different analysing methods depending on the elements. An example of a tapped AlSi block is seen in Figure 14.

The extracted AlSi-alloy samples were analysed with an optical emission spectrometer for metals, with combustion method for carbon and carrier gas method for oxygen.

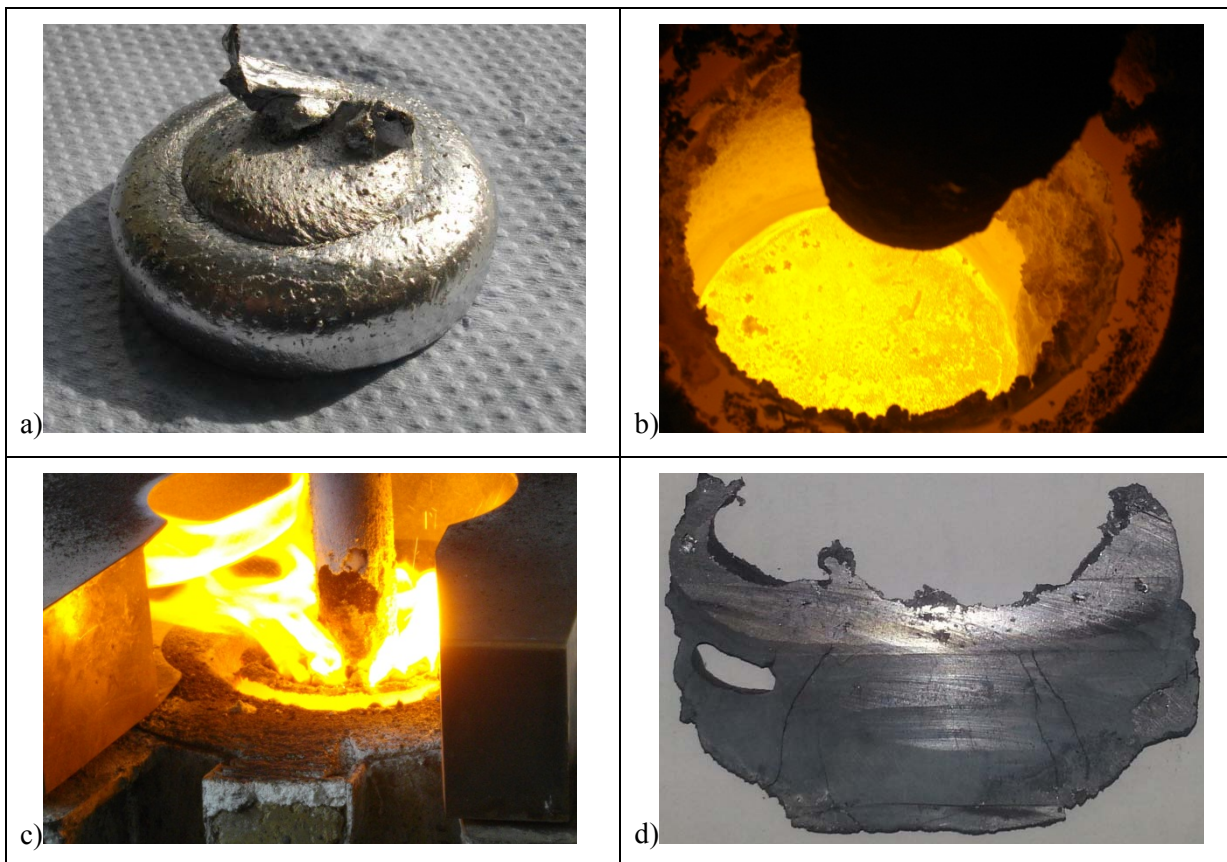


Figure 13: a) sampling during solidification; b) liquid melting pool after time on temperature; c) image during experiment; d) rest product inside the crucible

### 3.3 Experimental Results

In the experimental run with shorter feeding time and longer time at temperature we always received a smelting product after solidification rich in AlSi phases, but also rich in and mixed with carbides. This can be attributed to poor separation of the generated phases during solidification and diverse temperature profiles within the melt. After changing to a different course of action regard-



ing the feeding, but a shorter time at temperature we received a visible aluminium looking melting phase with a characteristic melting “skin” (Figure 12a). During solidification the AlSi melt was flooding on the top because of its lower density and was castable. Compared to all previous experiments (reduction of oxide residues and additional SiO<sub>2</sub>, [2]) a completely liquid melting pool (Figure 13b) was created at the end of the experimental series. It was obvious during the experiments that the used wood charcoal pellets had a better high temperature stability (Figure 12b) than all others, as they did not break up immediately after feeding.

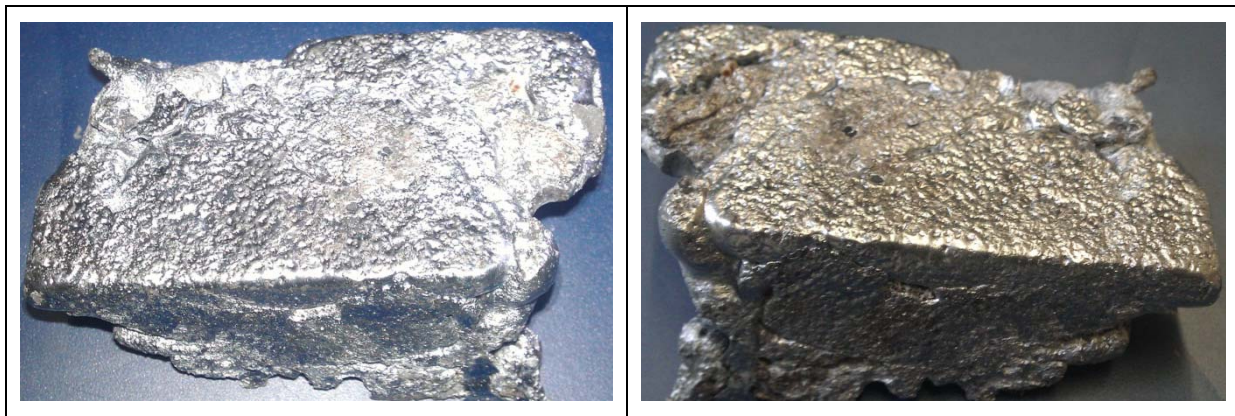


Figure 14: Pictures of carbothermally produced Al-Si alloy in experiment 10

For three representative experiments the results are shown in Table 1. Illustrated are the results of the calculated limits for the maximum aluminium recovery with Al/Si ratios of 0.26 and 0.35. In experiment 1 & 3 two samples were taken during solidification at temperature T1 (about 1600 °C) and T2 (about 1000 °C) and analysed.

Table 1: Chemical analysis of obtained Al-Si samples from co-reduction EAF trials, measured by Optical Emission Spectrometry and C and O<sub>2</sub> Analysis

Identification Number	Al wt.-%	Si wt.-%	Fe wt.-%	Mn wt.-%	Ti wt.-%	O <sub>2</sub> wt.-%	C wt.-%
Ex. 1:Si/Al 0.26 T1	72.53	25.58	1.62	0.028	0.032	0.03	0.34
Ex. 1:Si/Al 0.26 T2	71.37	25.95	2.32	0.034	0.032	0.06	0.06
Ex. 2: Si/Al 0.35 1	68.85	30.79	0.11	0.017	0.042	0.43	0.11



Ex. 3: Si/Al 0.35 T1	61.79	(37%) <sup>2</sup>	0.21	0.029	0.051	0.07	0.57
Ex. 3: Si/Al 0.35 T2	59.87	(39%) <sup>2</sup>	0.26	0.030	0.050	0.03	0.27

During the test campaign the purity of the produced alloy could be improved properly, reflecting in only small content of impurities. The values of iron in analysis Ex. 1 Si/Al 0.26 T1&T2 are attributed to the melting of a sampling spoon. SEM-EDS analyses in Figure 14 are supporting the results of optical emission spectroscopy.

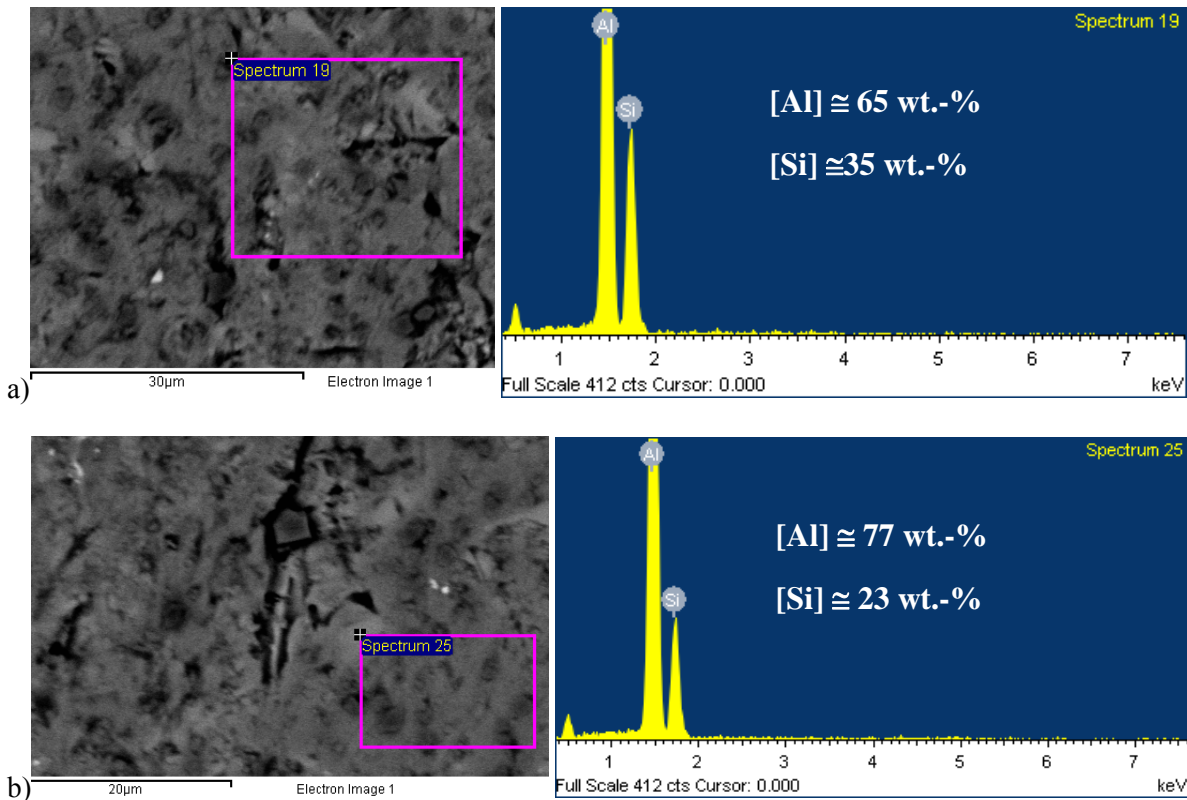


Figure 15: SEM-EDS analysis for two spectrums at two different positions on the surface of the block in Figure 13

SEM-EDS analysis of spectrums as well as analysis of different spots reveals variations of Al-Si concentrations, typical for AlSi alloys.

Due to the open system and high suction forces of the ring exhaustion a reasonable mass balance in these labscale EAF experiments is not useful, because a lot of the initial material was lost. There-

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<sup>2</sup> Due to non-existent required standard values for optical emission spectroscopy the analysis of silicon was only possible up to 33.60 %. Because no other elements were found the silicon value is normalized.



fore it is very difficult to give an estimation about reduction and metal yield. A comparison of the predicted thermodynamic analyses and conducted experiments show that the silicon content in the AlSi-alloys is a little bit higher than expected. In the experiments with a Si/Al ratio of 0.35 the discrepancy is higher than a Si/Al ratio of 0.25. Overall the feasibility of the process in lab-scale dimension was more successful for the experiments within the calculated limits of Si/Al 0.25 to Si/Al 0.35.

## 5 Conclusion

Overall the expectations to simplify the EAF process for carbothermic Alumina reduction by 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 stabilized successively. In the last experimental run after optimizing the feeding conditions, time on temperature and wood charcoal as reducing agent a fully liquid melting pool could be achieved. During solidification the Al-Si phase was separated due to different densities and melting points of the phases (carbides, oxycarbides). Thus the Al-Si alloy was floating at the top. The final product is an Al-Si alloy with silicon contents in the range of 20-40 wt.-%.

After successful synthesizing an Al-Si alloy through high temperature carbothermic reduction in a lab-scale electric arc furnace the further work is intended to check various refining options to increase the purity of the alloy. Some metallic impurities and non-metallic inclusions have to be removed from the melt before using it in aluminium cast houses. Possible refining methods could be remelting and controlled solidification of the melt, gas purging, filtration or hot centrifugation. Furthermore, in the framework of the ENEXAL project, up scaling to an already installed 1 MVA electric arc furnace is under consideration at the ALSA plant in Greece. There the aforementioned lab effects will be of little importance because the process conditions are more constant.

### Acknowledgements

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