

## EAF Carbothermic Co-Reduction of Alumina and Silica for the Direct Production of Al-Si Master Alloy

Christoph Kemper<sup>1</sup>, Efthymios Balomenos<sup>2</sup>, Dimitrios Panias<sup>2</sup>, Ioannis Paspaliaris<sup>2</sup>, Bernd Friedrich<sup>1</sup>  
<sup>1</sup>IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Intzestrasse 3, Aachen 5206, Germany  
<sup>2</sup>NTUA (National Technical University of Athens), Laboratory of Metallurgy, Zografos Campus, Athens, 157 80, Greece

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### Abstract

A key alternative for primary aluminum production could be the carbothermic reduction of alumina. Developed concepts face problems with the high solubility of carbon in liquid aluminum, the presence of the oxycarbide slag and the high volatilization of aluminum at elevated processing temperatures. In order to overcome some of these obstacles, in the framework of the ENEXAL FP7 project, research into the co-reduction of alumina and silica was made, aiming at the direct production of Al-Si master alloys. The latter are key commercial products for all casting applications, accounting for approximately 30% of all aluminum demand. As predicted by the thermodynamic study and verified by lab scale EAF experiments, the presence of silicon in the system suppresses volatilization phenomena, limits the oxycarbide slag formation and reduces carbon solubility in the metal phase.

### Introduction

Many technological concepts for an alternative aluminum production process have been developed during the last century, as the universally applied Hall-Héroult process is one of the most energy and CO<sub>2</sub> intensive industrial processes, with an electrical energy requirement of up to 56 MJ/kg of Al and with total GHG emissions up to 3.82 kg CO<sub>2</sub>equiv/kg of Al [1] (without taking into account the environmental footprint of electricity generation). A basic non-electrochemical alternative to the Hall-Héroult process is the carbothermic reduction of alumina, which has been proposed by various researchers in the last 50 years [2].

The main theoretical advantages of an EAF carbothermic production of aluminum over the established Hall-Héroult process would be an up to 37% decrease of the energy consumption per kg of Al, an up to 50% reduction in plant capital costs due to larger reactor volumes, a potential to recover energy through the utilization of the high temperature CO off-gases stream and the possibility for the new Aluminum industry to operate in “mini-mill” scale [1].

The greatest challenges in applying this process are the existence of the liquid “alumina-carbide slag” phase in the temperature region between 1850°C to 2160°C and the high aluminum volatilization phenomena occurring above 2200°C which reduce process efficiency [3]. Additionally the liquid metal produced above 2160°C is saturated in carbon (app 20% mol) so upon cooling forms a solid solution of aluminum and aluminum carbides. These fundamental thermodynamic obstacles of the Al-C-O system mandate the use of multi-stage reactors with substantial recycling of material. Such a complicated system has been researched for many years, leading to the “Advanced Reactor Process –ARP” where essentially four large scale reactors are combined in process where aluminum carbides are constantly circulated in the process [4]. The ARP has achieved the minimization of volatilization losses, but through its complexity

in mass and energy transfer, it is difficult to achieve the advantages mentioned earlier.

### Alumina and Silica Co-reduction

An alternative less complicated process could be the EAF co-reduction of alumina and silica. The presence of silicon in the system reduces the extent of aluminum vaporization, while the AlSi alloy formed has very low carbon content. Thus such a process could achieve the theoretical advantages described earlier, at the cost of course of producing an Al-Si master alloy instead of pure Al.

Historically Al-Si carbothermic production has been achieved industrially in the past, during the Second World War both in Germany and in Russia. The objective then was to achieve fast and large volume production of aluminum cast alloys for the war industry (airplanes). Yet after the end of the war, these processes were abandoned and focus was given in producing pure aluminum in centralized primary aluminum plants. Energy consumption, GHG emissions were not issue at that point, nor were Al-cast alloys significant part of the market.

Today Al-Si master alloys (AlSi25 and AlSi50) are used in casting applications for light-weight vehicles and constructions. In 2010 the overall demand for Al-casting alloys was 12 Mt or app 30% of the total Al demand (40Mt). In 2012 this number reached 14 Mt (33%) and by 2015 the demand is expected to reach 15Mt. It is also expected that in the period from 2000 to 2015 Al-casting alloy demand growth will surpass the demand growth of cast iron and steel [5]. Therefore it is evident that today a less energy and cost intensive route for primary Al-Si master alloys is again relevant and could have a significant impact on the aluminum industry.

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 [6]. The collaborative FP7 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) based on recipe 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 parameter for the investigation. To prove the quality of the AlSi-alloy chemical analysis were done as well as structure analysis.

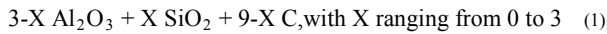
### Thermodynamic Study

The idea of utilizing a metal bath to reduce the activity of metallic aluminum has been explored in the work of Robert Frank [7], in which a process for using a tin or copper bath to collect the metallic aluminum was proposed. The dissolved aluminum 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 establish an industrially viable process the use of small amounts of silicon is examined as a route for the direct production of Al-Si master alloys. Aluminum and Silicon are elements with similar chemical behavior and similar to the Al-C-O system the Si-C-O 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 Aluminum in the liquid metal phase at thermodynamic equilibrium is presented in Figure 1 (all calculations using FactSage software [8]).

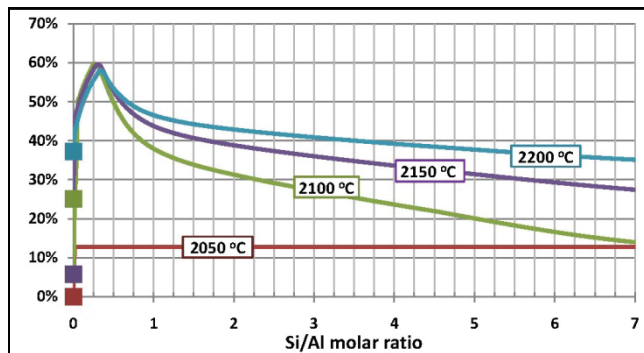


Figure 1. Calculated aluminum recovery (% mol) in the metal phase for different initial Si/Al molar ratio and temperatures, under thermodynamic equilibrium. The squares indicate the relevant recovery in a silicon free system.

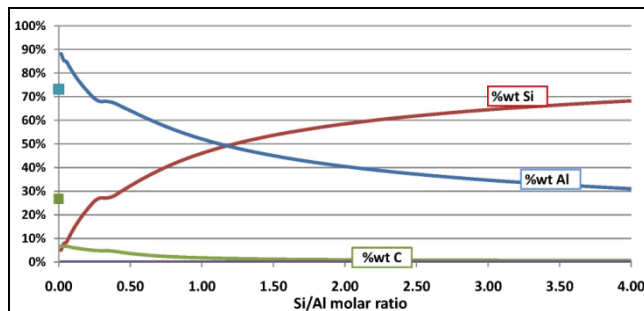


Figure 2: Calculated elemental weight distribution in the produced metal phase for different initial Si/Al molar ratios at 2100°C, under thermodynamic equilibrium. The squares indicate the relevant distribution in a silicon free system.

The maximum aluminum recovery (calculated as moles of aluminum present in the liquid metal phase to total moles of aluminum present in all phases of the system) is in the systems with Si:Al molar ratio between 0.25 and 0.35, or with X ranging from 1 to 1.15. As in the case of the simple carbothermic reduction of alumina described in [3], carbon excess in the feed will not influence the aluminum recovery as the system is at a state of thermodynamic equilibrium.

The calculated composition of the produced metal alloy at thermodynamic equilibrium for various Si/Al molar ratios at

2100°C, shown in Figure 2, reveals the “de-carbonization” effect of silicon in the produced alloy. Compared to the  $\text{Al}_2\text{O}_3 + 3\text{C}$  system at 2100°C, which would thermodynamically produce an alloy with 73%wt Al and 27%wt C the system of  $2 \text{ Al}_2\text{O}_3 + 1 \text{ SiO}_2 + 8 \text{ C}$  (Si:Al molar ratio 0.25) at the same temperature yields an alloy with 69%wt Al, 26%wt Si and 5 %wt C.

To further examine the effect of silicon presence in the system  $\text{Al}_{0.75}\text{-Si}_{0.25}\text{-C-O}$  in relation to the simple Al-C-O system, the calculated speciation of the liquid and gaseous aluminum phases are presented in figures 3a and 3b. As seen the area of the liquid metal phase is “enlarged” achieving both higher Al percentages and larger temperature ranges, effectively limiting the oxycarbide slag. The theoretical maximum aluminum recovery under thermodynamic equilibrium in the liquid metal phase is in the case of the Al-Si system 60 % at 2100°C, while in the alumina system it is 40 % at 2200°C. Furthermore in Figure 3b it is clearly seen that the presence of  $\text{SiO}_2$  in the system substantially reduces the production of alumina sub-oxide vapors, most likely due to the change in the activity of liquid aluminum in the metal phase. As described in [3] the production of aluminum suboxide is connected to the comproportionation reaction:

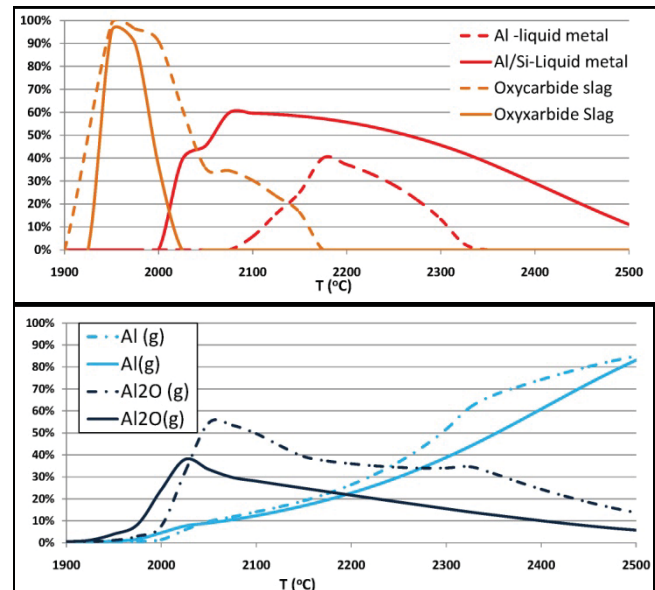
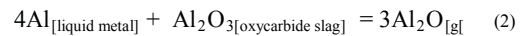


Figure 3. Calculated aluminum speciation (% mol) of liquid (above) and gaseous (below) phases at various temperatures under thermodynamic equilibrium for the system  $2 \text{ Al}_2\text{O}_3 + 1 \text{ SiO}_2 + 8 \text{ C}$  (solid lines) and the system  $\text{Al}_2\text{O}_3 + 3\text{C}$  (dash-dot lines).

Therefore thermodynamically it is feasible to achieve the direct production of Al-Si master alloy from the carbothermic co-reduction of alumina and silica, in process which will avoid extensive aluminum vaporization as well as carbon dissolution in the metal phase.

### Experimental Validation

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 AlSi alloy. The later 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 aluminum alloyed with silicon metal.

### Experimental Setup

The lab-scale electric arc furnace at RWTH-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 4. 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 %  $\text{Al}_2\text{O}_3$ . 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.

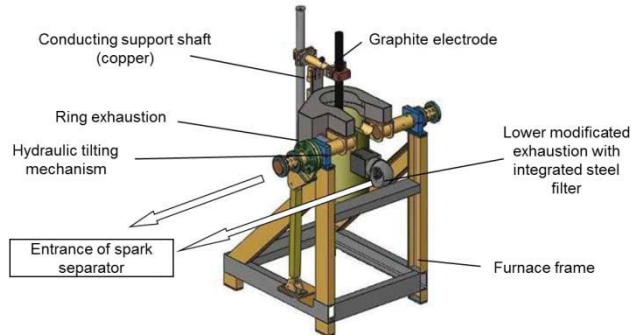


Figure 4: Schematic model of the RWTH-IME lab EAF

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 20-70 V and induced current of 120-700 A available.

For the reduction process 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 high temperature stability and prevention of chemical reaction between furnace feed and refractory material, their simple exchangeability.

### Experimental Process

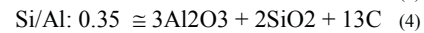
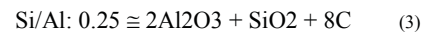
By co-reduction of alumina and silica it is aimed to limit the  $\text{Al}_4\text{C}_3$  formation and to produce an AlSi master alloy with relatively low vapor pressure, without changing the basic furnace design described in the section above. First experiments [6] have already shown that the reduction process can be controlled much more properly in this laboratory electric arc furnace, in contrast to previous tests with alumina alone.

The feeding material for the experimental campaign consisted of lignite coke or wood charcoal used as reducing agents, technical grade alumina from AoG (Aluminium S.A. plant in Greece) and silica sand. In order to achieve a good gas permeability of the charged material, the initial material has to be pelletized (Figure 5) due to its small grain size. In addition 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 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 up to 160°C for 24 h.



Figure 5: Alumina wood-charcoal pellets used in experiments.

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 utilization of the furnace practice had to be investigated and improved to produce an Al-Si alloy in accordance to the objectives. 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 rate 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).



Figure 6: Furnace operation and Melt Sampling

To increase the melt temperature above 2000°C in the lab-scale EAF with the aforementioned dimensions the feeding phase was prolonged (up to 1 h) and the amount of initial material and time at temperature reduced (20 min). The EAF under operation is shown in Figure 6. 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 optical pyrometer.

Besides sampling during solidification with a sampling spoon the crucible was removed from the furnace below a temperature of 1000°C and cast in a mold. Beneath this temperature the solubility of carbon in liquid aluminum is practically nil [9], so that the melt could be cast without any difficulties.

For quality control all smelting products were checked with different analyzing methods depending on the elements. An example of a tapped AlSi block can be seen in Figure 6.



Figure 7: Produced Al-Si block

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

#### Experimental Results

In the experimental runs a smelting product after solidification rich in AlSi phases but also rich in and mixed with carbides was always received and fractured out of the crucible. This can be attributed to insufficient separation of the generated phases during solidification and diverse temperature profiles within the melt. After changing to a different course of action regarding the feeding time and a shorter time at temperature, a visible aluminum looking melting phase with a characteristic melting “skin” was produced (Figure 7). During solidification the AlSi melt was floating on the top because of its lower density and melting point and was castable. Compared to all previous experiments (reduction of oxide residues and additional SiO<sub>2</sub>, [2]) a completely liquid melting pool was created at the end of the experimental series. It was obvious during the experiments that the used wood charcoal pellets had better high temperature stability than all others, as they did not break up immediately after feeding.

For four representative experiments the results are shown in Table I. Illustrated are the results of the calculated limits for the maximum aluminum recovery for the equations 3 & 4. In experiment 1 & 4 two samples were taken during solidification at temperature T1 (approx. 1500°C) and T2 (approx. 1000°C) and analyzed.

Table I. Chemical Analysis of produced alloys

Identification Number	Amount/%wt				
	Al	Si	Fe	O	C
Ex 1. AlSi21 T1	72.53	25.58	1.62	0.03	0.06
Ex 1. AlSi21 T2	71.37	25.95	2.32	0.06	0.34
Ex 2. AlSi21 T2	68.40	31.15	0.09	0.05	0.19
Ex 3. AlSi26 T2	68.85	30.79	0.11	0.43	0.11
Ex 4. AlSi26 T1	61.79	(37) <sup>1</sup>	0.21	0.07	0.57
Ex 4. AlSi26 T2	59.87	(39) <sup>1</sup>	0.26	0.03	0.27

<sup>1</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.



Figure 8: Photograph of produced Al-Si Melt and with characteristic “aluminum skin”

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 8 are supporting the results of optical emission spectroscopy. Additionally the SEM-EDS analysis reveals variations of Al-Si concentrations, typical for AlSi alloys.

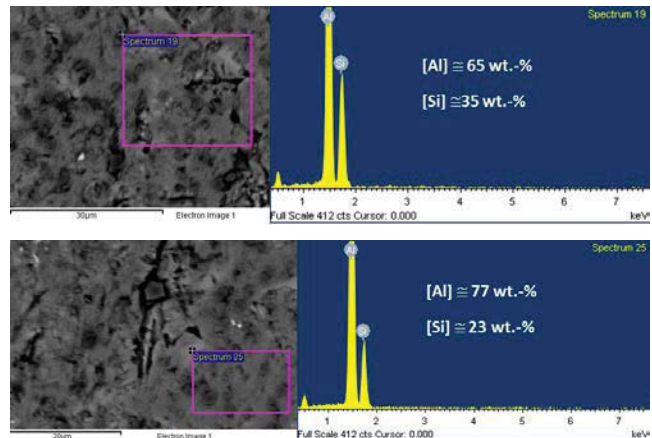


Figure 9: SEM photographs of the produced Al-Si alloy with surface EDS analysis.

In Table II the aluminum and silicon metal yields are stated, related to the initial amount of their oxides and their content in the alloy.

Table II. Metal yields of the four experiments analyzed in table I

Alloy	Mass/g				wt.-%	wt.-%
	Input Al	Input Si	Al in the alloy	Si in the alloy	Al metal yield	Si metal yield
Ex 1. AlSi21	648	168	222	81	34	48
Ex 2. AlSi21	648	168	242	110	37	65
Ex 3. AlSi26	648	224	222	119	34	53
Ex 4. AlSi26	648	224	200	130	31	58

The aluminum metal yield is obviously lower (<40%) than predicted in the thermodynamic analysis (60 %) presented earlier. This is attributed to the inadequate high temperature strength of

the pellets and the associated material losses through the gas exhaustion system in the small crucible dimensions. Furthermore not negligible amounts of metal were “lost” in the previously solidified oxycarbide phase. It should be mentioned that previous attempts to carbothermally reduce pure alumina without silica with the same experimental setup failed to produce any metallic phase.

#### Alloy Refining

The produced alloys were further processed to examine their potential refining methods. Possible refining methods could be remelting and controlled solidification of the melt, gas purging, filtration, salt treatment or vacuum treatment.

In lab the simplest option was tested, the produced AlSi blocks were remelted under protective gas in a resistance furnace and slowly and controlled solidified to remove impurities from the melt and to clean the alloy. The remelted blocks were sawed twice and analyzed with optical emission spectroscopy (Figure 9).

The results of the chemical analysis of the AlSi products of Experiment 3 & 4 are presented in Table III. It is obvious that the chemical composition of the remelted blocks in other metallic inclusions is within reach of the required values of standard AlSi specifications[10], also presented in Table III.



Figure 10: Refined and sawn blocks

Table III. Chemical analysis of refined alloy

Sample ID	Amount/%wt						Other
	Al	Si	Fe	Mn	Ca	C	
Ex 3 (1)	65.2	34.4	0.20	0.05	0.02	0.03	< 0.05
Ex 3 (2)	63.8	35.6	0.26	0.05	0.03	0.15	< 0.05
Ex 4 (1)	62.8	36.8	0.22	0.05	0.02	0.05	< 0.05
Ex 4 (2)	63.6	36.1	0.20	0.05	0.02	0.01	< 0.05
Al-Si Master alloy		Si	Max Fe	Max Mn	Max Ca	Max Others (each)	
AlSi25		23-27	0.40	0.15	0.10	0.05	
AlSi50		47-53	0.50	0.15	0.15	0.05	

#### Conclusions

Overall the expectations to simplify the EAF process for carbothermic Alumina reduction by implementation of silicon as an alloying 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 utilizing wood charcoal as a reducing agent a fully liquid melting pool was achieved. During solidification the AlSi phase was separated due to different densities and melting points of the phases (carbides, oxycarbides). Thus the AlSi alloy was floating at the top. The final product is an AlSi alloy with silicon contents in the range of 20-40 wt%.

A comparison of the thermodynamic model predictions and experimental results, at first shows that the silicon content in the Al-Si alloys is a little higher and the carbon content is much lower than expected. However the thermodynamic prediction of 69 %wt Al, 26 %wt Si and 5%wt C refers to an alloy at 2100°C at equilibrium. The same alloy at equilibrium at 1500°C (T1) will be a two phase system with a liquid alloy with 76.5 %wt Al, 23.0 %wt Si and 0.5 % C and some solid alumino-silicon carbides. Such an alloy prediction is much closer to the experimental values shown in Table I.

However the metal yields of both, Al and Si, are insufficient for the production process in general and have to be improved in further investigations. Due to the open system and high suction forces applied in the ring exhaustion of the lab scale EAF, a holistic mass balance was not possible, as, prior to melting charge material as well as evaporated components were carried away in the off-gasses. To lower and remedy these effects the next step is to attempt a scale up in an appropriate industrial EAF. In the framework of the ENEXAL project, this scale up will be attempted in a 1 MVA EAF pilot plant installed at the Aluminum SA plant in Greece, under actual industrial conditions. A larger furnace chamber filled-up with a packed bed of agglomerated raw materials advantages a temperature gradient inside the reactor, thus a condensation of the generated reaction gasses is possible. In addition the loss of large amounts of raw materials through the exhaustion should be avoidable, because the agglomerates won't break up with decreasing temperature. By working with a packed bed a tapping the whole melting pool is necessary, which includes a controlled cooling of the melt and a higher mass transfer. With decreasing material losses in an appropriate industrial furnace, both metal yields will increase significantly. It is expected that such tests will further advance the knowledge of this system and the process.

#### Acknowledgements

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