IN-SITU EXTRACTION OF Al-Sc BY METALLOTHERMIC REDUCTION VIA VACUUM INDUCTION MELTING

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Abstract

The extraction of metallic Sc from Sc-bearing compounds produced by prior processing steps in the value chain of European red mud / titanium tailings treatment is the final stage of material conversion. Potential metallothermic production routes are highlighted and experimentally validated. As the simulated energy balances are insufficient for an autogenous reaction, external heat sources are indispensable. Here, vacuum induction melting fulfills the energetic and atmospheric requirements. It is suited exceptionally well for aluminothermic ScF_3 extraction due to the fact that the reactants are liquid/solid and the side product gaseous. The final metallic product exhibits Sc concentrations above 15 Ma%, exceeding conventional master alloys by far.

Introduction

Efficient processing techniques for the extraction of Sc metal and alloys are one of the key steps to lower supply risks associated with this critical element[1]. Sc as alloying element for aluminium is a considered the most potent regarding its effect on the materials' strength, recrystallization behavior and weldability. However, with a global supply of 15 – 20 tons per year (2019)[2], the breakthrough of Sc-bearing technologies is yet to come, e.g. in aerospace applications.

Various approaches are described in literature for metallothermic reduction. For most, ScF_3 is dissolved in a suitable salt slag which is brought in contact with Al[3]. Hence, high Sc conversion yields (up to 91 % for Al-Sc 2 %) as well as the absence of harmful off-gases are strong advantages of these methods. Yet, the obtained Sc concentrations are quite low; in addition, the slags produced are mostly unusable as a valuable side-product. Thus, the approach chosen here is the utilization of pure ScF_3 and Al as input materials in order to achieve higher Sc contents with reported concentrations of up to 10 %[4]. The gaseous side product is mostly consisting of AlF AlF_3[5]. Co-reduction of Al_2O_3 and ScF_3 with Ca is also reported, with Al_3Sc formed in the metallic product[6].

As elevated temperatures are mandatory for metallothermic extraction, furnaces used for the reduction step are open induction furnaces[3], retort type reactors [4] or resistance

heating furnaces [5,7,8]. Another obstacle are the refractory materials: graphite[4,9] or tantalum[7,10–12] and MgO[13] are reported.

Due to the absence of harmful fluoridic compounds, Sc extraction from Sc_2O_3 is desired. Yet, metallothermic reduction of the oxide is thermochemically unfeasible for pure substances. Approaches described in the literature mostly comprise in-situ conversion of the oxide to fluoride during the respected processes. *Harata et al.*[8] successfully added Al and Ca as reducing agent to Sc_2O_3 and produced an alloy with roughly 9 Ma% Sc, which indicates a complete reduction of the oxide. Other researchers state that it is sufficient to skip the master alloy production step by directly introducing Sc_2O_3 to the aluminium melt. [14]

Thermochemistry

Initial approaches[15,16] are refined further with the use of the "Equilib" and "Reaction" module of FactSage 7.3[17] using databases FactPS, FTlite and FThall. Here, we focus on the aluminothermic reduction with special emphasis on the effect of pressure.

In-situ Al-Sc extraction

The reaction mechanism of the aluminothermic ScF_3 reduction is governed by the by-products behavior. Depending on pressure, temperature and Al activity, AlF and AlF_3 are formed at various ratios that thus determine the rate, equilibrium and obtainable Sc content in the metallic product.

Two main reactions are identified, hereafter named R1 and R2, whereas R2 is the gross reaction of R1 and R1.1 (Table 1):

Table 1: Reaction mechanisms of the aluminothermic ScF_3 reduction

Reaction	
R1	$ScF_3 + 4\,Al = Al_3Sc + AlF_3$
R1.1	$AlF_3 + 2\,Al = 3\,AlF$
R2	$ScF_3 + 6\,Al = Al_3Sc + 3\,AlF$

The effect of pressure and Al3Sc activity on the thermochemical equilibrium is calculated (Figure 1). Note that the pressure has a strong effect on R2, whereas R1 rather depends on the Sc product's activity.
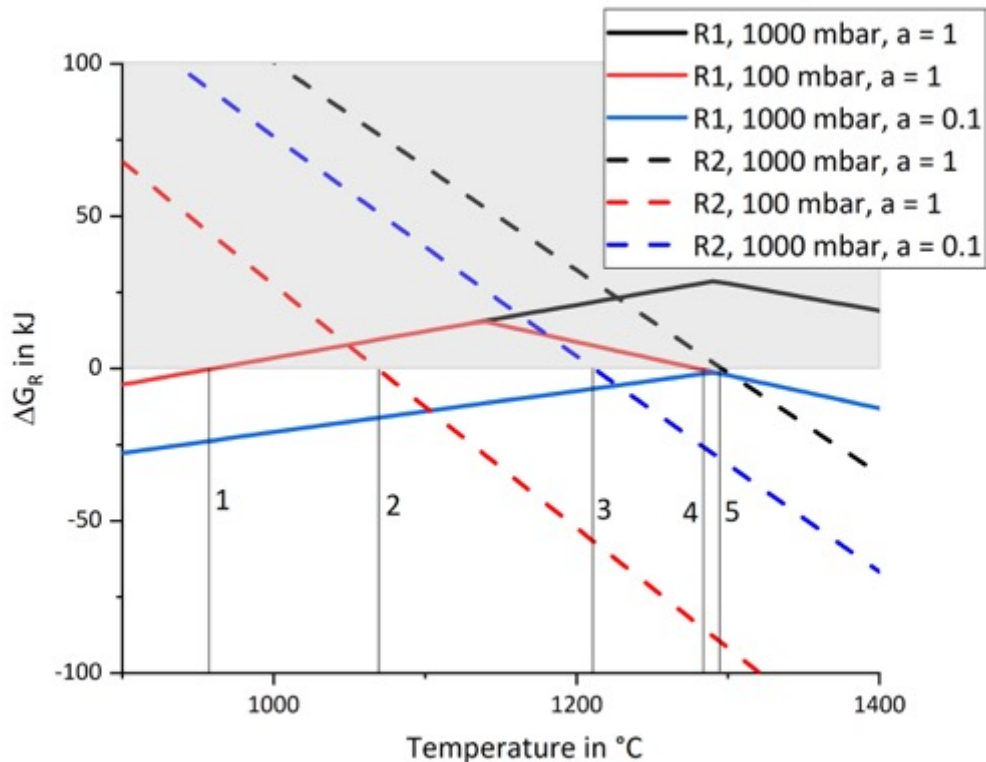
Figure 1: Gibbs free energy plot for R1 and R2 under various conditions. Equilibrium temperatures 1-5 indicated by lines.

Hence, temperature regimes are

1:   Up to 960 °C, R1 is the prevailing mechanism, independend from pressure and Al$_3$Sc activity.

1-2:   960 °C – 1070 °C: R1 is only spontaneous if Al$_3$Sc is chemically bound (a < 0.1).

2-3:   1070 °C – 1210 °C: If pressure is below 100 mbar, R2 is spontaneously reacting and becomes the prevailing mechanism above 1100 °C.

3-4:   1210 °C – 1285 °C: R2 also occurs at 1000 mbar if Al$_3$Sc activity is decreased (a < 0.1).

4-5:   1285 °C – 1295 °C: R1 runs spontaneously if the pressure is below 100 mbar.

5:   Above 1295 °C, R2 occurs at 1000 mbar and single phase Al$_3$Sc (a =1).

Thus, at non-vacuum conditions, the Sc extraction is limited to low concentration levels (960 °C: 6.8 Ma% Sc in Al) if Al$_3$Sc remains as pure phase. By applying vacuum and constant Al$_3$Sc removal and dissolution by liquid Al, significantly higher Sc concentrations are attainable as thermochemical equilibra are constantly on the product side at any temperature.

Experimental

Process development: Al-Sc via VIM

In this chapter, the aluminothermic reduction of ScF_3 as a semi-continuous process scheme is presented. The experiments are carried out in a vacuum induction furnace (VIM, VSG 10 by PVA TePla) to ensure sufficient bath movement and temperature homogeneity. Any crucibles used are Al_2O_3-based with an Al_2O_3 thermocouple protective tube attached to the Y_2O_3 coated walls. Each trial is started with an initial mass of 250 g Al to which pressed ScF_3 pellets are added at discrete time intervals. Based on the theoretical liquidus temperature as a function of Sc content within the melt, the liquid metal phase is overheated by 50 – 100 °C to avoid freezing during ScF_3 feeding. Ar pressure is increased during the process from 0.1 to max. 250 mbar to avoid material spillage. A water-cooled condenser unit placed upon the crucible collects volatile fluoridic compounds. A bottom-cooled steel mould solidifies the material after tapping, from which the cyclindrial ingots are taken and prepared for XRF. A boron nitride pressing tool immerses floating pellets under the melt surface. Table 2 displays the main parameters and results for each heat.

Table 2: Experimental parameters and results

Heat #	Process time (hrs)	ScF₃ pellets	Avg. hold. (min)	ΔT Avg. (°C)	Max temp (°C)	Avg. Sc (Ma%)	Sc Yield
V1	01:44:56	6 (10 g)	17:22	53.94	1097	2.61	23.56%
V2	04:02:19	19 (6 g)	13:56	114.0	1284	17.29	79.39%
V3	03:36:41	16 (10 g)	13:59	63.17	1202	13.54	59.51%
V4	03:33:35	21 (6 g)	11:39	118.5	1370	8.26	31.29%
V5	01:13:58	8 (6 g)	15:00	126.3	1097	0.77	7.71%
V6	03:59:13	17 (6 g)	18:21	112.8	1284	9.1	47.16%
V7	03:05:46	14 (6 g)	21:41	119.2	1200	10.96	58.26%
V8	01:49:13	14 (6 g)	17:21	97.88	1195	6.7	38.32%

A maximum Sc yield of 73.39 % is obtained at 17.29 Ma% Sc. The average heating rate has a major impact on the process' performance, as around 1 K/min delivers the highest Sc yields (Figure 2). At least 1200 °C should be reached in order to synthesize Al-Sc alloys at satisfying Sc concentrations.
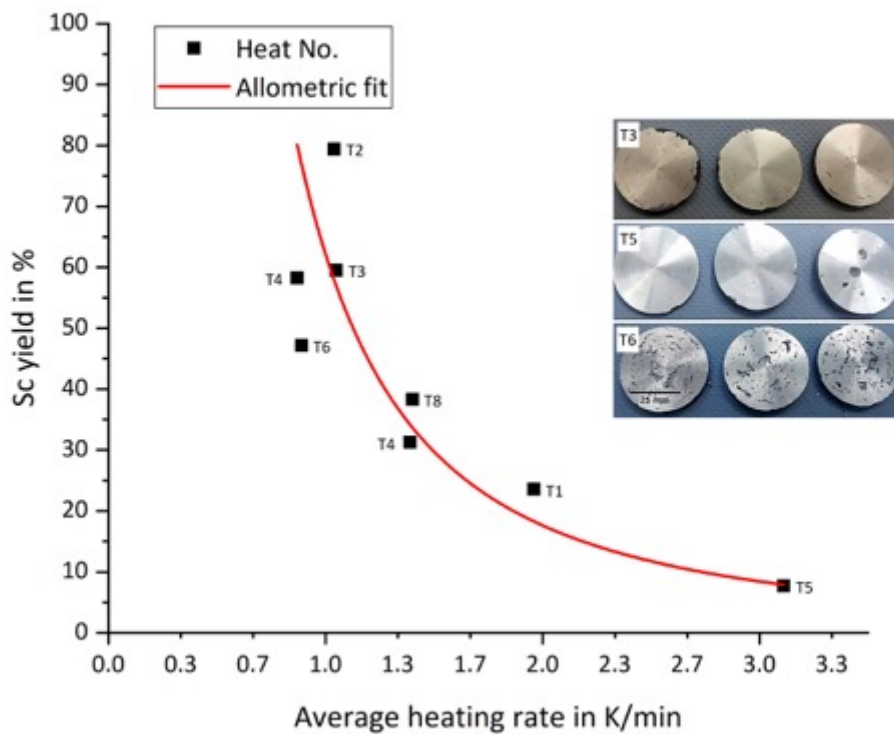
Figure 2: Heating rate impact on the average Sc yield for each heat

Discussion

From the various approaches to Sc/Al-Sc reduction via Ca, Al and Ca/Zn derived from thermochemical considerations, aluminothermic reduction of ScF_3 offers the most feasible and scalable processing route in vacuum induction furnaces. These furnaces are suited exceptionally well for this process as the combination of adjustable pressures, high bath turbulence and feeding installations meet the requirements derived from thermochemical considerations. A semi-continuous operation is thus possible, with high Sc concentrations and satisfactory yields at acceptable processing times. In additional, the use of oxidic refractories avoids costly materials such as Tantalum. While other approaches with Ca are unfeasible as the evaporation poses a serious problem to the furnace infrastructure, combinations of Ca and Al/Al_2O_3 could potentially work as well (Figure 3).
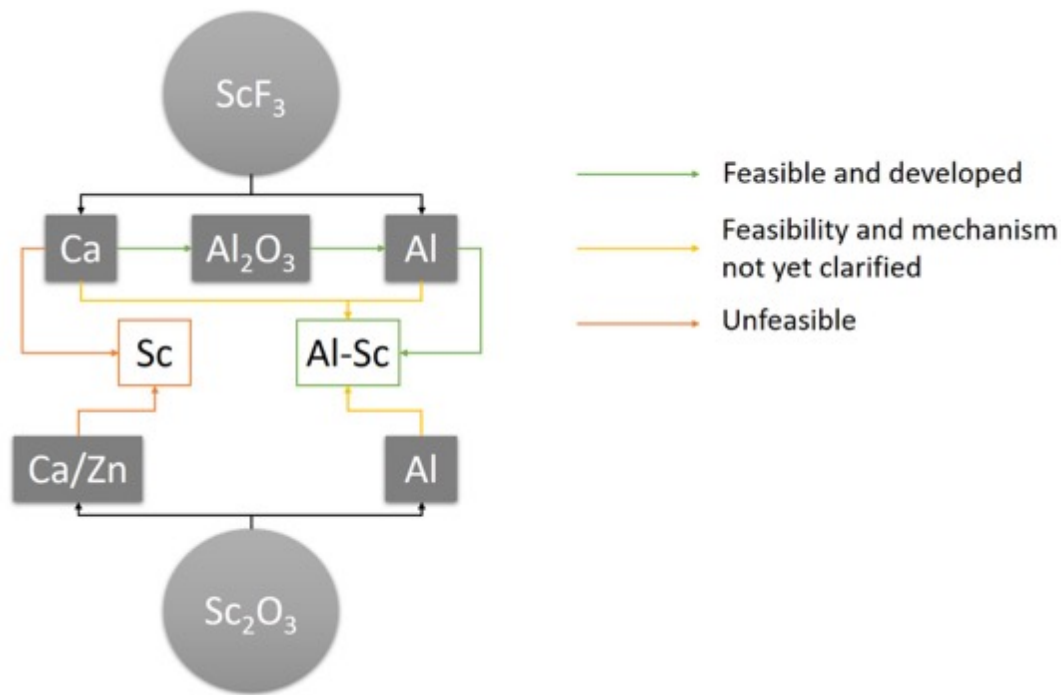
Figure 3: Extraction pathways investigated with feasibility indications

Acknowledgments

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