

Proceeding Paper

# Production of Al-Sc Alloy by Electrolysis from Cryolite Melt Using Secondary Feedstock Material †

Ana Maria Martinez \*, Samuel Senanu, Henrik Gudbrandsen, Karen Sende Osen, Anne Støre, Zhaohui Wang and Ole Kjos

SINTEF, Sem Saelands Vei 12, 7034 Trondheim, Norway; Samuel.Senanu@sintef.no (S.S.); Henrik.Gudbrandsen@sintef.no (H.G.); Karen.S.Osen@sintef.no (K.S.O.); Anne.Store@sintef.no (A.S.); Zhaohui.Wang@sintef.no (Z.W.); Ole.Kjos@sintef.no (O.K.)

\* Correspondence: anamaria.martinez@sintef.no

† Presented at International Conference on Raw Materials and Circular Economy, Athens, Greece, 5–9 September 2021.

**Abstract:** Electrolysis experiments to produce Al-Sc alloys were carried out in galvanostatic mode using a cryolitic melt with a NaF/AlF<sub>3</sub> molar ratio of 2.2 at 980 °C, using both synthetic and waste feeds. After elucidation of the cryolite electrolyte bath chemistry when adding Sc<sub>2</sub>O<sub>3</sub>, small-laboratory scale trials allowed for the demonstration of the process and the study and for the optimisation of the electrolysis parameters. Experiments in large-scale electrolysis cells allowed us to run long-term trials in continuous operation, while the on-line monitoring of the cell off-gases ensured the environmentally benign performance of the process. The aluminium product obtained contained 0.6–2.6 wt% Sc, depending on the current density applied. The material is suited to prepare Al-Sc master alloys for 3D printing powders.



**Citation:** Martinez, A.M.; Senanu, S.; Gudbrandsen, H.; Osen, K.S.; Støre, A.; Wang, Z.; Kjos, O. Production of Al-Sc Alloy by Electrolysis from Cryolite Melt Using Secondary Feedstock Material. *Mater. Proc.* **2021**, *5*, 41. <https://doi.org/10.3390/materproc2021005041>

Academic Editor: Konstantinos Simeonidis

Published: 30 November 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Keywords:** electrolysis; Al-Sc alloy; molten cryolite; waste valorisation

## 1. Introduction

Al-Sc alloys are employed in many advanced applications due to their attractive properties, such as strength, weldability, corrosion resistance and light weight [1]. Despite the high demand for these alloys, owing to the aforementioned properties, Al-Sc are not employed in significant volumes by the industry due to the very high prime cost of production. Currently, Al-Sc alloys are produced by mixing Sc with overheated liquid Al, followed by melt crystallisation [2]. There are several drawbacks in these methods, namely: high production costs, high price of pure Sc, high losses during alloy preparation and difficulties in controlling the cooling process parameters to obtain a uniform alloy crystallisation. Therefore, innovative reduction technologies for both Sc and Sc-Al master alloy production are sought.

Previous work has been published suggesting molten salt electrolysis as a suitable method in the manufacture of Al-Sc alloys from fluoride- or chloride-based molten salts [3–6], using reasonably priced Sc<sub>2</sub>O<sub>3</sub> as raw material.

The Hall–Héroult process is currently the dominant industrial method for producing Al metal. The process involves the electrolytic reduction of alumina (Al<sub>2</sub>O<sub>3</sub>) in a molten fluoride electrolyte consisting mainly of cryolite (Na<sub>3</sub>AlF<sub>6</sub>) contained in an electrochemical reduction cell at temperatures around 955–965 °C [7]. The molten cryolite dissolves the alumina to obtain aluminium- and oxygen-containing fluoride ions, the first ones being reduced at the cathode to produce the liquid metal, while the second ones are oxidised at the carbon anode to produce CO<sub>2</sub>.

Modifying the Hall–Héroult process for Al metal production to the production of Al-Sc alloys using the same conditions and electrolysis cells set-up, while using Al<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> feed material, will simplify the implementation of the process at the industrial scale.

However, information about the chemistry and electrochemistry of the process, and the control of the optimal parameters over time are crucial for the successful industrialisation of the process.

This work is focusing firstly on the elucidation of the cryolite electrolyte chemistry when adding  $\text{Sc}_2\text{O}_3$ , including oxide solubility determinations when adding synthetic  $\text{Sc}_2\text{O}_3$ , and discarded dross material from current Al-Sc alloy manufacturing as a source of electroactive species, and secondly the demonstration of Al-Sc production at a small- as well as large lab scale. Electrolysis in a large lab scale set-up was carried out for 24 h in continuous operation, while performing on-line monitoring of the cell off-gases to ensure the environmentally benign performance of the process.

## 2. Experimental

### 2.1. Chemicals

$\text{AlF}_3$  (Norsink, ~10 wt%  $\text{Al}_2\text{O}_3$  content) was sublimated to eliminate the oxide content down to <1 wt%. The corresponding amounts of  $\text{AlF}_3$  and NaF (p.a., Supelco®) were weighed and mixed in order to get a cryolite-based electrolyte with a cryolite ratio (CR) equal to 2.2.

$\text{Sc}_2\text{O}_3$  (anhydrous 99.9% (REO), Strem Chemicals Inc., Bischheim, France) was carefully kept in a dry atmosphere. The discarded dross material from Al-Sc alloy manufacturing was provided by KBM Affilips B.V and was sieved at +75  $\mu\text{m}$ . An XRD analysis and a subsequent quantification of the phases showed higher amounts of  $\text{Sc}_2\text{O}_3$  in the fine fraction, which was calcined at 1200 °C for 8 h, and kept in a dry atmosphere before its use. The quantification of the phases obtained by the XRD analysis of the calcined dross gave the following composition: 0.7 wt% aluminium nitride; 6 wt%  $\text{Sc}_2\text{O}_3$ ; 82 wt%  $\text{Al}_2\text{O}_3$ ; 1 wt% Al; 11 wt% aluminium oxide nitride.

### 2.2. Oxide Solubility Determinations

The oxide feed:  $\text{Sc}_2\text{O}_3$  and calcined fine fraction of the dross were added in the form of pellets into the cryolite melt. The additions were made every 24 h. During that time, the melt was kept under stirring at ca. 90 rpm. All material in contact with the melt was graphite, i.e., the stirring blade (which was connected to an electrical motor suspended above the furnace) and a protective cup for the thermocouple (type S, Pt/Pt-10 pct Rh) that allowed for an accurate control of the working temperature inside the melt. The stirring was stopped 2 h before the melt samples were taken, to allow the settling down of possible solids in suspension. The samples were taken with the help of a 4-mm-diameter Mo wire, and the oxide content was analysed by the carbothermal inert fusion method using LECO TC-436 DR (Leco Corp., Benton Harbor, MI US). To determine the residual content of oxygen in the salt mixture, samples of the melt were analysed prior to any oxide addition.

An X-ray diffraction analysis using a Bruker D8 Advance Davinci 1 X-ray diffractometer equipped with a LynxEye detector was used to obtain diffractograms across a 2-theta range of 10° to 80° on the samples to investigate the phases present in the melt during the dissolution. A study to investigate the dissolution of dross in a cryolite melt with the same composition and temperature as for the pure  $\text{Sc}_2\text{O}_3$  was also carried out.

### 2.3. Electrolysis Experiments

The trials in a small laboratory cell were carried out from a cryolite melt (CR = 2.2) containing 10 wt%  $\text{Sc}_2\text{O}_3$  at 980 °C.  $\text{Al}_2\text{O}_3$  was not added. The experimental lab-scale cell consisted of a programmable vertical gas-tight furnace with a mullite liner that housed a graphite crucible (76.5 cm inner diameter) used as electrolyte container.  $\text{Si}_3\text{N}_4$  was used as side-lining to avoid the graphite crucible being polarised. Steel and  $\text{TiB}_2$  disks with a diameter of 6 cm, placed at the bottom of the crucible, were used as cathodes, whereas graphite was used as the anode material, inserted from above and leading to a horizontal electrode arrangement, as in the industrial Hall-Héroult cells. Electrolysis was run until a depletion of the oxides in the cryolite melt was achieved, thus incurring the anode effect,

i.e., a current blockage was reached. The electrolysis was then stopped, and the cell cooled down before inspection.

A long-term electrolysis trial was carried out in an open tubular furnace placed in a fume hood. A graphite crucible (22 cm inner diameter) was used as electrolyte container, its bottom being the cathode. The anode material was graphite, and a Si<sub>3</sub>N<sub>4</sub> bounded SiC tube was used as side-lining. Al<sub>2</sub>O<sub>3</sub> was fed using an automatic feeder from the top of the electrolysis cell, and Sc<sub>2</sub>O<sub>3</sub> was added manually every 2 h. Electrolyte was also added to maintain the bath composition and compensate for evaporation losses. A Fourier Transform Infrared Spectrometer (FTIR) apparatus (Protea ProtIR 204m) was used for the online analysis of the cell off-gases (CO, CO<sub>2</sub>, C<sub>2</sub>F<sub>6</sub>, CF<sub>4</sub>). A 500 mL min<sup>-1</sup> Argon flow was used as carrier gas and kept constant during the experiment to obtain the best dynamics in the FTIR analyser. The existing models were used to transform the FTIR readings to actual gas concentrations, upon calibration of the apparatus. The HF content in the laboratory environment was monitored using a tunable diode laser equipment (Lasergas II Single Gas Monitor, NEO Monitors AS, Skedsmokorset, Norway).

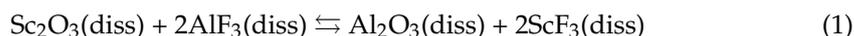
All the electrolysis experiments were run at galvanostatic conditions (constant applied current); 0.79–0.93 A cm<sup>-2</sup> at a small lab scale and 0.45 A cm<sup>-2</sup>, on average, at a large scale. The temperature (maintained at 980 °C and measured with a thermocouple type S) and the cell voltage were recorded by means of a multichannel Keithley 2000 Multimeter.

The microstructure and chemical composition of the cathode products after eliminating the electrolyte remains by washing the metal with an AlCl<sub>3</sub> solution, were investigated by means of scanning electron microscopy using LV-SEM HITACHI S-3400N equipped with an energy dispersive spectrometer. An element analysis of the metal samples was achieved by the ICP-MS apparatus (Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) with SPS 4 Autosampler).

### 3. Results and Discussion

#### 3.1. Bath Chemistry upon Sc<sub>2</sub>O<sub>3</sub> Additions

From a thermodynamic point of view, the raw material used in the process for obtaining the Al-Sc compound, i.e., Sc<sub>2</sub>O<sub>3</sub>, reacts with AlF<sub>3</sub> according to the reaction showed in Equation (1), which is displaced to the right at the operating temperature, i.e., 980 °C.

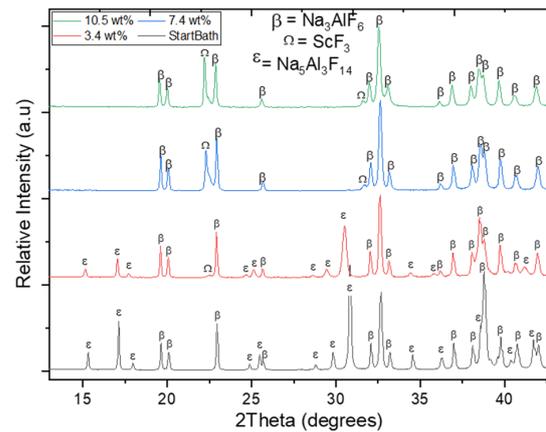


To optimise the electrolysis process, the occurrence of this reaction needs to be elucidated, so that the conditions for a stable electrolysis operation can be established. This was done through a systematic XRD analysis and a quantification of the phases of the bath samples upon Sc<sub>2</sub>O<sub>3</sub> additions into the 2.2NaF-AlF<sub>3</sub> melt.

Figure 1 shows the results obtained. The amount of cryolite phase (Na<sub>3</sub>AlF<sub>6</sub>) increases upon Sc<sub>2</sub>O<sub>3</sub> additions, whereas the amount of chiolite phase (Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>) decreases, until it is almost non-existent (oxide saturation reached). Moreover, the amounts of ScF<sub>3</sub> measured went from zero, when no Sc<sub>2</sub>O<sub>3</sub> had been added, to almost constant, when reaching oxide saturation. Table 1 gathers the amounts determined for the different phases. The cryolite ratio of the bath increases with the amount of Sc<sub>2</sub>O<sub>3</sub> as expected from Equation (1), thus showing that this must be followed up closely in long-term electrolysis for Al-Sc production with Sc<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as feed.

**Table 1.** Quantification of the phases of bath samples taken at each of the  $\text{Sc}_2\text{O}_3$  additions shown in Figure 1. The analysis was done using the TOPAS Software after XRD diffractograms of the samples. Values in wt%.

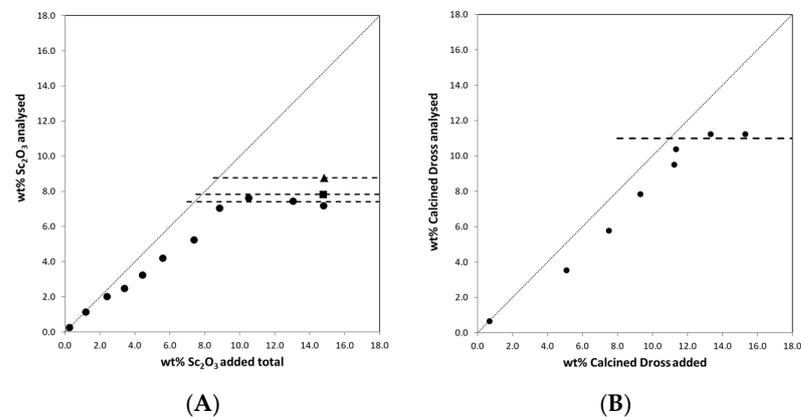
Phase	0 wt% $\text{Sc}_2\text{O}_3$	3.4 wt% $\text{Sc}_2\text{O}_3$	7.4 wt% $\text{Sc}_2\text{O}_3$	10.5 wt% $\text{Sc}_2\text{O}_3$
$\text{Na}_3\text{AlF}_6$	55	65	95	94
$\text{Na}_5\text{Al}_3\text{F}_{14}$	45	35	0	0
$\text{ScF}_3$	0	0.5	5.5	6.5
CR ( $n_{\text{NaF}}/n_{\text{AlF}_3}$ )	2.2	2.4	3.0	3.0



**Figure 1.** XRD diffractograms of bath samples taken upon  $\text{Sc}_2\text{O}_3$  additions to the molten cryolite. wt% of  $\text{Sc}_2\text{O}_3$  added prior to sampling are indicated in the insert.

### 3.2. Oxide Solubility Determinations

The elucidation of the oxide-saturation values in the  $2.2\text{NaF-AlF}_3$  melt at different temperatures was carried out upon  $\text{Sc}_2\text{O}_3$  and dross additions. The results obtained are shown in Figure 2. The ratio oxide analysed/oxide added is deviating from linearity, probably due to the reaction showed in Equation (1), leading to a change in electrolyte composition and CR. In addition, the influence of  $\text{ScF}_3$  on the solubility of  $\text{Al}_2\text{O}_3$  is unknown, and it might have a negative effect. Moreover, the results showed that discarded dross material can be used as feed in the electrolysis process for direct Al-Sc production. The oxide saturation value obtained is similar to that previously reported at this operating temperature, i.e., 11 wt% [8], showing that all oxide added in the dross is dissolved in the cryolite melt and does not lead to sludge.

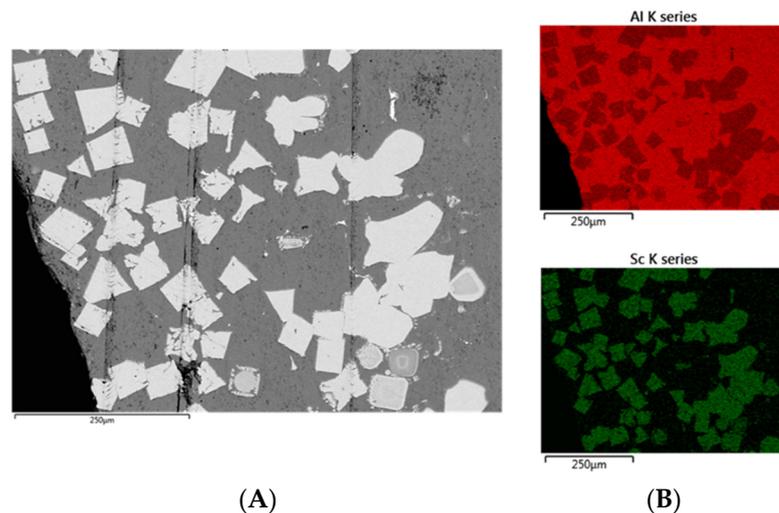


**Figure 2.** (A) Oxide solubility determinations in cryolite melt, CR = 2.2. Oxide source added as  $\text{Sc}_2\text{O}_3$ . The operating temperature, (●) 980 °C, was increased at the end to investigate the effect of the temperature at saturation point, i.e., (■) 1000 °C and (▲) 1020 °C. (B) Oxide solubility determinations in cryolite melt, CR = 2.2. Oxide source added as dross after calcination of the fine fraction. T = 980 °C

### 3.3. Electrolysis at Small Lab Scale

Several electrolysis trials in a small laboratory cell were carried out using both steel and  $\text{TiB}_2$  cathodes, from a cryolite melt (CR = 2.2) containing 10 wt%  $\text{Sc}_2\text{O}_3$  at 980 °C.  $\text{Al}_2\text{O}_3$  was not added in any case, but just formed after the reaction showed in Equation (1). A good wettability of the metal product was obtained in the case of the steel cathode. However, in the case of inert  $\text{TiB}_2$ , metal drops of different sizes were collected from the bottom of the cell. The poor wettability could be attributed to the inert nature of the  $\text{TiB}_2$  material. The current efficiencies determined by the amount of charge passed and the amount of metal harvested were in the order of 85–77%.

The SEM-EDS analysis of the metal products confirmed the presence of intermetallic  $\text{Al}_3\text{Sc}$  phases in the aluminium matrix (cf. Figure 3). A precipitation of the intermetallic phase occurred upon slow cooling of the electrolysis cell, but a uniform distribution of scandium in the aluminium metal is expected owing to the electromagnetic forces created during electrolysis, as reported previously [6]. The amount of Sc in the metal product was analysed by ICP-MS and increased with the current density, ranging from 1.87 wt% Sc at 0.79  $\text{A cm}^{-2}$  to 2.6 wt% Sc at 0.93  $\text{A cm}^{-2}$ .



**Figure 3.** (A) SEM micrograph of the metal product obtained with the  $\text{TiB}_2$  cathode, and (B) EDS analysis.

### 3.4. Long-Term Electrolysis Trial with On-Line Monitoring of Cell Off-Gases

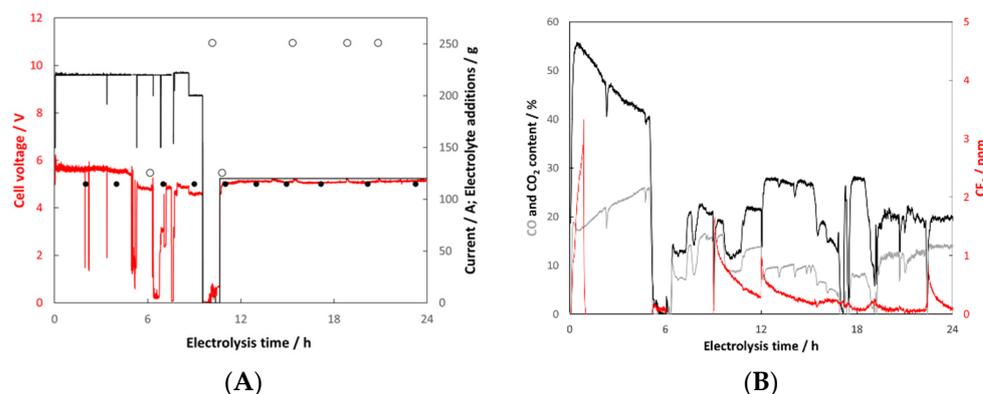
A long term electrolysis trial was carried out to demonstrate the process in a continuous operation for 24 h, while feeding  $\text{Al}_2\text{O}_3$  and  $\text{Sc}_2\text{O}_3$ . In this case, the bottom of the electrolyte graphite container acted as cathode. At the same time, an on-line monitoring of the cell-off gases was carried out to control both the electrolysis process ( $\text{CO}/\text{CO}_2$  and  $\text{CF}_4/\text{C}_2\text{F}_6$ ) and the safe working environment (HF). Electrolyte additions throughout the trial allowed for the maintenance of the bath composition and a compensation for evaporation losses.

The cell voltages' read-outs showed a smooth operation throughout the whole period (cf. Figure 4A), which was also confirmed by the analysis of the off-gases (cf. Figure 4B), measuring  $\text{CF}_4$  levels < 1 ppm, with an estimated LOQ (level of quantification) of 0.5 ppm. The recovered gas was highly concentrated, approximately 20–30 times that of an industrial plant, due to the higher dilution ratio in the gas treatment systems in industrial plants. Therefore, to compare the measured  $\text{CF}_4$  concentrations with industrial figures, they should be divided by at least a value of 20. Given the added uncertainty of a small-scale laboratory cells,  $\text{CF}_4$  emissions can be estimated to be equal to those of a commercial aluminium electrolysis cells.

The CO/CO<sub>2</sub> ratio increased with the electrolysis time, probably due to a certain back reaction between dissolved Al and CO<sub>2</sub> and the Boudouard reaction between the anode gas and the graphite material in the cell, according to Equations (2) and (3), respectively:



The total metal harvested after the trial was ~750 g, obtaining a current efficiency of ~63%. The Al<sub>3</sub>Sc phases were also confirmed by SEM-EDS, and the ICP-MS analysis of the metal gave a Sc content of ~0.6 wt% in the Al matrix, with a current density of 0.45 A cm<sup>-2</sup>, on average.



**Figure 4.** (A) Cell voltage recorded during the electrolysis trial. Galvanostatic operation at 220 A during the first 9 h, and then 120 A. Al<sub>2</sub>O<sub>3</sub> was continuously fed through an automatic feeder. (●) Sc<sub>2</sub>O<sub>3</sub> and (○) electrolyte additions are also shown in the graph; (B) On-line analysis of the cell off-gases.

#### 4. Conclusions

Electrolysis from a cryolite melt at CR = 2.2 and 980 °C has demonstrated to be a suitable method to prepare the Al-Sc alloy, while using the same electrolysis cell arrangement as in current industrial aluminium production.

The formation of ScF<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> upon Sc<sub>2</sub>O<sub>3</sub> addition into the cryolite melt has been demonstrated. This reaction leads to the necessary electroactive species for the electrolysis process but may change the acidity of the melt (AlF<sub>3</sub> content). This parameter must be monitored for the well performance of the electrolysis process in continuous operation.

The results showed that it is possible to electrodeposit Sc in the Al matrix due to the underpotential deposition of Sc, i.e., at activities lower than 1. The amount of Sc obtained depended on the cathodic current density applied.

A uniform distribution of scandium in the aluminium matrix can be achieved via the electromagnetic forces created during electrolysis, though the phases found by the SEM-EDS analysis corresponded to an intermetallic Al<sub>3</sub>Sc compound, due to its formation upon the slow cooling of the cell after the electrolysis trials.

**Author Contributions:** Conceptualisation, A.M.M.; methodology, all authors; investigation, all authors; data curation, all authors; writing—original draft preparation, A.M.M.; writing—review and editing, all authors.; supervision, A.M.M.; project administration, A.M.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work has received funding from the European Union’s Horizon 2020 and Innovation Programme under Grant Agreement No. 730105.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

## References

1. Zakharov, V.V. Effect of Scandium on the Structure and Properties of Aluminum Alloys. *Met. Sci. Heat Treat.* **2003**, *45*, 246–253. [[CrossRef](#)]
2. Røyset, J.; Ryum, N. Scandium in aluminium alloys. *Int. Mater. Rev.* **2005**, *50*, 19–44. [[CrossRef](#)]
3. Wang, Z.J.; Guan, C.Y.; Liu, Q.C.; Xue, J.L. Formation of Intermetallic Phases in Al-Sc Alloys Prepared by Molten Salt Electrolysis at Elevated Temperatures. In Proceedings of the 6th International Symposium on High-Temperature Metallurgical Processing, TMS2015, Orlando, FL, USA, 15–19 March 2015; pp. 215–222.
4. Nikolaev, A.Y.; Suzdaltsev, A.V.; Zaikov, Y.P. Electrowinning of Aluminum and Scandium from  $\text{KF-AlF}_3\text{-Sc}_2\text{O}_3$  Melts for the Synthesis of Al-Sc Master Alloys. *J. Electrochem. Soc.* **2019**, *166*, D252–D257. [[CrossRef](#)]
5. Harata, M.; Yasudab, K.; Yakushiji, H.; Okabe, T.H. Electrochemical production of Al-Sc alloy in  $\text{CaCl}_2\text{-Sc}_2\text{O}_3$  molten salt. *J. Alloys Compd.* **2009**, *474*, 124–130. [[CrossRef](#)]
6. Shtefanyuk, Y.; Mann, V.; Pingin, V.; Vinogradov, D.; Zaikov, Y.; Tkacheva, O.; Nikolaev, A.; Suzdaltsev, A. Production of Al-Sc Alloy by Electrolysis of Cryolite-Scandium Oxide Melts. In *Light Metals 2015*; Hyland, M., Ed.; Springer International Publishing: Cham, Switzerland, 2016; pp. 589–593. [[CrossRef](#)]
7. Thonstad, J.; Fellner, P.; Haarberg, G.M.; Hives, J.; Kvande, H.; Sterten, A. *Aluminium Electrolysis: Fundamentals of the Hall-Héroult Process*; Aluminium-Verlag Marketing and Kommunikation GmbH: Düsseldorf, Germany, 2001.
8. Grjotheim, K.; Krohn, C.; Malinovsky, M.; Matiasovsky, K.; Thonstad, J. *Aluminium Electrolysis: Fundamentals of the Hall-Héroult Process*; Aluminium-Verlag: Düsseldorf, Germany, 1982.