

A MODERN WAYS FOR Al-Sc MASTER ALLOYS PRODUCTION

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ABSTRACT

A brief review of the features of the up-to-date methods for producing the Al-Sc master alloys is presented. The key approaches including the direct fusion of aluminum with scandium, the aluminothermic synthesis using scandium salts or oxide as a scandium source and the electrowinning in molten salts using scandium salts or oxide as a scandium salts have been discussed. The mechanism features of methods are briefly described in this article. The advantages and disadvantages of each approach are analyzed, along with the comparative evaluation of parameters of the most promising ways for further development. Parameters, data regarding the process temperature, scandium content in the obtained master alloys as well as the degree of scandium extraction from its sources were studied.

In conclusions, the results of recent achievements in the development of the energy-effective and resource-saving method for the continuous production of the AlSc₂ master alloys by electrolysis of oxide-fluoride melts with scandium oxide, which was performed at the Institute of high-temperature electrochemistry, have been presented.

Keywords: Aluminum, scandium, master alloy, flux, scandium oxide, oxide-fluoride melt, aluminothermy, electrolysis.

INTRODUCTION

The aluminum-scandium (Al-Sc) master alloys are widely used in the fabrication of alloys for the car and aerospace industries, as well as for the military-industrial sector [1-4]. The increasing interest in alloys with each passing year is due to the fact that the functional details and protective coatings manufactured from them possess the improved exploitation parameters and technical features. Nowadays, the selling market of the standardized Al-Sc master alloys with scandium content of 2-5 wt% [5] is fairly fully represented by foreign and domestic manufacturers (Intermix-met, Aleastur, UC AMG Advanced Metallurgical Group, Huizhou Top Metal Material, Scandium International Mining Corp).

Nevertheless, the production output of master alloys and alloys based on aluminum increases, and a search and development of energy-efficient and resource-saving methods seem to be of great interest.

In the present article, the data demonstrating the current state and perspective directions in the field of the Al-Sc master alloys production are discussed.

4. METHODS AND DISCUSSION

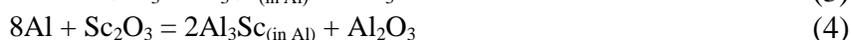
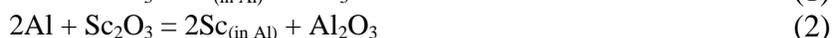
4.1. Direct fusion of scandium with aluminum

The simplest way to operate and control the composition of the obtained Al-Sc master alloy can be a direct fusion of the liquid or powdered aluminum with scandium. This way allows obtaining master alloys with the scandium content up to 35 wt% with the extraction degree close to 100%. However, the cost of the obtained master alloys is rather high, as it includes

the expenses for the production and storage of the pure initial reagents, as well as an appliance of the vacuum distillation in order to remove admixtures in conditions of the high temperature process. In addition, the disadvantage of this method is the inhomogeneity of the structure of the obtained master alloys due to a significant difference in the melting temperatures of the pure reagents [6]. For this reason, the aluminothermic reduction of scandium compounds is currently the most common among manufacturers.

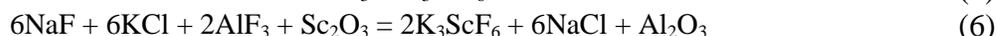
4.2. Aluminothermic synthesis

A principle of the method consists in a chemical reduction of the scandium compounds contained in the molten salt flux (NaF-KCl, NaF-KCl-AlF₃, and others [7-11]) according to the following overall reactions:



Scandium is a more electronegative metal compared to aluminum [12], therefore, the reactions (1) and (2) are difficult to proceed in the forward direction. One of the main ways of transition of scandium to aluminum during the alloys and master alloys production can be considered the intermediate formation of the intermetallic compounds according to the reactions (3) and (4). Their dissolution in the liquid aluminum bulk determines the kinetics and the equilibrium constant of the reaction.

In the sci-tech literature, another scheme of the similar technique is presented. Thus, according to works [7-11], a formation of the potassium and sodium fluoride-scandates takes place in the molten fluxes NaF-KCl-ScF₃ and NaF-KCl-AlF₃-Sc₂O₃:



The reaction mixture (granulate) mixes with aluminum, and fluoride-scandates plays the role of the main scandium source:



The reduced scandium interacts with aluminum with the formation of Al₃Sc. The authors [7-11] explain the given scheme on the basis of the XRD data, according to which the K₃ScF₆ and Na₃ScF₆ compounds are formed in the NaF-KCl-ScF₃ and NaF-KCl-AlF₃-Sc₂O₃ melts.

In fact, both schemes can be realized during the aluminothermic synthesis of alloys and master alloys. However, due to the high melting point of K₃ScF₆ (1170 °C [13]) and Na₃ScF₆ (885 °C [14]) the dominant scheme, from the kinetic point of view, seems to be including reactions (1)-(4). The fluoride-scandates and oxifluoride-scandates are also formed when the ScF₃ or Sc₂O₃ is in excess in the molten flux. The participation of more fusible fluoride-scandates KScF₄ (810 °C [13]) and NaScF₄ (660 °C [14]) in the aluminothermic reduction has not been described in the literature yet.

The method given above allows obtaining the Al-Sc master alloys with a quite high content (5 wt%) and an average extraction of scandium (70-90%). The variations of the flux compositions and ways of mixing aluminum with the flux results in an increase of the extraction degree up to 99.5% [11, 15, 16].

The advantages of this method is an easiness of implementation, a possibility of conducting the synthesis without using an inert atmosphere at a rather low temperature (790-1050 °C), and a quite high content and extraction of scandium. The main disadvantage is the accumulation of the oxide compounds (Al₂O₃, in particular) in the molten flux due to their presence in the initial reagents, which makes the flux unsuitable for further use. At the same time, the significant amount of the valuable scandium-containing compounds remains in the waste flux [15, 16].

4.3. Electrowinning in melts

Electrolysis of scandium-containing melts (LiCl-KCl-ScCl₃-AlCl₃, LiF-NaF-ScF₃-AlF₃, LiF-ScF₃-Sc₂O₃, NaF-AlF₃-LiF-Sc₂O₃, NaF-ScF₃-Sc₂O₃, CaCl₂-Sc₂O₃) [17-21] allows avoiding or reducing to minimum the loss of valuable reagents and performing the continuous obtaining the alloys and master alloys Al-Sc. When using a graphite cathode, the co-electrowinning of aluminum and scandium takes place, whereas using a liquid aluminum cathode, the primary process is the aluminothermic reduction of scandium compounds [19], and the electrolysis is necessary to increase the extraction of aluminum and scandium from the melt to the Al-Sc master alloy.

In comparison with the aluminothermic approaches, the electrolytic method can be performed at temperature below the aluminum melting point, in such a case, the solid Al-Sc master alloy with homogeneous distribution of scandium and intermetallic compounds will be formed at the cathode. The main obstacles for the practical implementation of this method are the use of relatively expensive reagents (LiCl, ScCl₃, AlCl₃, LiF, ScF₃), the need to develop and design a more complex reactor-electrolyzer including the selection and testing the constructive and electrode materials. In the electrolysis of a number of the above mentioned melts, the use of a protective atmosphere and the evaluation of the chlorine and chlorine-containing toxic gases at the anode are implied, which significantly reduces the acceptability of the technologies for producing Al-Sc master alloys.

The most promising and simplest way seems to be a fabrication of the Al-Sc alloys and master alloys under the conditions of existing technology for the aluminum production in the operating electrolyzer [22-26]. The principle of this method is that the electrolyzer can be fed by the Sc₂O₃ instead of the Al₂O₃. Moreover, it should be taken into account that the latter will also be presented in the melt. During the electrolysis in the NaF-AlF₃-Sc₂O₃-Al₂O₃ melt the following parallel processes take place:

- the aluminothermic reduction of the Sc₂O₃ according to the reactions (2) and (4);
- the aluminum and scandium electrowinning according to the overall reactions:



The portions of the reaction (2), (4), (11), and (12) in the overall process of the scandium withdrawal to aluminum are determined by a number of factors (such as electrolyzer design, value of current, mass ratio of the melt to aluminum, temperature, molar ratio of [NaF]/[AlF₃], amount of the Sc₂O₃ and Al₂O₃, content of scandium in aluminum, etc). In general, according to the different data [22-24], the reactions (2) and (4) seem to be dominant; therefore, it is the electrolytic decomposition of oxides and the relevant technological parameters that allow organizing the continuous production of the Al-Sc alloy and master alloy with a required content of scandium [26].

Due to its attractiveness, the possibility of industrial implementation of this method directly on the pilot electrolyzers has been investigated as early as the 80th of the past century [27], but did

not receive any development. The specificity of this method is that the Al-Sc master alloy can be obtained with a relatively low scandium content (not higher than 1.3 wt%) during electrolysis in the NaF-AlF₃-Sc₂O₃-Al₂O₃ at the acceptable cathode current density for the aluminum production (up to 1 A/cm²) in the operating electrolyzer [23, 24]. In order to obtain a standardized master alloy AlSc2 [5], it is required an increase in the cathode current density up to 2-3 A/cm² or a feeding the electrolyzer with a more expensive ScF₃ [23]. This is not possible within the framework of the existing technology for aluminum production, because the first one will result in the alkali metal deposition, the salt passivation of the electrode in electrolyzer, and will stop the process; and the second one will lead to significant changes in the physic-chemistry of the melt and the electrode processes taking place in this melt (anode process, in particular).

There are known attempts to obtain the Al-Sc alloys in the melts based on the low-melting KF-AlF₃ system with an addition of Sc₂O₃ at 750-850 °C [28, 29]. It was shown that the scandium content in the obtained samples significantly depends on the cathode current density (0.44 and 0.73 wt% at 0.5 and 1.0 A/cm²), and the additional ultrasonic treatment of the cathode aluminum increases the scandium concentration in the Al-Sc alloys (from 0.73 to 1.10 at cathode current density of 1.0 A/cm²). The scandium electrowinning was registered at the potential of -0.9 V against the liquid aluminum. Despite the positive preliminarily results, the work has not been continued yet.

Systematical physic-chemical studies and electrolysis tests in the melts based on the KF-AlF₃ system [32-36] with additions of NaF, Sc₂O₃, and Al₂O₃, performed in Institute of High-Temperature Electrochemistry UB RAS [30, 31], made it possible to find the operating parameters ranges for a continuous obtaining the Al-Sc master alloys with the scandium content of 2 wt% and higher in an enlarged lab electrolyzer. The electrolyzer consisted of a graphite crucible, which was placed in the resistance furnaces. The graphite crucible was filled with the 39KF-10NaF-51AlF₃ mixture (wt%)(4 kg), 200 g Sc₂O₃, and 4 kg of aluminum.

When the operating temperature reached 820 °C, the anode made of dense graphite was immersed into the molten mixture. The electrolysis was carried out at the current of 80 A between graphite anode and liquid aluminum cathode. Based on the lab tests it was estimated that in order to provide continuous producing the aluminum master alloy it is necessary to discharge the electrolyzer with the rate of 2 kg per 3 h, and, correspondently, to charge 2 kg of pure aluminum with the next portion of Sc₂O₃. It were completed eight discharges of the Al-Sc master alloy with total mass of 15.5 kg during this enlarged lab experiment. The chemical composition of the obtained Al-Sc master alloy was, wt%: scandium - 1.99-2.12; iron – 0.006; silicon – 0.007; copper – less than 0.001; sodium – 0.0002; lithium - not more than 0.0001; potassium – 0.0003. The content of scandium and admixtures in the obtained ingots corresponded to the AlSc2 master alloy, which is in a good agreement with the national and foreign standards [5], and the scandium extraction from its oxide reached 90-95%.

From the stated above it can be assumed that along with the traditional aluminothermic production of the Al-Sc master alloys with the scandium content of 2 wt% and higher, it seems promising to obtain the master alloys during electrolysis in the KF-NaF-AlF₃-Sc₂O₃ oxide-fluoride melts. Comparative characteristics of these methods are given in Table.

Table. Comparative characteristics of the methods for producing the Al-Sc master alloys

Parameter	Aluminothermic reduction	Electrolysis in the KF-NaF-AlF ₃ -Sc ₂ O ₃ melts

Required reagents	salts KCl-NaF-AlF ₃ ; aluminum; ScF ₃ (preferentially)	salts KF-NaF-AlF ₃ ; aluminum or Al ₂ O ₃ ; Sc ₂ O ₃
Temperature, °C	790-1050	750-900
Sc in Al, wt%	up to 5	5 and higher (under study)
Sc extraction, %	70-90 (preferentially)	90-95
Electricity consumption	- melting in an induction furnace; - remelting in crystallization bath	- electrolysis; - remelting in crystallization bath
Advantages	-simplicity of operation; - high extraction degree and content of scandium	- high extraction degree and content of scandium; - relatively simplicity of operation; - the possibility of continuous production of the master alloy with the required content of scandium
Disadvantages	- the necessity of the KCl-NaF-AlF ₃ flux regeneration; - use of rather expensive ScF ₃	- necessity of developing the electrolyzer's design

CONCLUSIONS

Key features, mechanisms, and advantages of the methods for producing the Al-Sc master alloys are presented and discussed. Among these methods a novel method for AlSc₂ master alloy production as well as parameters of the method were proposed. Data regarding the process temperature, scandium content in the obtained master alloys, the degree of scandium extraction from its sources were comparatively studied.

Actuality and competitiveness of the energy-effective and resource-saving method for the continuous production of the AlSc₂ master alloys by electrolysis of oxide-fluoride melts with scandium oxide, which was performed at the Institute of high-temperature electrochemistry, have been shown.

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