A MODERN WAYS FOR Al-Sc MASTER ALLOYS PRODUCTION

Andrey V. Suzdaltsev[1], Andrey Yu. Nikolaev[1,2], Yuriy P. Zaikov[1,2]

[1]*Institute of High-Temperature Electrochemistry UB RAS, Yekaterinburg, Russia*
[2]*Ural Federal University, Yekaterinburg, Russia*

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 is 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-AlF_3, and others [7-11]) according to the following overall reactions:

$$Al + ScF_3 = Sc_{(in\ Al)} + AlF_3 \quad (1)$$

$$2Al + Sc_2O_3 = 2Sc_{(in\ Al)} + Al_2O_3 \quad (2)$$

$$4Al + ScF_3 = Al_3Sc_{(in\ Al)} + AlF_3 \quad (3)$$

$$8Al + Sc_2O_3 = 2Al_3Sc_{(in\ Al)} + Al_2O_3 \quad (4)$$

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 fluorine-scandates takes place in the molten fluxes NaF-KCl-ScF_3 and NaF-KCl-AlF_3-Sc_2O_3:

$$3NaF + 3KCl + ScF_3 = K_3ScF_6 + 3NaCl \quad (5)$$

$$6NaF + 6KCl + 2AlF_3 + Sc_2O_3 = 2K_3ScF_6 + 6NaCl + Al_2O_3 \quad (6)$$

$$3NaF + ScF_3 = Na_3ScF_6 \quad (7)$$

$$2Na_3AlF_6 + Sc_2O_3 = 2NaAlOF_2 + Na_3ScF_6 + NaScOF_2 \quad (8)$$

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

$$K_3ScF_6 + Al = K_3AlF_6 + Sc_{(in\ Al)} \quad (9)$$

$$Na_3ScF_6 + Al = Na_3AlF_6 + Sc_{(in\ Al)} \quad (10)$$

The reduced scandium interacts with aluminum with the formation of Al_3Sc. The authors [7-11] explain the given scheme on the basis of the XRD data, according to which the K_3ScF_6 and Na_3ScF_6 compounds are formed in the NaF-KCl-ScF_3 and NaF-KCl-AlF_3-Sc_2O_3 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 K_3ScF_6 (1170 °C [13]) and Na_3ScF_6 (885 °C [14]) the dominant scheme, from the kinetic point of view, seems to be including reactions (1)-(4). The flouride-scandates and oxifluoride-scandates are also formed when the ScF_3 or Sc_2O_3 is in excess in the molten flux. The participation of more fusible fluoride-scandates $KScF_4$ (810 °C [13]) and $NaScF_4$ (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 (Al_2O_3, 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-$ScCl_3$-$AlCl_3$, LiF-NaF-ScF_3-AlF_3, LiF-ScF_3-Sc_2O_3, NaF-AlF_3-LiF-Sc_2O_3, NaF-ScF_3-Sc_2O_3, $CaCl_2$-Sc_2O_3) [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 ($LiCl$, $ScCl_3$, $AlCl_3$, LiF, ScF_3), 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 Sc_2O_3 instead of the Al_2O_3. Moreover, it should be taken into account that the latter will also be presented in the melt. During the electrolysis in the NaF-AlF_3-Sc_2O_3-Al_2O_3 melt the following parallel processes take place:

- the aluminothermic reduction of the Sc_2O_3 according to the reactions (2) and (4);
- the aluminum and scandium electrowinning according to the overall reactions:

$$Sc_2O_3 + 3C + 6e^- = 2Sc_{(in\ Al)} + CO + CO_2 \quad (11)$$

$$Al_2O_3 + 3C + 6e^- = 2Al + CO + CO_2 \quad (12)$$

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 $[NaF]/[AlF_3]$, amount of the Sc_2O_3 and Al_2O_3, 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 $NaF-AlF_3-Sc_2O_3-Al_2O_3$ at the acceptable cathode current density for the aluminum production (up to 1 A/cm^2) 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/cm^2 or a feeding the electrolyzer with a more expensive ScF_3 [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 $KF-AlF_3$ system with an addition of Sc_2O_3 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/cm^2), 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/cm^2). 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 $KF-AlF_3$ system [32-36] with additions of NaF, Sc_2O_3, and Al_2O_3, 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 $39KF-10NaF-51AlF_3$ mixture (wt%)(4 kg), 200 g Sc_2O_3, 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 Sc_2O_3. 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 $KF-NaF-AlF_3-Sc_2O_3$ 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 $KF-NaF-AlF_3-Sc_2O_3$ melts

Required reagents	salts $KCl-NaF-AlF_3$; aluminum; ScF_3 (preferentially)	salts $KF-NaF-AlF_3$; aluminum or Al_2O_3; Sc_2O_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.

REFERENCES

1. Royset J, Ryum N: 'Scandium in aluminium alloys overview: physical metallurgy, properties and applications'. International Materials Reviews 2005 50 19-46.
2. Zakharov VV: 'Kinetic of decomposition of the solid solution of scandium in aluminum in binary Al-Sc alloys'. Metal Science and Heat Treatment 2015 57 410-4.
3. Ovsyannikov BV, Zamyatin VM: 'Behavior of scandium in aluminum alloys of different alloying systems' Materials Science Forum 2014 794-796 1002-7.
4. Kotenkov PV, Popova EA, Pastukhov EA, Bykov AS: 'Survivability of Al-Sc-Zr master alloy'. Tsvetnye Metally 2013 (12) 77-80.
5. GOST R 53777-2010 'Ligatury alyuminievye. TU'; CEN Standard EN AM-94004.
6. Yang Sh, Gao B, Wang Zh, Shi Zh, Ban Y, Kan H, Cao X, Qiu Zh 'Preparation of Al-Sc alloys by molten salts electrolysis'. Light Metals 2007 54-7.
7. Makhov SV, Moskvitin VI: 'Fundamentals of the kinetics of the aluminothermic reduction of scandium from chloride-fluoride-scandate melts'. Rus J Non-Ferrous Metals 1998 (2) 13-6.
8. Makhov SV, Moskvitin VI: 'Modern technology of production of aluminum-scandium

ligature’. Tsvetnye Metally 2010 (5) 95-6.
9. Skachkov VM, Yatsenko SP: ‘Obtaining of Sc, Zr, Hf and Y base metals on the basis of aluminum by method of high-temperature exchange reactions in salt melts’. Tsvetnye Metally 2014 (3) 22-6.
10. Skachkov VM, Varchenya PA, Ovsyannikov BV, Yatsenko SP: ‘Injection of scandium-containing process powders into aluminum alloys’ Tsvetnye Metally 2013 (12) 81-6.
11. Yatsenko SP, Skachkov VM, Yatsenko AS: ‘Receipt of ligature on basis of aluminium by method of high-temperature exchange reaction in molten salts. V. Injection of technological powders in liquid aluminium’. Rasplavy 2011 (4) 41-6.
12. Turkdogan ET: Physical Chemistry of High Temperature Technology, 1st ed. NY, Academic Press, 1980.
13. Sokolova YuV, Cherepanin RN, Sagalova TB: ‘Synthesis and some properties of potassium fluoro-scandates’. Rus J Non-Ferrous Metals 2006 (4) 40-4.
14. Brown D: Halides of the transition elements. Halides of the lanthanides and actinides. London, John Wiley, 1968
15. Shubin AB, Shunyaev KYu: Method for obtaining aluminium-scandium alloy combination, Pat. RU2507291, Feb. 2014.
16. Gorokhov DS, Poponin NA, Kukushkin YuM, Kazantsev VP, Rychkov VN: Procedure for production of aluminium-scandium addition alloy for alloys on base of aluminium, Pat. RU2426807, March 2011.
17. Castrillejo Y, Vega A, Vega M, Hernandez P, Rodriguez JA, Barrado E: ‘Electrochemical formation of Sc-Al intermetallic compounds in the eutectic LiCl-KCl. Determination of thermodynamic properties’. Electrochimica Acta 2014 118 58-66.
18. Tian Y, Sun B, Zhai Yu: ‘Preparation of Al-Sc alloy in chloride system with molten salt electrolysis’. Transactions of Nonferrous Met. Soc. China 1998 8 626-31.
19. Yang Sh, Gao B, Wang Zh, Shi Zh, Ban Y, Kan H, Cao X, Qiu Zh: ‘Preparation of Al-Sc alloys by molten salts electrolysis’. Innovations in Electrometallurgy 2007 54-7.
20. Harata M, Yasuda K, Yakushiji H, Okabe TH: ‘Electrochemical production of Al-Sc alloy in $CaCl_2$-Sc_2O_3 molten salt’. J Alloys and Compounds 2009 474 124-30.
21. Nikolaev AYu, Suzdaltsev AV, Zaikov YuP: ‘Electroreduction of aluminium and scandium from the fluoride and oxide-fluoride melts’. Butlerov Communications 2018 56 (10) 75-83.
22. Schwellinger P: Method for the production of an aluminum-scandium master alloy, Int. appl. WO2006/079353A1, Aug.2006.
23. Moskvitin VI, Makhov SV: ‘On possibility of fabrication of aluminum-scandium alloying composition in aluminum electrolyzer’. Tsvetnye Metally 1998 (7) 43-6.
24. Zaikov Yu, Tkacheva O, Suzdaltsev A, Kataev A, Shtefanyuk Yu, Pingin V, Vinogradov D: ‘Lab scale synthesis of Al-Sc alloys in NaF-AlF_3-Al_2O_3-Sc_2O_3 melt’. Advanced Materials Research 2015 1088 213-6.
25. Qian Y, Xue J, Liu Q, Zhu J: ‘Preparing Al-Sc-Zr alloys in aluminum electrolysis process’. Light Metals 2013 1311-4.
26. Zaikov YuP, Suzdaltsev AV, Nikolaev AYu, Tkacheva OYu, Vinogradov DA, Pingin VV, Shtefanyuk YuM, Mann VKh: Electrolytic method for continuous production of aluminium alloy with scandium, Pat. RU2599312, Oct. 2016.
27. Napalkov VI, Makhov SV: Alloying and modifying of aluminium and magnesium. Moscow, MISiS, 2002.

28. Liu Q, Xue J, Zhu J, Qian Y, Feng L: 'Processing Al-Sc alloys at liquid aluminum cathode in KF-AlF_3 molten salt'. ECS Transactions 2012 50 (11) 483-9.
29. Liu Q, Xue J, Zhu J, Guan Ch: 'Preparing aluminium-scandium inter-alloys during reduction process in KF-AlF_3-Sc_2O_3 melts'. Light metals 2012 685-9.
30. Tkacheva O, Redkin A, Kataev A, Rudenko A, Dedyukhin A, Zaikov Y: 'Novel molten salts media for production of functional materials'. MATEC Web of Conferences 2016 67 06044.
31. Dedyukhin AE, Apisarov AP, Tkacheva OYu, Zaikov YuP, Redkin AA: 'Alumina solubility and electrical conductivity in potassium cryolites with low cryolite ratio' in book: Molten Salts and Ionic Liquids: Never the Twain? 2012 75-84.
32. Shtefanyuk Yu, Mann V, Pingin V, Vinogradov D, Zaikov Yu, Tkacheva O, Nikolaev A, Suzdaltsev A: 'Production of Al-Sc alloy by electrolysis of cryolite-scandium oxide melts'. Light Metals 2015 589-93.
33. Nikolaev AYu, Suzdaltsev AV, Polyakov PV, Zaikov YuP: 'Cathode process at the electrolysis of KF-AlF_3-Al_2O_3 melts and suspensions'. J Electrochemical Society 2017 164 (8) H5315-21.
34. Suzdaltsev AV, Filatov AA, Nikolaev AYu, Pankratov AA, Molchanova NG, Zaikov YuP: 'Extraction of scandium and zirconium from their oxides during the electrolysis of oxide–fluoride melts'. Rus Metallurgy (Metally) 2018 (2) 133-8.
35. Mann VKh, Pingin VV, Vinogradov DA, Shtefanyuk YuM, Zaikov YuP, Suzdaltsev AV, Nikolaev AYu, Tkacheva OYu: Method for producing aluminum-scandium ligature, Int. appl. WO2016/171584A1, Oct. 2016.
36. Zaikov YuP, Suzdaltsev AV, Nikolaev AYu, Tkacheva OYu, Vinogradov DA, Pingin VV, Shtefanyuk YuM, Mann VKh: Method of continuous production of aluminium ligature with 2 wt.% of scandium, Pat. RU2629418, Sept. 2017.