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Lab Scale Synthesis of Al-Sc Alloys in $NaF-AlF_3-Al_2O_3-Sc_2O_3$ melt

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Abstract. The liquidus temperature in the [NaF-AlF_3(30 mol.%)]-Sc_2O_3 molten system with the Sc_2O_3 additions up to 12 wt% was measured by the thermo analysis. The effect of the cathode current density (0, 0.25, 0.50, and 1.0 $A \cdot cm^{-2}$), the Sc_2O_3 content (1, 2, 4, and 8 wt%) in the NaF-AlF_3(30 mol.%)-Al_2O_3-Sc_2O_3 electrolyte, the rate of the molten aluminum agitation (0, 100 rotates/min), the synthesis duration (30-210 min) on the Sc content in the aluminum alloy at 980 °C was studied. The Al-Sc alloys with the scandium content of 0.15-1.30 wt%, depending on the synthesis conditions, and with the uniform Sc distribution throughout the aluminum matrix were produced.

Introduction

The most part of the worldwide produced aluminum is used in electrical engineering and automotive industry. However, recently with a rapid pace of development and modernization of Hi-Tech, robotics, automotive and space industry there was a demand for master alloys based on aluminum metal with additions of Si, B, Ti, Sc, Zr, and other elements. Even an insignificant additive of the majority of the listed elements to aluminum modifies its structure and changes the technological properties. For instance, the addition of 0.2 wt% scandium to aluminum improves it durability, corrosion resistivity, weldability and stability to the recrystallization [1]. The cost of the Al-Sc master alloy currently produced by mixing Sc with liquid Al is rather high; moreover, the scandium distribution throughout the aluminum matrix is not uniform enough.

At present, some research schools are focused on development of an alternative way for the aluminum alloy's production. One of the approaches is electrolysis in a conventional cryolite-alumina [2, 3] or in a potassium-cryolite-based electrolytes with Sc_2O_3 additives [4]. In this connection the purposes of this work were to measure the Sc_2O_3 solubility in the NaF-AlF_3 melt with composition close to conventional electrolyte at temperatures 950-980 °C and to study the effect of different technological parameters (Sc_2O_3 content in electrolyte, cathode current density, duration of electrolysis, agitation of aluminum) on concentration and distribution of scandium in aluminum during electrolysis in the NaF-AlF_3-Al_2O_3-Sc_2O_3 electrolyte.

Sc_2O_3 solubility in NaF-AlF_3

Experimental. The NaF-AlF_3(30 mol.%) electrolyte was prepared by melting reagents mixed in corresponding amounts. The following chemicals were used for electrolyte preparation: NaF (chemically pure grade, Vekton); AlF_3 (pure grade, Vekton); Sc_2O_3 (99.9 wt%).

The solubility measurements were performed by thermo analysis. A platinum crucible filled with a preliminary prepared sodium cryolite electrolyte was placed inside a furnace and heated about 30 degrees above the expecting melting point. Then, during cooling (2-3 degrees/min), temperature change was registered with a frequency of 1 measurement per second. The first bend on the cooling curve was ascribed to the liquidus temperature. The heating-cooling cycle was repeated after each addition of Sc_2O_3.

Results. A part of phase diagram obtained in the quasi-binary system [NaF-AlF_3(30 mol.%)]-Sc_2O_3 with the Sc_2O_3 concentration varied from 0 to 12 wt% is shown in Fig.1. It is represented by a simple eutectic at the Sc_2O_3 concentration 8.5 wt% and temperature 920 ˚C. The Sc_2O_3 solubility in the NaF-AlF_3(30 mol.%) melt was found to be 10 wt% at 950 ˚C.

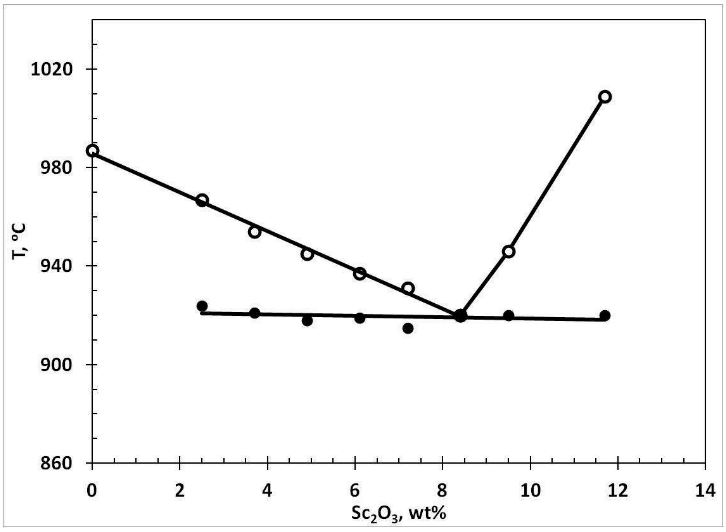

Fig.1 Part of the phase diagram in the [NaF-AlF_3(30 mol.%)]-Sc_2O_3 quasi-binary system

The alumina solubility in sodium cryolite decreases in presence of scandium oxide. It was found that the alumina solubility in the [NaF-AlF_3(30 mol.%)]-Sc_2O_3(2 mol.%/4.9 wt%) molten mixture is about 8 wt% at 950 °C.

Synthesis of Al-Sc alloy

Experimental. The Al-Sc alloys were obtained by two methods: electrolysis and aluminothermy. Experimental cells in both procedures had a similar design. The electrolysis cell was supplied with a graphite anode and a graphite current lead to a cathode (liquid aluminum on the bottom of an alumina crucible). The cathode current density was changed from 0.2 to 1 A/cm^2. The [NaF-AlF_3(30 mol.%)]-Al_2O_3-Sc_2O_3 molten mixtures with the Sc_2O_3 concentration ranged from 1 to 8 wt% and the Al_2O_3 content about 1 wt% were tested as electrolytes in both procedures. First of all a pre-testing electrolysis at 1.08 V in a cell with graphite electrodes during 2 hours was conducted in order to remove electropositive impurities in the prepared electrolyte. After that the aluminum metal was added into the crucible. All tests were carried out at 980 °C. When applied the molten aluminum was agitated with a graphite stirrer (100 rotates/min). The melt and alloy compositions were analyzed by ICP and SEM EDX.

Results. The Al-Sc alloy synthesis was carried out by electrolysis in the NaF-AlF_3(30 mol.%)-Al_2O_3-Sc_2O_3 electrolytes with varied concentration of Sc_2O_3 at different cathode current density, duration and with and without aluminum agitation. The synthesis parameters for both procedures (with applying current and without) and characteristics of obtained alloys in the tests performed in the cryolite-alumina melts with the Sc_2O_3 content of 2 and 8 wt% are presented in Table 1. The scandium content in the obtained alloys was in the range of 0.15-1.30 wt% depending on electrolysis condition. Apparently, the Sc_2O_3 amount added into the melt has the most impact on the scandium content in the obtained alloy; at the same time the cathode current density increase or the mechanical agitation of aluminum have no significant effect.

According to SEM analysis, typically the scandium distribution in the aluminum matrix was uniform. An example of micrograph of the Al-Sc alloy obtained in electrolyte with 2 wt% of Sc_2O_3 by electrolysis (sample #3) and aluminothermy (sample #7) and the scandium distribution in Al (EDX) are shown in Figs. 2 and 3. However, the increased Sc_2O_3 concentration in electrolytes results in formation of intermetallic compounds. The micrograph of the Al-Sc metallographic section and the scandium distribution map in a sample obtained in the electrolyte with 8 wt% of Sc_2O_3 during test without current and agitation (sample #11) is shown in Fig.4. The elemental analysis of the differently colored areas in the photomicrography indicates the presence of the intermetallic compounds with high scandium concentration (grey area). These points at a certain excess of the scandium concentration in the aluminum matrix comparing to the ICP analysis data.

TABLE 1. THE SYNTHESIS PARAMETERS AND CHARACTERISTICS OF OBTAINED AL-SC ALLOYS IN NAF-ALF$_3$(30 MOL.%)-AL$_2$O$_3$-SC$_2$O$_3$ ELECTROLYTES

Sample #	Sc_2O_3 in electrolyte, wt%	stirring, rotates/min	*t*, min	*i*, A cm^{-2}	*U*, V	Sc in Al, wt%	
						ICP	EDX*
1		100	120	0.25	3.2…3.3	0.23	0.21/0.28
2		100	60	0.50	3.4…3.6	0.25	0.27/0.32
3		100	120	0.50	3.4…3.6	0.27	0.25/0.35
4	2	0	30	0	-	0.21	0.23/0.24
5		0	60	0	-	0.24	-
6		0	120	0	-	0.24	-
7		0	180	0	-	0.23	0.26/0.26
8		0	30	0	-	0.65	-
9		0	60	0	-	0.72	-
10	8	0	90	0	-	0.90	-
11		0	120	0	-	1.02	0.86/1.44
12		100	120	0.50	3.1…3.4	1.25	-
13		100	120	1.00	3.2…3.4	1.30	-

*Average value/Maximum value

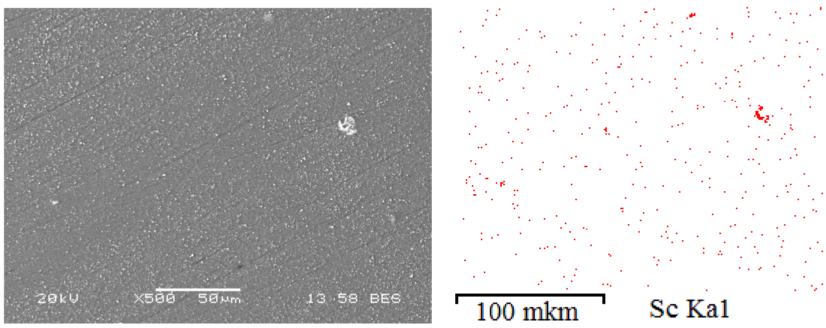

Fig.2 Micrographs of the Al-Sc alloy metallographic section (sample #3, Table 1) and distribution map of scandium in aluminum.

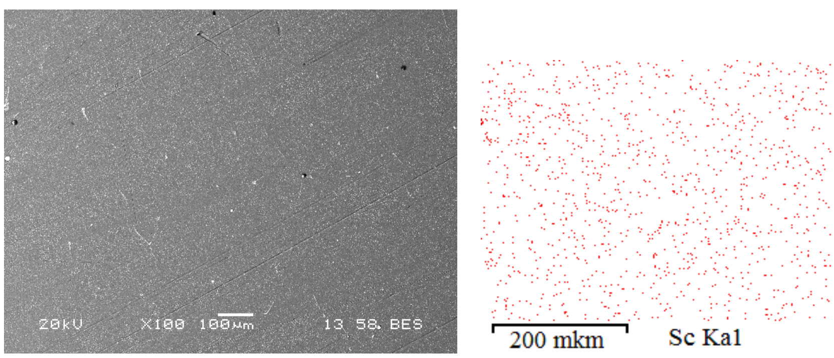

Fig.3 Micrographs of the Al-Sc alloy metallographic section (sample #7, Table 1) and distribution map of scandium in aluminum.

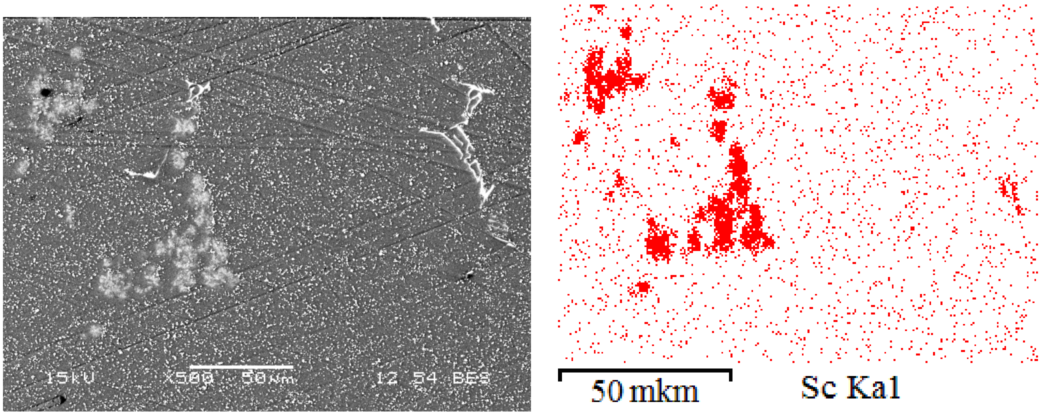

Fig.4 Micrographs of the Al-Sc alloy metallographic section (sample #11, Table 1) and distribution map of scandium in aluminum.

Summary

The Sc_2O_3 has a good solubility in the NaF-AlF_3 melts at 950-980 °C. The alumina additions to the cryolite electrolyte decrease the Sc_2O_3 solubility; nevertheless it is still sufficient to perform the Al-Sc synthesis.

The Al-Sc alloys with scandium content from 0.15 to 1.30 wt% were synthesized in the NaF-AlF_3(30 mol.%)-Al_2O_3-Sc_2O_3 with the Sc_2O_3 content changed from 1 to 8 wt% in the lab cell at 980 °C. Since the Sc_2O_3 amount added into the melt impacts the scandium content in the Al-Sc alloys the most effectively then it was suggested that the chemical mechanism of the Sc_2O_3 reduction in the cryolite-alumina melts dominated the electrochemical one.

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