

APPLICATION OF ALKALINE METAL FLUORIDES FOR DOPING OF ALUMINUM

Skachkov V.M., Pasechnik L.A., Yatsenko S.P.

Institute of Solid State Chemistry UB RAS,

91, Pervomaiaskaya st, Ekaterinburg, 620990 (Russia)

e-mail: yms@weburg.me

Abstract. High-temperature exchange reactions between liquid aluminum and fluoride salt systems containing scandium, yttrium, zirconium, and hafnium compounds have been studied. High-temperature reactions in other salt systems have been compared. Advantages and disadvantages of application of alkaline metal fluorides for doping of aluminum have been shown.

Keywords: salt melt, aluminum, scandium, yttrium, zirconium, hafnium, high-temperature exchange reactions

Introduction

In construction, mechanical engineering, aircraft building, rocket production, and many other sectors of the national economy they use mainly aluminum alloys since pure aluminum has poor technical characteristics, and doping of aluminum alloys with rare-earth scattered elements finds an ever-greater application, which considerably improves their service properties [1,2]. Small additions of scandium, yttrium, zirconium, and hafnium restrict grain growth of aluminum alloys, stabilize the crystal structure at high temperatures, increase the mechanical and corrosion properties, and improve weldability and plasticity. The presence of only 0.3 wt.% Sc increases the tensile strength of annealed aluminum sheets from 55 to 240 MPa, and in Al-5%Mg alloy – from 260 to 400 MPa. The effect of scandium manifests itself at smaller concentrations in the presence of zirconium. Yttrium additions of not more than 0.1 wt.% reduce the oxidation rate, especially in hard aluminum alloys. Hafnium in aluminum alloys binds such harmful impurities as iron, alkaline metals etc. into intermetallic compounds (IMC). The introduction of 1 wt.% Hf leads to the production of ultrastrong alloys exhibiting enhanced resistance to vibrational damage; such alloys have a grain size of ~ 40-50 nm [3-10]. Aluminum is usually doped by introducing master alloys, that can be obtained by different methods, into a melt. A good review of scandium doping methods is given by researchers of the Institute of High-Temperature Electrochemistry UB RAS in work [11]. The aluminothermal method for doping of aluminum and aluminum-based alloys, both castable and wrought, holds much promise. It is not obvious that high-temperature exchange reactions in salt melts can be used to introduce refractory,

scattered, and rare metals into aluminum. The authors have doped aluminum with small additions (less than 1 wt.%) of scandium, yttrium, zirconium, and hafnium.

Experimental

Melting of salts and high-temperature exchange reactions were carried out in a Nabertherm L 9/11 muffle furnace. X-ray phase analysis (XPA) of melted (reaction) salts was performed on Shimadzu and DRON-2.0 diffractometers in $\text{CuK}\alpha$ radiation with the angle interval $10^\circ \leq 2\Theta \leq 70^\circ$, a scanning step of 0.03° , and 2 s time in point. The phases were identified using the Powder Diffraction File JCPDS-ICDD PDF2 (sets 1-47). The produced reaction salts were ground in an agate mortar and stored in an desiccator. The high-temperature exchange reactions were carried out in alundum crucibles at 750-780 °C; the salts were fed into the aluminum melt by means of a laboratory-scale injection plant (Fig. 1), and bottled carbon dioxide served as a transporting agent. The elemental analysis of the melts was performed on a Spectromass 2000 mass-spectrometer with inductively bound plasma.

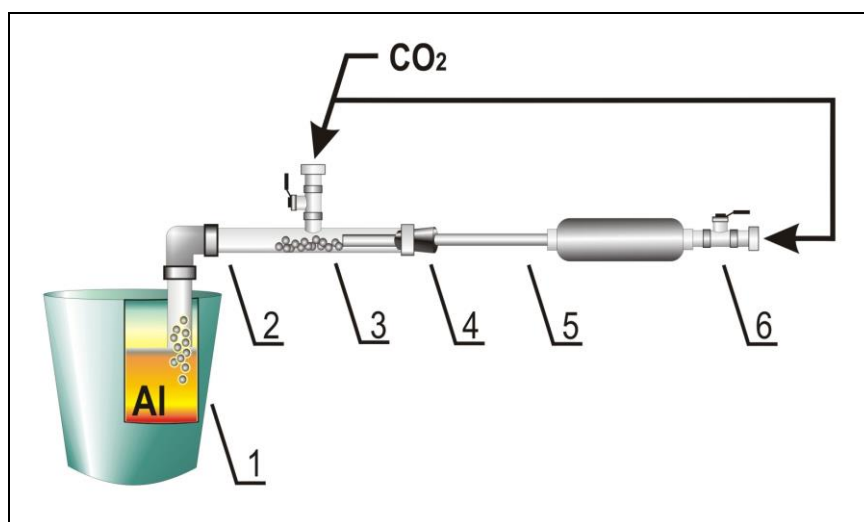


Fig. 1. The diagram of the laboratory plant for injection of reaction salts into aluminum salt: 1 – crucible for aluminum; 2 – single-nozzle tuyere; 3 – salt powder; 4 – plug; 5 – accelerating nozzle; 6 – pulse gate; CO_2 – protective gas; Al – liquid aluminum

Granular aluminum (p.a.) TU 6-09-02-529-92; NaF (p.a.) GOST 4463-76; KF (pure) GOST 20 848-75; Sc_2O_3 (pure) TU 48-4-417-87; Y_2O_3 (pure) TU 48-4-191-72; ZrO_2 (pure) TU 6-09-2486-77; HfO_2 (pure) TU 48-4-201-72 were used for synthesis.

Results and discussion

The application of aluminothermal methods for the production of master alloys and alloys by injection of a gas-powder suspension through aluminum melt has been comprehensively

examined by the authors and described in [12]. The suspension consists of inert gas (argon Ar or carbon dioxide CO₂) and a ground salt mixture of sodium fluoride and potassium chloride with additions of aluminum fluoride, which contains oxides or fluorides of metals introduced into the alloy at 700-900 °C. A corresponding patent [13] has been acquired, and aluminum-scandium alloys have been obtained by the injection method in industrial furnaces at OAO *KUMZ*, which was described in [14].

Mixtures of alkaline metal salts dissolve oxides and fluorides of other metals during melting forming complex compounds that easily interact with molten aluminum. This makes it possible not to use such expensive compounds as for example potassium fluozirconates (hafnates). The application of sodium and potassium fluoride melts for the dissolution of oxides holds much promise, which is demonstrated with an example of scandium oxide solubility in different salt systems (Fig. 2, curve 8). It was determined from the XPA data (Fig. 3) that scandium oxide dissolves during melting with sodium and potassium fluorides forming 2-potassium sodium hexafluoroscandiate (scandium cryolite-elposolite) K₂NaScF₆. Yttrium oxide behaves in similar salt mixtures like scandium oxide. Zirconium and hafnium dissolve giving rise to oxyfluorides of variable composition, in much the same way as they behave during the formation of oxyfluorides from their dioxides when treated with concentrated solutions of hydrofluoric acid. As a result, Hf(Zr)F₄·nH₂O is precipitated, and oxyfluorides are formed during drying in air at 200-250 °C. The products of their thermal decomposition are Hf₄F₁₂O₂ and Zr₄F₁₀O₃.

A large number of salt systems (Fig. 2) based on fluoride-chloride salts of alkaline (Li, Na, K) and alkaline-earth (Ca) metals with introduced scandium, yttrium, zirconium, and hafnium fluorides or oxides have been studied to search for the optimal conditions of their displacement with more active aluminum. The eutectics melting temperatures vary depending on the composition of salt mixtures from 454 °C (for LiF-NaF-KF) to 965 °C (cryolite Na₃AlF₆) [15]. The use of calcium salts allows a considerable reduction of the concentration of sodium in the final alloy, whose admixture may substantially increase the volume of rejects in the production of rolled stock. We have established the solubility values of scandium fluoride and oxide as a function of temperature; the application of scandium oxide lowers slightly its direct yield in the solution compared with scandium fluoride. For example, at 800 °C the solubility value in a calcium salt mixture is 0.6 wt.% for Sc₂O₃ and 3.4 wt.% for ScF₃.

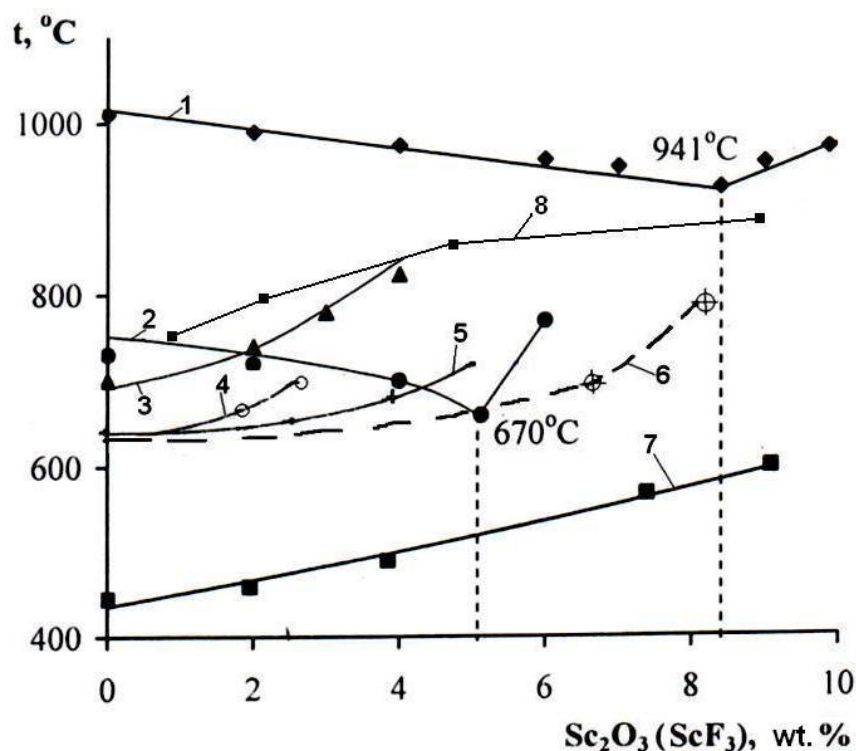


Fig. 2. Segments of liquidus curves of salt systems with scandium oxide and fluoride:

1 - $\text{Na}_3\text{AlF}_6 - \text{Sc}_2\text{O}_3$; 2 - $(0.53\text{NaF} + 0.47\text{AlF}_3) - \text{Sc}_2\text{O}_3$; 3 - $(0.09\text{Na}_5\text{Al}_3\text{F}_{14} + 0.91\text{KCl}) - \text{Sc}_2\text{O}_3$;
 4 - $(0.86\text{CaCl}_2 + 0.14\text{CaF}_2) - \text{Sc}_2\text{O}_3$; 5 - $(0.86\text{CaCl}_2 + 0.14\text{CaF}_2) - \text{ScF}_3$; 6 - $(0.82\text{Li}_3\text{AlF}_6 + 0.18\text{K}_3\text{AlF}_6) - \text{ScF}_3$;
 7 - $(0.59\text{KF} + 0.29\text{LiF} + 0.12\text{NaF}) - \text{ScF}_3$; 8 - $(0.4\text{NaF} + 0.6\text{KF}) - \text{Sc}_2\text{O}_3$

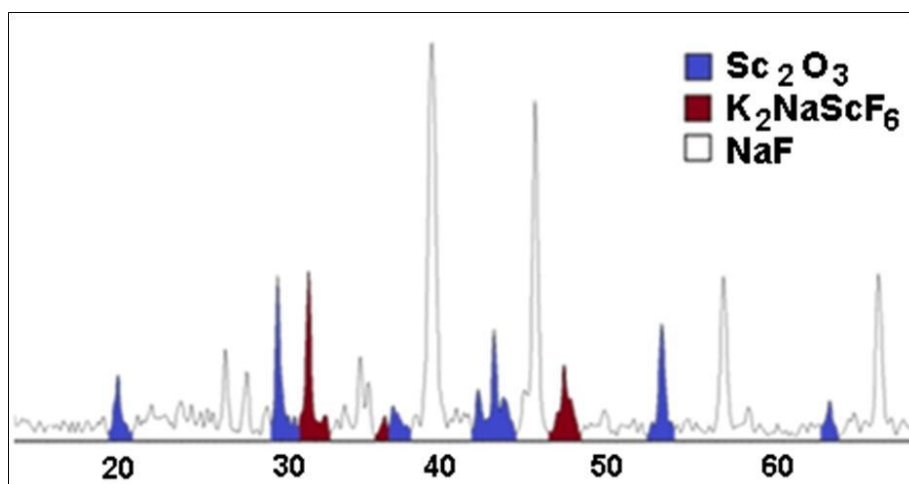


Fig. 3. XRD pattern of salt system with scandium oxide: $(0.4\text{NaF} + 0.6\text{KF}) - \text{Sc}_2\text{O}_3$

The application of sodium and potassium fluorides instead of chlorides not only increases the reactivity in high-temperature exchange reactions, but also reduces metal loss during evaporation since fluorides are less volatile than chlorides, although fluorides have higher melting temperatures (Table 1) [16,17].

Table 1

Melting and boiling temperatures of metal chlorides and fluorides		
Substance	Melting temperature t, °C	Boiling temperature t, °C
LiCl	614	1380
LiF	870	1681
NaCl	801	1465
NaF	992	1705
KCl	776	1406
KF	857	1500
CaCl ₂	772	1600
CaF ₂	1418	2500
AlCl ₃	(192,6) under pressure	sublimates 181,2
AlF ₃	(1290) under pressure	sublimates 1272
ScCl ₃	956	975
ScF ₃	1552	1607
YCl ₃	703	1510
YF ₃	1155	-
ZrCl ₄	(437) under pressure	sublimates 333
ZrF ₄	(910) under pressure	sublimates 903
HfCl ₄	(432) under pressure	sublimates 315
HfF ₄	-	sublimates 974

The eutectic 0.4NaF + 0.6KF melts at 721 °C [18], which allows the exchange reactions to be carried out at temperatures below 800 °C. The thermodynamic calculations for the displacement reaction, for example, displacement of scandium by aluminum into alloy at 800 °C, give a value of yield of ~80%. It was determined experimentally that an increase in the temperature of interaction lowers the yield of scandium from the salt melt, whereas the process temperature of 700-750 °C provides a direct yield of scandium into alloy of 95% and more.

The economic effectiveness of production of alloys with unique properties (mechanical, thermal, corrosion, radiation etc.) can be enhanced by injection of prepared reaction powder into liquid aluminum. Vigorous agitation of alloy during injection promotes uniform distribution of introduced components and acceleration of the high-temperature reaction, which considerably reduces the doping time in whole. Besides, some impurities are removed from aluminum. The chemical composition of the alloy impurities during doping of A85 grade aluminum was determined as (initial Al – numerator, after melting – denominator, wt.%): Cu - 0.01/0.0019; Mg - 0.01/0.0007; Zn - 0.01/0.001; Mn - 0.01/0.003; Si - 0.05/0.038; Na - 0.0014/0.0012; and hydrogen < 0.29 m³/100 g.

On completing the injection with carbon dioxide and 5 min exposure, the slag was discharged (730-750 °C) and the obtained alloy was poured out into a cast-iron mold lined with hexagonal boron nitride. An averaged alloy sample was taken and analyzed; the results are presented in Table 2.

Table 2

Interaction of liquid aluminum with scandium, yttrium, zirconium, and hafnium oxides/fluorides/oxyfluorides dissolved in fluoride melt (0.4NaF + 0.6KF)

No.	Oxide, fluorides	In alloy, %				Direct yield, %			
		Sc	Y	Zr	Hf	Sc	Y	Zr	Hf
1	Sc ₂ O ₃	0.91	-	-	-	93	-	-	-
2	ScF ₃	0.98	-	-	-	96	-	-	-
3	Y ₂ O ₃	-	0.95	-	-	-	61	-	-
4	YF ₃	-	1.15	-	-	-	69	-	-
5	ZrO ₂	-	-	1,00	-	-	-	92	-
6	Zr ₄ F ₁₀ O ₃	-	-	1,05	-	-	-	94	-
7	HfO ₂	-	-	-	0,9	-	-	-	82
8	Hf ₄ F ₁₂ O ₂	-	-	-	1,1	-	-	-	88

Note: The presented results are average data of three identical meltings.

The mass ratio of the fluoride melt to the aluminum melt during melting was determined by the solubility of the chosen metal oxides. For the salt/metal ratios less than 0.5 for Zr, 0.8 for Sc, and 1.0 for Y and Hf, the process of reduction of rare metals is inhibited, therefore the components pass into the alloy to a lesser extent, while salt/metal ratios of more than 1.2 lead to efficiency loss and a larger volume of recycling salts. Replacement of oxides to fluorides and oxyfluorides of the metals of the input increases direct access from 2 to 7%.

The injection method of alloy production allows one to combine necessary amounts of different ingredients in the form of fluoride and oxide compounds in the injected powder. Metals, that are electrochemically more positive than aluminum, can be reduced simultaneously, for example, scandium and zirconium, scandium and hafnium, yttrium and zirconium, yttrium and hafnium etc., which further facilitates the technology of alloy production. Note that the reaction powder should be produced by preliminary alloying of fluorides with the corresponding oxides or fluorides and subsequent grinding. Ground powder is very hygroscopic and should be used immediately or stored in a damp-proof place.

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