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Salt flux compositions for reprocessing and producing Al-Mg-based alloys and composites

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Abstract. Al-Mg alloys and composite materials based on Al-Mg alloys are widely used in various fields due to their unique characteristics. In this paper, compositions of salt fluxes for processing alloys, as well as for the synthesis of Al-Mg-based composites, are thermodynamically justified and experimentally tested. The NaCl-KCl (chloride-fluoride flux) with MgF₂ additives is recommended for further studies.

1. Introduction

The demand for new alloys and metal matrix composites (MMCs) based on aluminum is growing [1–4]. This is due to the fact that small additions of modifiers (Sc, Zr, B, etc.) or reinforcement particles (C, Al₂O₃, TiB₂, TiC, ZrB₂, etc.) to aluminum significantly improve their performance.

Various methods for the synthesis of aluminum alloys and aluminum metal matrix composites, as well as techniques for modifying their structure and properties under thermomechanical influences, have been proposed and experimentally tested in different studies [5–8]. Despite the large volume of positive results, the developed methods have a number of disadvantages (complexity, low efficiency, high cost, etc.) and they require further optimization.

One of the lines of research in the synthesis and processing of alloys and composites based on the Al-Mg system is liquid-phase methods, which include bringing the initial alloy into contact with reinforcement particles, alloying elements or compounds of alloying elements.

To increase the efficiency of the methods for inserting the reinforcement particles, it is necessary to carry out synthesis under conditions of oxygen removal from the reaction mixture by vacuuming or dissolving in a coating-refining salt flux. A well-proven method includes alloying aluminum in a molten oxide-salt flux under conditions of the electrolytic decomposition of oxides from the flux [9].

The paper deals with primary thermodynamic assessments and experimental studies aimed at selecting a salt flux for reprocessing Al-Mg alloys, as well as for the synthesis of Al-Mg-TiC-based composites.

2. Thermodynamic evaluation

The following flux compositions for the synthesis and processing of alloys are known from [9–12]: NaCl-KCl-NaF, CaF₂-CaO, KF-KCl, and KF-AlF₃. The main criteria for choosing a flux are

- the ability to maintain the operating temperature between 800 and 950 °C;
- the stability of the flux composition (low vapor pressure, inertia to the atmosphere);
- the chemical stability of alloy or composite compounds in the flux.



Table 1 shows the thermodynamic evaluation [13] of the reactions of flux components with the Al-1.7Cu-2.1Mg-6Zn alloy and a TiC reinforcer. The obtained values of the standard Gibbs energy (ΔG^0) of probable reactions indicate that the alloy components are resistant to the chemical effects of the NaCl-KCl flux with the CaF₂, LiF or MgF₂ fluoride additives. It is highly likely that magnesium will interact with NaF, especially when the temperature increases. The main cause of TiC instability may be its contact with atmospheric oxygen, leading to its oxidation and possible formation of MgTiO₃, MgTi₂O₅, and Mg₂TiO₄ magnesium titanates [13].

Table 1. Thermodynamic evaluation of reactions between an Al-Mg alloy and salt fluxes.

Reaction	ΔG^0 , kJ [13]		
	800 °C	850 °C	900 °C
Chemical stability of alloy components			
Mg + 2NaCl = MgCl ₂ + 2Na	147.6	147.1	146.7
Mg + 2KCl = MgCl ₂ + 2K(g)			
Mg + 2NaF = MgF₂ + 2Na	-8.0	-9.5	-10.8
Mg + CaF ₂ = MgF ₂ + Ca	109.0	109.6	109.9
Mg + 2KF = MgF₂ + 2K(g)			
Mg + 2LiF = MgF ₂ + 2Li			
3Mg + 2AlF₃ = 3MgF₂ + 2Al			
Al + 3NaCl = AlCl ₃ + 3Na	440.9	439.0	437.2
Al + 3KCl = AlCl ₃ + 3K(g)			
Al + 3NaF = AlF ₃ + 3Na	163.5	161.2	159.1
Al + 6NaF = Na ₃ AlF ₆ + 3Na	56.8	52.8	48.8
2Al + 3CaF ₂ = 2AlF ₃ + 3Ca			
2Al + 3MgF ₂ = 2AlF ₃ + 3Mg			
Al + KF = AlF ₃ + K(g)			
Chemical stability of TiC			
TiC + 3Al = Al ₃ Ti + C	56.2	58.7	61.2
TiC + Al = AlTi + C	105.7	106.1	106.4
TiC + 1/2Mg = 1/2MgC ₂ + Ti	208.2	207.3	206.4
TiC + 2/3Mg = 1/3Mg ₂ C ₃ + Ti	190.6	189.8	188.9
TiC + 4NaCl = TiCl ₄ + 4Na + C	865.5	863.1	860.8
TiC + 4NaF = TiF ₄ + 4Na + C	686.5	678.5	670.6
4TiC + 2MgF ₂ = TiF ₄ + 2MgC ₂ + 3Ti	1362.7	1354.7	1346.5
TiC + O₂ = TiO₂ + C	-577.2	-567.0	-560.8
TiC + 3/2O_{2(g)} = TiO₂ + CO_(g)	-784.0	-780.1	-776.3
TiC + 2O_{2(g)} = TiO₂ + CO_{2(g)}	-973.2	-965.0	-956.8

3. Experiment

Experimental verification of the composition stability was performed on the example of the Al-1.7Cu-2.1Mg-6Zn alloy (analog of the 7075 alloy), which was melted under the NaCl-KCl-NaF, NaCl-KCl-NaF-MgF₂, NaCl-KCl-MgF₂, and KF-AlF₃ salt fluxes in the air atmosphere.

The alloy was remelted under a flux in a corundum crucible placed in a pit-type resistance furnace. A mixture of salts was loaded into the crucible and heated to a working temperature of 900 °C. The temperature in the furnace was measured and maintained constant (± 2 °C) using Pt/Pt-Rh thermocouples and a USB-TS01 thermocouple module (National Instruments, USA).

The Al-1.7Cu-2.1Mg-6Zn alloy of a certified chemical composition in the form of cylinders weighing up to 250 g, with a length of 10 to 20 mm and a diameter of 10 mm, was loaded into the molten salt flux or melted together with it. After melting, the reaction mixture was mechanically stirred by a graphite agitator for 60 minutes. Then, after finishing the mixing process, the crucible with the flux and the alloy was removed from the furnace. The main part of the flux was poured out into a

graphite mold, and the alloy was poured out into a steel mold. The resulting castings were used to make samples for further analysis. The flow of the experiment can be traced from the photos in Fig. 1.

In a special series of experiments, we studied the effect of mixing conditions of a micro-sized (1 to 5 μm) TiC powder in the Al-1.7Cu-2.1Mg-6Zn alloy on the stability of the carbide and its insertion into the alloy. The volumetric stability of the alloy composition was assessed using a Spectromaxx spectrometer. To do this, the castings were cut into 4-5 samples. The porosity of the castings was estimated by comparing their density with the density of the original alloy.



Figure 1. Photos of the experimental process flow.

4. Results and discussion

4.1. Selection of the casting mode

Before the experiments, we worked out the casting mode that would allow us to obtain solid castings with the most uniform distribution of the components in the blastic Al-1.7Cu-2.1Mg-6Zn alloy. To produce composites, a mode was chosen that included casting the alloy into a steel mold heated to 280-300 °C and then slowly cooling the castings together with the mold in the furnace. In order to obtain statistical results, the mold was made with the possibility of obtaining three castings (Fig. 1). Figure 2 shows typical photos of castings without visible cracks and with significant cracks and fractures.



Figure 2. Photos of the Al-1.7Cu-2.1Mg-6Zn alloy castings.

4.2. The stability of the alloy composition

Table 2 shows the composition of the Al-1.7Cu-2.1Mg-6Zn alloy before and after remelting under fluxes of different compositions. The table shows that the salt flux of the NaCl-KCl-MgF₂ composition is the most suitable for processing the alloy under study. When other fluxes are used, the magnesium-thermal recovery of its components occurs, as well as the redistribution of the alloy composition. The obtained experimental data are consistent with the thermodynamic estimates given in Table 1.

Table 2. The compositions of the original and remelted Al-1.7Cu-2.1Mg-6Zn alloy.

Element	Alloy	Alloy after contact with			
		NaCl-KCl-NaF	NaCl-KCl-NaF-MgF ₂	NaCl-KCl-MgF ₂	KF-AlF ₃
Al	89.3-89.5	90.1-90.8	90.0-90.2	89.2-89.7	91.5-91.7
Mg	2.08-2.13	1.40-1.52	1.58-1.64	1.96-2.04	0.015
Cu	1.68-1.75	1.48-1.67	1.61-1.70	1.75-1.88	1.57-1.70
Zn	5.90-6.00	5.55-5.88	5.60-5.75	5.80-6.00	5.53-5.77
Si	0.1	0.1	0.09	0.1	0.15
Fe	0.23	0.22	0.22	0.23	0.25
Mn	0.33	0.32	0.32	0.33	0.33
Cr	0.13	0.13	0.13	0.13	0.14
Ti	0.026	0.025	0.028	0.022	0.02
Na	0.001	0.014	0.012	0.001	<0.0001

4.3. Selection of TiC liquid-phase mixing conditions

To assess the chemical stability of the TiC powder and the principal possibility of its insertion into the Al-1.7Cu-2.1Mg-6Zn alloy, preliminary experiments were performed with the following variants of TiC powder mixing:

- 1) mixing TiC with salts before melting;
- 2) putting TiC in Al foil into the molten salt-alloy mixture being stirred;
- 3) putting TiC in Al foil into the liquid alloy being stirred without using a salt flux;
- 4) putting a tablet compacted from alloy+TiC powders into the molten salt-alloy mixture being stirred;
- 5) melting a mixture of TiC powders and the Al-1.7Cu-2.1Mg-6Zn alloy under a graphite powder layer in a corundum crucible with an internal diameter of 15 mm without stirring;
- 6) putting a salt-TiC mixture pre-melted in a high-purity argon atmosphere into the liquid Al-1.7Cu-2.1Mg-6Zn alloy in a graphite crucible.

The chemical stability and insertion of TiC into the alloy were evaluated by the weight of titanium in the alloy using a Spectromaxx spectrometer. For all the mixing conditions, the degree of TiC insertion did not exceed 5%, while the content of titanium in the alloys did not increase in cases of using the NaCl-KCl-MgF₂ salt flux. The reason for low TiC insertion may be poor wettability of the powder of the selected granulometric composition with the liquid alloy. To optimize the proven liquid-phase method for the synthesis of Al-Mg-Cu-Zn-TiC composites, it is recommended to introduce additional mixing conditions (induction, ultrasound) or to use a coarser TiC powder.

5. Conclusions

The composition of the NaCl-KCl-MgF₂ coating-refining flux has been thermodynamically and experimentally selected for remelting Al-Mg-based alloys and synthesizing Al-Mg-alloy-based composites at temperatures exceeding 800 °C.

Preliminary experiments on mixing the TiC reinforcer into the Al-1.7Cu-2.1Mg-6Zn alloy under different conditions have been performed. A good chemical stability of TiC in the selected salt flux has been shown, and recommendations have been made for optimizing the liquid-phase synthesis of composites based on the Al-Zn-Mg-Cu-TiC system.

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