Study of the complex interaction process of flux with an aluminum melt

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Abstract. In this work, the process of interaction of an aluminum melt with an experimental complex modifying flux is investigated. The conditions for the reactions and the possible composition of the decomposition products of the CMF in the melt are determined.

The study of processes proceeding during the aluminum melt processing by experimental complex modifying flux (CMF) containing potassium fluorotitanate, barium carbonate and graphite was carried out [1]. Thermocouples chromel-alumel and tungsten-rhenium with electrode diameter 0.5 mm were used to study the temperature at the melt-flux boundary and the temperature in the melt. Information data was collected using CA and TR(A)-3 thermocouples and USB-9162A module available from National Instruments. Temperatures were recorded on a computer using a specially program written in the Lab View 7.1 engineering environment.

At the same time, the temperature at the melt-flux boundary and the temperature in the melt were controlled (figure 1).

The flux heated to 250 °C in an amount of 2 wt. % of the heat size was poured onto the melt surface. The temperature at the melt-flux boundary sharply decreased from 702 to 503 °C. The melt temperature remained constant at 764 °C. Subsequently, the temperature at the melt-flux boundary gradually increased and after a time (approximately 2 minutes) it became 10-15 °C higher than the melt temperature and stabilized. The flux forms a caked crust on the surface of the melt. After holding the melt for 1-3 minutes under these conditions, the resulting crust was kneaded. In the place of destruction of the flux crust, local burning occurs and the combustion reaction spreads over the entire surface of the flux. At the time of the combustion reaction initiation, a temperature perturbation of up to 1040 °C is observed at the melt-flux boundary. As the combustion reaction spreads over the entire flux surface, the temperature at the melt-flux boundary rises to 1332 °C. As a result, the melt temperature rises to 830 °C.

The process of interaction of the melt with the flux can be divided into two stages.

At the first stage, the flux deposited on the melt surface is heated. At that, the flux sintering and the solid crust formation occurs. The flux temperature exceeding the melt temperature on 10-15 degrees can be explained by the physicochemical processes occurring in the flux. The process of potassium fluorotitanate and barium carbonate interaction with the melt begins.

Thermodynamic calculations of the Gibbs energy [2] showed that when the flux is heated to a temperature above 660-670 °C, the K₂TiF₆ salt interacts with the aluminum melt. Solid compounds KF and AlF₃ are formed by the following reaction:
The reaction proceeds with the release of heat; therefore, upon further heating, the compounds KF and AlF$_3$ fuse and form potassium cryolite, which is in a liquid state at these temperatures.

The decomposition of the K$_2$TiF$_6$ salt causes diffusion of titanium atoms into the aluminum melt. As a result, fine particles of titanium aluminide are formed:

$$\text{Ti} + 3\text{Al} \rightarrow \text{TiAl}_3.$$  \hspace{1cm} (2)

Thus, titanium forms a dispersed suspension of TiAl$_3$ particles in the melt, which serve as additional crystallization centers and are modifiers of the $\alpha$-solid solution.

In parallel with the decomposition of K$_2$TiF$_6$, the melt interacts with BaCO$_3$ according to the following reaction:

$$3\text{BaCO}_3 + 2\text{Al} \rightarrow 3\text{BaO} + \text{Al}_2\text{O}_3 + 3\text{CO}.$$  \hspace{1cm} (3)

In the future, it is possible to reduce barium oxide with an aluminum melt ($\Delta G^\circ = -167$ kJ/mol) and transfer the barium into the melt [3] according to reaction:

$$3\text{BaO} + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Ba}.$$  \hspace{1cm} (4)

Thus, barium enters the melt, where it is a eutectic modifier in the alloy being studied.

Potassium, the reduction of which is possible from potassium cryolite, practically has not absorbed by aluminum and does not have a modifying effect on the eutectic structure of the alloy being studied [4].

In the second stage, as a result of a significant increase in temperature at the melt–flux boundary, an exothermic reaction of carbide synthesis is possible.

According to earlier studies [5], the two-stage process for the titanium carbide synthesis is most likely. In the first stage, aluminum interacts with titanium according to reaction (2) with the formation of TiAl$_3$, then the reaction takes place:

$$\text{TiAl}_3 + \text{C} \rightarrow \text{TiC} + 3\text{Al}.$$  \hspace{1cm} (5)

between titanium aluminide and carbon.
Since, under these conditions, $\Delta G^0 < 0$, this reaction is thermodynamically possible and is consistent with the data from earlier studies [6].

At the same time, potassium cryolite promotes the interaction of titanium with carbon due to wetting of graphite particles and removal of oxide films from the surface of the melt. Obviously, simultaneously with the exothermic reactions of the carbides synthesis, the potassium cryolite decomposition at high temperatures, and then partially its transition to a gaseous state occurs.

![Figure 2. Surface morphology and elemental composition.](image)

The formed particles of titanium carbide in the melt will serve as additional crystallization centers and act as modifiers of the $\alpha$-solid solution in the alloy being studied.

The analysis of the sample after the processing of aluminum melt by CMF was carried out. The surface morphology and elemental composition according to scanning electron microscopy (SEM) are presented in figure 2.

In the sample obtained after processing of the melt by CMF, the dispersed phase particles predominate. Using local energy-dispersive analysis, it was determined that the dispersed particles shown in figure 2 are the phase of titanium carbide.
References
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