Alloying and modification of molten silumin in salt melt

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Abstract. Processes of structure formation in iron-containing silumins made by smelting in a salt melt are studied. The effect of the composition and the temperature-time characteristics of the ionic medium on the phase composition of metallic materials is analyzed. The “salt melt – silumin” system is simulated in thermodynamic terms.

1. Introduction

Silumins (alloys with 4-22% silicon) constitute the main group of cast aluminum compounds. These alloys are used in more than 90% of all castings since they can be processed nearly by all casting methods.

Mechanical, corrosion and casting properties are the most important characteristics of silumins determining their processibility and applications. All these properties depend on the chemical composition and the structure of silumins. A modification treatment [1] is used to alter the structure of liquid and solid silumins.

Silumins are heterophase alloys whose structure includes crystalline formations predominantly with covalent bonds (silicon and iron-containing phases). They are shaped as lamellar or needle inclusions, which act as stress concentrators and considerably impair the mechanical properties. High mechanical properties can be achieved if the concentration of iron in silumins is a minimum. For example, the recommended concentration of iron for applications in the US defense and aircraft industries is as low as 0.2% [2].

The neutralization of the adverse effect of iron is very topical for making of silumins from industrial waste. The concentration of iron in ingots reaches 1.1-1.3 mass %; it can increase up to 2.5 mass % when alloys are smelted in cast-iron crucibles [3]. Iron forms various compounds (FeAl₃, Al₅SiFe, Al₃SiFe, etc.) in silumins. All these phases have a coarse-crystalline structure and, hence, considerably impair the mechanical properties, especially plasticity [2, 3].

The adverse effect of iron on the strength properties is eliminated by introduction of compensating elements, which suppress formation of the needle phase β. The methods include, e.g., additional alloying with manganese amounting to 50-100% of the iron concentration of the alloy. Iron and
manganese are bound together to form the phase \( \text{Al}_{12}\text{Si}_{2}(\text{FeMn})_3 \), which is often shaped as China script and depresses embrittlement. However, if the total concentration of manganese and iron is over 0.8 mass \%, primary crystals of \( \text{Al}_{12}\text{Si}_{2}(\text{FeMn})_3 \) looking like hexagonal globules can appear. They do not embrittle the alloys, but considerably impair their machinability. Compounds are most often alloyed with manganese using Al-Mn master alloys [2, 5]. However, considering poor solubility of transition metals in aluminum, formation of unwanted excess brittle aluminides can hardly be avoided with this alloying method. New advanced methods have been developed recently for processing of metal melts.

2. Experimental technique
The starting material was the AL9 silumin (0.2-0.4\% Mg, 6.0-8.0\% Si, the balance Al) enriched with iron. The melt was prepared at a temperature of 900 °C, stirred carefully, and poured into metallic molds at 710 °C.

The experiments were performed in air in a shaft resistance furnace with graphite heaters. Alundum crucibles served as the melt container. Chemically pure reagents were used. Weights of salts and Mn\(_2\)O\(_2\) were mixed and charged to a crucible, which was placed in the furnace. An alumel-chromel thermocouple in an alundum casing was installed in the crucible for temperature measurements. Once the salts melted, a weight of the metal was added to the crucible and the mixture was allowed to stand at the given temperature for some time. The metal to salt melt ratio was 0.5 to 1.93, while the atomic ratio of iron in the alloy and manganese in the salt melt was 1:(4.25-9.44). The salt and metal melts were poured into a graphite mold, the metal was separated from the salt upon crystallization, and the metal structure was analyzed. The experimental conditions are given in table 1.

| Experiment No. | T, °C | \( \tau \), min | Salt melt composition, mass % | Charged Mn\(_2\)O\(_2\), mass % | Metal-to-salt mass ratio | Remarks |
|---------------|-------|------------------|-------------------------------|-----------------------------|-------------------------|---------|
| 1             | 835   | 120              | BaCl\(_2\) – 72               | AlF\(_3\) – 15.5            | 13.04                   | 1.29    | AL9+0.6%Fe |
|               |       |                  | NaF – 12.5                   |                             |                         |         |           |
| 2             | 791   | 136              | BaCl\(_2\) – 72               | AlF\(_3\) – 15.5            | 16.67                   | 1.93    | AL9+1.0%Fe |
|               |       |                  | NaF – 12.5                   |                             |                         |         |           |

3. Results and discussion
The "salt melt – silumin" system was analyzed in theoretical terms using the ASTRA.4 software package and the ASTRA.BAS databank [6]. The investigation was performed over the temperature interval of 1000-1400 K at a total pressure of 10\(^5\) Pa (1 atm) in Ar and a model air atmosphere (20 mass % O\(_2\) and 80 mass % Ar). The metal phase was assumed to be an [Al]-[Si]-[Mg]-[Fe]-[Mn]-[Na] ideal solution over the whole temperature interval. The ion melt was described by the model of ideal solution of interaction products (ISIP) [7] at temperatures of 1000 to 1400 K. Molten aluminum and the salt melt enter into the following reactions:

\[
3(\text{MnO}_2) + 4\text{Al} = 2(\text{Al}_2\text{O}_3) + 3[\text{Mn}], \tag{1}
\]

\[
6(\text{NaF}) + \text{Al} = 3[\text{Na}] + (\text{Na}_3\text{AlF}_6), \tag{2}
\]

\[
3(\text{BaCl}_2) + 2\text{Al} = 3[\text{Ba}] + 2(\text{AlCl}_3), \tag{3}
\]

where (...) are components (cluster, group, complex ion) of the salt melt, whose composition can change depending on the salt melt composition, and [...] is the aluminum alloy component. The progress of the reactions (1)-(3) depends on conditions of the interaction between the metal and salt melts.
In the computer-aided experiments, part of the aluminum alloy interacts with oxygen at high temperatures in the model air atmosphere by the reaction

\[ 2[\text{Al}] + 1.5\text{O}_2 \rightarrow (\text{Al}_2\text{O}_3), \]  

leading to a small (~0.1%) decrease in [Al] at \( T = 1000 \text{ K} \) as compared to the interaction in argon.

Thus, the presence of NaF, BaCl\(_2\) and MnO\(_2\) in the melt leads to formation and assimilation of sodium, barium and manganese in silumin respectively. Sodium and barium modify silumin, while manganese alloys silumin.

The experiments 1 and 2 differ by the melt heating temperature, the amounts of the metal and the salt, and their mass ratio. The chemical composition of silumin is given in table 2. The Fe concentration was not over 0.5-0.6% in the experiment 1.

**Table 2. Chemical composition of silumin.**

| Experiment No. | W/o smelting | 1 | 2 |
|---------------|--------------|---|---|
| Fe            | 0.43         | 0.57 | 1.04 |
| Mn            | 0.01         | 2.03 | 2.54 |
| Fe + Mn       | 0.44         | 2.6  | 3.58 |
| Mn/Fe         | 0.023        | 3.56 | 2.44 |

![Figure 1. Microstructure of the AL9 alloy before smelting (Neophot-2 optical microscope).](c)

\( (\alpha + \text{Si}) \) _eutectic_ 
\( \alpha \) _solid solution_
The main structural components of the casting before smelting are Al dendrites of the $\alpha$-phase solid solution (figure 1a) and the coarse-plate Al-Si eutectic on dendrite cell boundaries (figure 1b). Iron is present as excess needle FeSiAl$_5$ crystals (figure 1a), which impair plasticity characteristics of the metal because of their shape. Furthermore, the skeleton Mg$_2$Si phase (figure 1c) is observed in the region of the eutectic.

Figure 1. Microstructure of the AL9 alloy before smelting: (a) $\alpha$ solid solution, (b) (MnFe)$_3$Si$_2$Al$_{15}$, (c) $\alpha$ solid solution + Si eutectic.

Figure 2. Microstructure of the AL9 alloy after smelting in the salt melt, experiment 1 (Neophot-2 optical microscope).

The examination of the structure of the casting after smelting in the salt melt shows that the phase composition of the alloy and the morphology of its structural components change (figure 2a, b). For example, it is seen from the comparison (figures 1b and 2b) that the salt medium has a modifying effect on the main Al-Si eutectic. Specifically, Si plates become shorter and thinner. Dendrites of the $\alpha$-phase remain unchanged. Also, primary crystals including Mn (figure 2b) are formed in the alloy instead of individual Al$_5$FeSi crystals with Fe. These crystals have a sufficiently complicated growth form of the dendrite type and are about 40 $\mu$m in size. The analysis of their morphology, size and location suggests that they crystallize first from the aluminum melt. Local X-ray analysis was performed in a JCXA-733 microscope for identification of this phase. The photographs in figure 3 were taken using reflected electrons (figure 3a) and characteristic Mn, Fe and Si radiation (figures 3b-d). These photographs prove that all the elements enter into the composition of the intermetallics. The conversion from the weight to atomic percent demonstrates that the phase composition approaches (Fe, Mn)$_3$Si$_2$Al$_{15}$. This is in agreement with the data reported in [4, 5]. The Fe-Mn ratio in the aluminides is 1:13, i.e. the intermetallics most probably are the solid solution of Fe in the ternary Mn$_3$Si$_2$Al$_{15}$ phase [2] in the given experimental conditions.
Figure 3. Images of the AL9 alloy structure after smelting in the salt melt, experiment 1: (a) reflected electrons; (b) characteristic Mn radiation; (c) characteristic Fe radiation; (d) characteristic Si radiation (JCXA-733 scanning electron microscope).

Silumin with the Fe concentration as high as 1% was smelted in the salt medium in the experiment 2. It is seen from table 2 that the composition of the salt melt does not differ from its composition in the experiment 1. The concentration of MnO$_2$ is larger, while the melt temperature is higher than the temperature in the first experiment. All these characteristics of the process influence the structure of the casting as seen from results of metallographic and chemical analyses.

This statement is readily illustrated in figure 4a, b. Firstly, a eutectic, which has a complex phase composition and consists of dispersed Si crystals and chain-forming faceted crystals, appears on the $\alpha$-phase boundaries in the casting (figure 4a). X-ray structural analysis (figure 5a-c) revealed that the composition of these aluminides corresponds to the ternary Mn$_3$Si$_2$Al$_{15}$ phase, in which Fe is partially dissolved. According to [4], the melting point of this eutectic is 573 °C, which is close to the melting point of the Al-Si eutectic equal to 577 °C.

Figure 4. Microstructure of the AL9 alloy after smelting in the salt melt, experiment 2 (Neophot-2 optical microscope).
Secondly, although the Mn concentration is high, the concentration of primary aluminides decreases in the alloy structure. This observation agrees with the data [5], according to which the ratio of eutectic and primary phases in the structure is determined by the Mn-Fe concentration ratio in the melt. That is, the smaller the ratio, the lower the concentration of primary phases formed during crystallization.

Thus, the Mn concentration of silumin can be increased to 2-2.5% by smelting in the salt medium. Dissolution of Mn in liquid silumin changes the aluminum melt composition, which, in turn, influences the kinetics, the morphology and the composition of solid phases formed during crystallization. For example, alloying of silumin with Mn leads to formation of more dispersed aluminides including Mn, Fe and Si, which are uniformly distributed between dendrites of the α-phase in the region of the Al-Si eutectic. Moreover, the salt medium causes modification of the Al-Si eutectic. It may be thought that the uniform distribution of the intermetallics in the cross section of the casting and the presence of the modified Al-Si eutectic must improve mechanical properties of the casting. Therefore, the permissible concentration of Fe in the alloy can be increased without the loss of plasticity and strength.
4. Conclusion
Specific features of the structure formation during smelting of silumins in molten salts were analyzed by methods of metallography, X-ray structural analysis and X-ray spectrum analysis.

The salt composition and the melt temperature influence alloying of the compounds with manganese. It was shown that the manganese concentration of silumin can be increased to 2.5% if a combination of salts (BaCl$_2$, AlF$_3$, NaF and MnO$_2$) is used as the medium.

The effect of Mn on the morphology and the composition of iron-containing aluminides in silumin was analyzed with the aim of improving its structure and properties.

It was shown that smelting of silumin in molten haloid salts can be used for refinement of ingots by transferring excess Fe to transition-metal aluminides having a complex composition.

Acknowledgment
This study was supported by RFBR-Ural (project No. 07-03-96088).

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