

Effect of Ultrafine Powders on the Structural Formation Processes and Mechanical Properties of Al–7%Si Alloy

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Abstract. The multi-component system interaction mechanisms associated with ultrafine powders (TiO₂ and ZrO₂) and fluorine-containing salts (K₂ZrF₆, Na₃AlF₆ and Na₅Al₃F₁₄) with the Al–7%Si melt are studied. The formation of a multi-phase system with a high concentration of crystallization centres ($N \approx 7 \cdot 10^{12}$ U/cm³) was identified. We experimentally show that the injection of an ultrafine powders modifying mixture containing refractory metal oxides and fluorine-containing salts into a Al–7%Si melt leads to a significant reduction in the a silicon plate size (by 1.5 times) and the Fe-containing phases (by 4 times). An equal distribution of the eutectic phase (α -Al + β -Si) is established in the Al–7%Si alloy. As a result of microstructural changes when the modifying mixture was injected, a factor of 2 increase in the Al–7%Si alloy ductility was observed.

INTRODUCTION

Aluminium-silicon alloys (silumins) are widely used as modern construction materials in aircraft engineering and motor-vehicle construction. As a result of the increasing requirements associated with the operating characteristics of machines, the development of new technological approaches dedicated to improving the properties of aluminium-silicon alloy castings are being sought. Quality improvements to the structural and mechanical properties of silumins castings may be achieved by changing the melting processing method used. However, improvements in the material quality by changing the mechanism are also possible [1]. Crystallization processes mainly depend on the injection of modifying mixtures into the melts.

In recent years, many works have been devoted to the metallurgical modification of Al-Si alloys [1-5]. Experimental data on silumin modification via the addition of different salts including strontium, sulphur, phosphorus and nickel, have been presented. Different fluxing agents based on sodium salts, potassium and potassium fluoroaluminates (K₂ZrF₆) are mainly used, which provide simultaneous refinement and melt modification, resulting in strong grain refinement [1]. Today, one trend is modification using ultrafine refractory particles [6, 7]. When injected into the melt via powder particles, they are absorbed by the melt as a result of their small size and equally spread throughout the volume. These particles act as centres of potential crystallization [4]. Modification by ultrafine powder leads to the formation of a uniform crystallographic structure, which is determined by the creation of a high concentration of crystallization centres in any single melt volume unit [8]. Moreover, the after effects associated with the injected additives depend to a great extent on the degree of their absorption and the possibility any chemical interactions with the melt components.

The use of ultrafine oxides in modifying the mixtures is interesting from a crystallization process control perspective. It is possible to inject fluorine-containing salts, which provide oxide absorption into the metal melt to form an appropriate amount of crystallization centres in the melt. A number of studies have shown that the use of cryolite together with refractory metals oxides as a part of the modifying mixtures lead to a high-degree of

absorption and the formation of a micro-crystalline structure in cast irons [9]. It is supposed that the use of a mixture containing fluorine-based salts and refractory oxides for silumins can also provide a significant microstructural improvement. This work is devoted to studying of the influence ultrafine powders of titanium oxide and zirconium and fluorine-containing salts (K_2ZrF_6 , Na_3AlF_6 and $Na_5Al_3F_{14}$) on the formation of structural phases and mechanical properties of Al–7%Si alloy.

MATERIALS AND METHODS

The Al–7%Si alloy is produced at the Research and Development Center “Polus” (Tomsk, Russia), and has the following chemical composition: Si 7.2%, Mg 0.4%, Fe 0.4%, Mn 0.2%, Zn 0.3%, Cu 1.0%, Ni 0.9%, Cr 0.03%, Ca 2.9%, Na 2.3%, Ti 0.01%, Ag 0.004% and Al balance. The initial materials include: 1) Al7 alloy (National State Standard 11069-2001), 2) Al–12%Si alloy (National State Standard 1583-93) and 3) Mg95 alloy (National State Standard 1583-93). The melting was carried out in furnaces using steel crucibles (temperature $\sim 600^\circ\text{C}$) [10]. The samples used for mechanical testing were cast into a metal mould according to the National State Standard 1583-93.

The modifying agents used in the additive mixture included ultrafine powders of: TiO_2 , ZrO_2 , K_2ZrF_6 , Na_3AlF_6 and $Na_5Al_3F_{14}$, which is equal to 0.4 wt. % per melt ton. Ultrafine powders of TiO_2 and ZrO_2 (with impurity of Nb, Hf, Mg, Fe, Cr, Sr and Mo at ≤ 5 wt. %) were acquired using a thermo-chemical method from soluble salts of rare metals. The average size of the particles used in the modifying mixture (MM) was 1.2 μm .

The phase composition of the castings was examined using a Shimadzu XRD 6000 X-ray diffraction meter. The localization phase of the Al–7%Si alloy and the basic structural characteristics were studied using a scanning electron microscope (Vega II LMU) combined with an energy dispersive X-ray micro-analysis system (INCA Energy 350). The mechanical tensile tests were carried out on a tensile testing machine UMM-5.

RESULTS AND DISCUSSION

Interaction Mechanisms of the Modifying Mixture with the Al–7%Si Melt and the Formation of the Crystal Structure

When the modifying mixture is injected into the Al–7%Si melt, a multi-phase system is formed. The oxide particles in the modifying mixture sit in a suspended state in the melt. The chemical reactions related to the restoration of the elements from the oxides are possible at the high temperatures in the “melt + MM” system. The composition of the polyfluoride salts containing aluminium and sodium are: Na_3AlF_6 and $Na_5Al_3F_{14}$, and are significant. One characteristic feature of inorganic polyfluorides, including cryolite, heolite, and so on, is their weak intermolecular connections. The compounds Na_3AlF_6 and $Na_5Al_3F_{14}$ are fusible components of a mixture and are decomposed stage by stage to fluorides salts (NaF and AlF_3) upon reaching the melting temperature. In the same way, potassium fluoroaluminat (K₂ZrF₆), which is used in iron and steel production as a modifier in aluminium melts, is decomposed into fluoride salts. In turn, high temperatures cause the fluoride salts to melt and/or decompose. The absorption dependence that the modifying mixture has on the solid particles in the wet state of the melt is a significant feature in the melt crystallization processes. The formation of liquid layers of fluoride salt at the boundary of the oxide particles/melt allows a reduction of the surface energy at the interface, promoting a uniform distribution of the MM throughout the volume. The formation of oxide particles on the surface of the shell of the liquid fluoride salt reduces the surface energy and ameliorates the crystallization processes. Moreover, a portion of the MM refractory particles, including the titanium oxide and zirconium with impurities Nb, Hf, Cr, S and Mo that have melting points ranging from $T = 1521\text{--}2758^\circ\text{C}$, play a role of “micro-refrigerators”, which increase the cooling speed of the melt and change the crystallization conditions. These processes are significant in the formation of a finely crystallized eutectic structure (Al + Si), and the silicon crystal formation increases the casting cooling speed.

It is noted that chemical reactions are possible during the mixing of the MM with the Al–7%Si melt, including decomposition and recovery of the fluorine-containing salts of the active elements of the oxides. During experimental melting, gaseous compound disengagement was noticed during the injection of the MM into the melt. According to the thermodynamic calculations using the Gibbs equation (and taking into account the heat capacity of the system’s components) [11], chemical reactions can occur from changes in the enthalpy and entropy and aggregate as a result of polymorphic transformations under standard conditions and at the melting temperature (Table 1). The decay products of the fluorine-containing complex salts (sodium fluoride and aluminium) can

participate in the recovery of refractory metals oxides to a metallic state. The reaction of the MM Al–7%Si melt and thermodynamic characteristics are shown in Table 1.

TABLE 1. Chemical reactions of the interaction of modified mixture with alloy and its thermodynamic characteristics

Reactions	ΔH_{298}^0 , kJ/mol	ΔS_{298}^0 , kJ/mol	ΔG_{298}^0 , kJ/mol	ΔG_{1023}^0 , kJ/mol
Reduction:				
$3\text{TiO}_2 + 4\text{Al} = 3\text{Ti} + 2\text{Al}_2\text{O}_3$ (1)	–519.7	–70.7	–498.6	–444.8
$3\text{ZrO}_2 + 4\text{Al} = 3\text{Zr} + 2\text{Al}_2\text{O}_3$ (2)	–69.4	–45.9	–55.7	–13.7
Interaction of the oxides with fluoride of Na and Al				
$3\text{TiO}_2 + 3\text{NaF} + 4\text{Al} = 3\text{NaAlO}_2 + \text{AlF}_3 + 3\text{Ti}$ (3)	–344.4	–47.24	–330.3	–296.1
$3\text{ZrO}_2 + 3\text{NaF} + 4\text{Al} = 3\text{NaAlO}_2 + \text{AlF}_3 + 3\text{Zr}$ (4)	105.9	–22.79	–112.7	129.2
$3\text{TiO}_2 + 6\text{AlF} = 3\text{Ti} + 2\text{AlF}_3 + 2\text{Al}_2\text{O}_3$ (5)	–1914.5	–1113.9	–1582.0	–747.9
$3\text{ZrO}_2 + 3\text{AlF} = 3\text{Zr} + 2\text{AlF}_3 + 2\text{Al}_2\text{O}_3$ (6)	–1464.2	1089.5	–1139.5	–349.7
$3\text{TiO}_2 + 3\text{KF} + 4\text{Al} = 3\text{KAlO}_2 + \text{AlF}_3 + 3\text{Ti}$ (7)	–558	–71.43	–536.7	–484.9
$3\text{ZrO}_2 + 3\text{KF} + 4\text{Al} = 3\text{KAlO}_2 + \text{AlF}_3 + 3\text{Zr}$ (8)	–107.7	–46.4	–93.9	–60.3
$2\text{Na}_3\text{AlF}_6 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{NaF} + 6\text{HF}$ (9)	715.56	712.9	–503.1	–13.8

The table shows that under normal conditions (ΔG_{298}^0) all the above reactions can occur. The most probable reactions that may occur from the injection of a refractory oxide mixture into the Al–7%Si melt (ΔG_{298}^0) are the aluminio-thermic reduction (1) and oxide reduction reactions (5 and 6). When the melting temperature is reached, the aluminio-thermic reduction of titanium (1) and interactions of TiO_2 and ZrO_2 with aluminium fluoride (5 and 6) take place. The system energy reaches –747.9 kJ/mol and –349.7 kJ/mol, respectively (Table 1). As a result of the oxidation process, the formation of aluminium oxides is also possible.

The formation of gaseous products as a result of the decomposition reactions of the fluorine-containing salts and interaction with the melt can lead to the removal of impurities from the surface of the melt. As the TiO_2 and ZrO_2 ultrafine particles and the fine metallic Ti and Zr particles are lightweight, they may diffuse into the volume of the melt, resulting in them being equally distributed and capable of acting as crystallization centres. A quantitative calculation of the concentration of the particles introduced into the Al–7%Si melt from the MM results in $N = 7 \cdot 10^{12}$ U/cm³, which is sufficient to form a fine-grained structure with silumin main phases (Al, Si, AlFeSi and Al₃FeSi) [8]. Silicon, which is found in the melt, does not participate during the chemical reaction with the melt. However, it crystallizes in the form of separate phase plates and has a significant influence on the mechanical characteristics.

Thus, considering the interaction of the ultrafine powders with the Al–7%Si melt, in the “melt + MM” mixture, we observe that a series of processes take place: 1) melting and decomposition of the complex salts K_2ZrF_6 , Na_3AlF_6 and $\text{Na}_5\text{Al}_3\text{F}_{14}$ to form aluminium fluorides, potassium, sodium, gaseous products and metal particles of Zr and Ti that are recovered from the oxides; 2) the formation of a multi-component system of “solid (oxide and metal particles), liquid (metal melt and fluoride salt) and gaseous products”; 3) the formation of a surface layer of liquid fluoride salts at the “solid particle/melt” interface, leading to a reduction in the surface energy at the interface; and 4) the facilitation of the diffusion of particulate-points during melt crystallization throughout the volume.

Mixture Modification Influence on the Structural/Phase State of the Al–7%Si Melt

The quality of the resulting Al–7%Si casting when injected with the modifying mixture was estimated according to a solid dendritic α -Al solution, the size of the Si plates and the Fe-containing phase. According to the X-ray diffraction analysis, the initial castings contain a α -Al solid solution, which contains the β -Si, α -(Al₂FeSi) and β -(Al₃FeSi) phases (Fig. 1 a). The α -(Al₂FeSi) phase has an orthorhombic crystal matrix with the following matrix parameters: $a = 0.799$ nm, $b = 1.516$ nm and $c = 1.521$ nm with a space group P . The β -(Al₃FeSi) phase has a monoclinic matrix with the following matrix parameters: $a = 0.612$ nm, $b = 0.612$ nm and $c = 4.15$ nm with a space group $Cmma$.

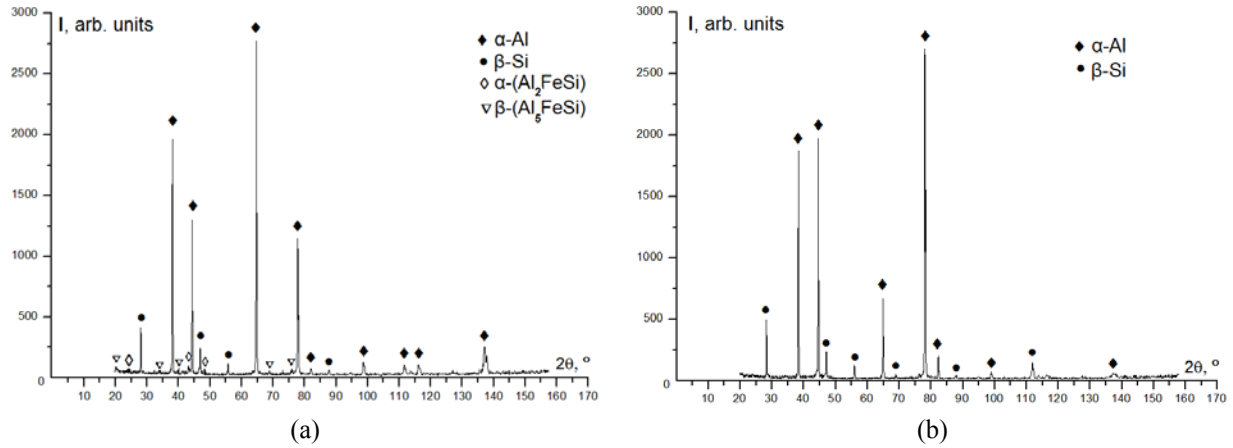


FIGURE 1. XRD spectra of the Al-7%Si alloy: a – initial state; b – after introducing of the MM

The microstructure of initial casting consists of long-branched α -Al dendritic crystals and is situated within the interdendritic eutectic space (α -Al+ β -Si) (Fig. 2, a, b).

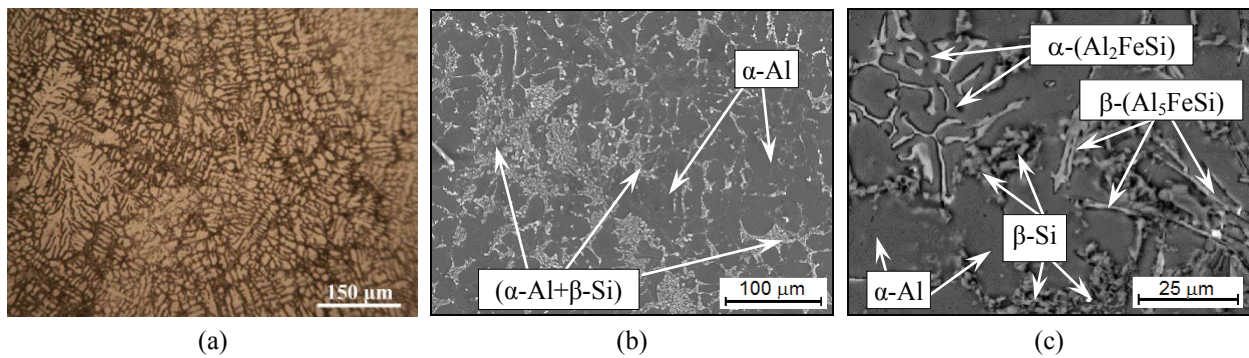


FIGURE 2. Images of the microstructure of the initial Al-7%Si alloy: a – optical micrograph; b – in a secondary electron regime; c – in a scattering regime

The accumulation of eutectic (α -Al+ β -Si) and inequigranularity of the α -Al solid solutions, which exist at sizes from ~ 8 – $80 \mu\text{m}$, are seen in the melt structure. The average dendritic α -Al size is $\sim 22 \pm 9 \mu\text{m}$ and the Si plates are $\sim 12.5 \mu\text{m}$ (Fig. 3, a).

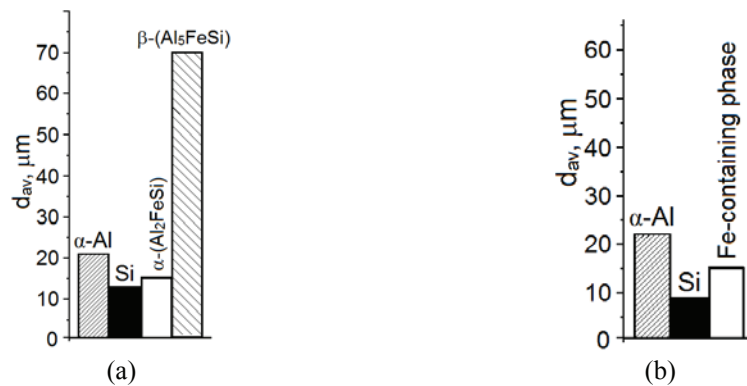


FIGURE 3. The histogram of the size distribution of the alloy's structural components Al-7%Si alloy: a – initial state; b – after introducing of the MM

The results of the X-ray fluorescence analysis are confirmed using scanning electron microscopy (SEM). The α -(AlFeSi) and β -(Al₅FeSi) phases are easily observed using the backscattered electron mode (mode BSE, phase contrast, Fig. 2, c). When examining the Al-7%Si castings using SEM, an energy dispersive X-ray micro-analysis was performed at local points in the different phases and calculated using the theoretical chemical composition, which corresponds to the phases determined based on the X-ray fluorescence results. The α -(Al₂FeSi) phase crystallizes in the form of streaks with a skeletal shape and a size of approximately 15 μ m. The β -(Al₅FeSi) phases take the form of plates with a size of \sim 70 μ m (Fig. 2, c and Fig. 3, a). When performing the local energy dispersive X-ray micro-analyses, we found that for the α -Al solid solution, a small amount of Si, Cu and Zn (no more than 3 wt. %) was found to be present in the α -(AlFeSi) phase. Also, impurities of Ni, Zn, Cu, Mg and Mn are present in the β -(Al₅FeSi) phase.

The addition of the MM containing 0.4 % ultrafine powder in the Al-7%Si alloy influenced the phase composition and structure of the castings. According to the X-ray phase analysis, the main phases modified in the casting are the α -Al and β -Si solid solutions, whereas the Fe-containing α -(AlFeSi) and β -(Al₅FeSi) phases are not observed in the X-ray diffraction pattern (Fig. 1, b). The modified Al-7%Si alloy has a dendritic structure, in which eutectic dendrite colonies constitute an α -Al solid solution (Fig. 4, a). Eutectic dendrite growth occurs at the MM particles, which act as crystallization centres and facilitate the α -Al nucleation process. A decrease in the size of the eutectic (α -Al + β -Si) phase is observed (Fig. 4, a, b) after the injection of the MM in the structure of the modified casting. The average size of the α -Al dendrites is 24 ± 8 μ m (Fig. 3, b).

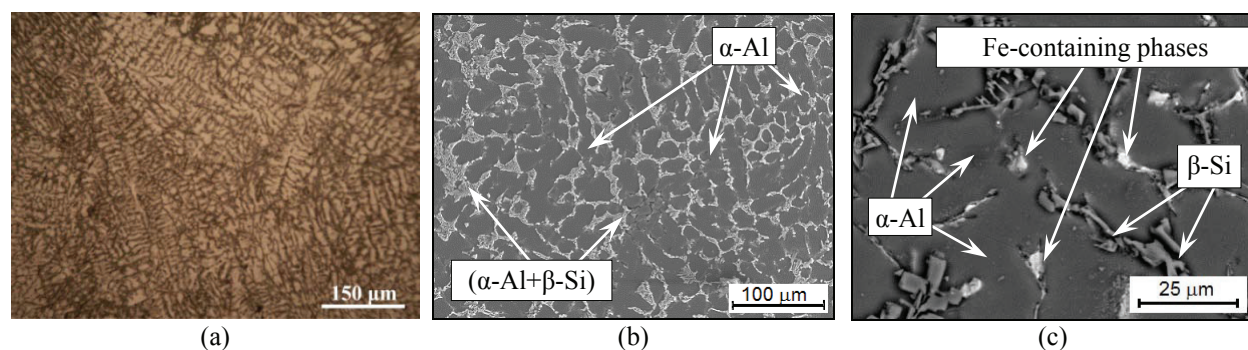


FIGURE 4. Images of the microstructure of the modified Al-7%Si alloy: a – optical micrograph; b – in a secondary electron regime; c – in a scattering regime

Finely divided silicon phase crystals are situated in the eutectic interdendritic spaces. Grinding of the silicon crystals in the eutectic is explained by the fluoride salts that form and create a shell on the surface of the nascent silicon crystals, leading to a slowing of their growth. The injection of the MM leads to a decrease in the size of the Si plates, with their average size becoming \sim 9 μ m (Fig. 3, b), which is almost 1.5 times lower than the one of the initial casting. Conservation of the volume fraction of silicon inclusions is also observed. The crystallization process inhibits the silicon crystal growth and leads to an increase in the nucleation rate of the α -Al solid solution. The formation of a modified finely structured Al-7%Si alloy occurs due to the large amount of crystallization centres.

According to the scanning electron microscopy data and the local energy dispersive X-ray micro-analysis using the backscattered electron mode (phase contrast), Fe-containing phases are present in the modified alloys. The size and shape of these phases (Fig. 4, c) is greatly changed. The average size of the Fe-containing phases decreases to about 15 μ m (Fig. 3, b). The local energy dispersive X-ray micro-analysis of the Fe-containing phases shows that they contain impurities, such as the Mn, Ni, Cu and Mg. The α -Al solid solution of the modified castings includes Si, Cu and Zn impurities. The amounts of these impurities are almost identical to those in the original casting, indicating that the introduction of the modifying mixture does not affect the α -Al solid solution. Rather, it promotes a reduction in the size of the Si crystals and the shape and size of the Fe-containing phases.

According to TEM studies it was established the formation of the Fe-containing phases with composition close to Al_xSiFe. According to the phase diagram this compounds are solid solutions of iron and silicon in aluminum with variable composition. It was obtained that adding of the modifier will change the size, shape, and the stoichiometry of the phases. It was established the formation of plate-like structures of the Al₂SiFe phase by TEM. The evolution of the Fe-containing phase structure is essentially determined by the crystallization conditions and will be discussed in detail in the following publications of the scientific team.

Figure 5 shows two endothermic peaks in the DTA pattern of the Al–7%Si alloy. The peak at 594 is related to the precipitation of α -Al, and the second peak at 565.8 °C is associated with the formation of the Al and the binary Al-Si eutectic alloy. However, we note that the precipitation of the Al phase occurs over a wide range of temperatures. As part of the experiment, the melt was solidified at a moderate cooling rate. After the addition of the MM, the temperature of the peaks exhibited a slight decrease. Such a trend reveals that the addition of MM can indeed decrease the eutectic temperature, resulting in a well modified Al–7%Si alloy. In addition, the peak at 530.8 °C corresponds to the minor phases in the alloys.

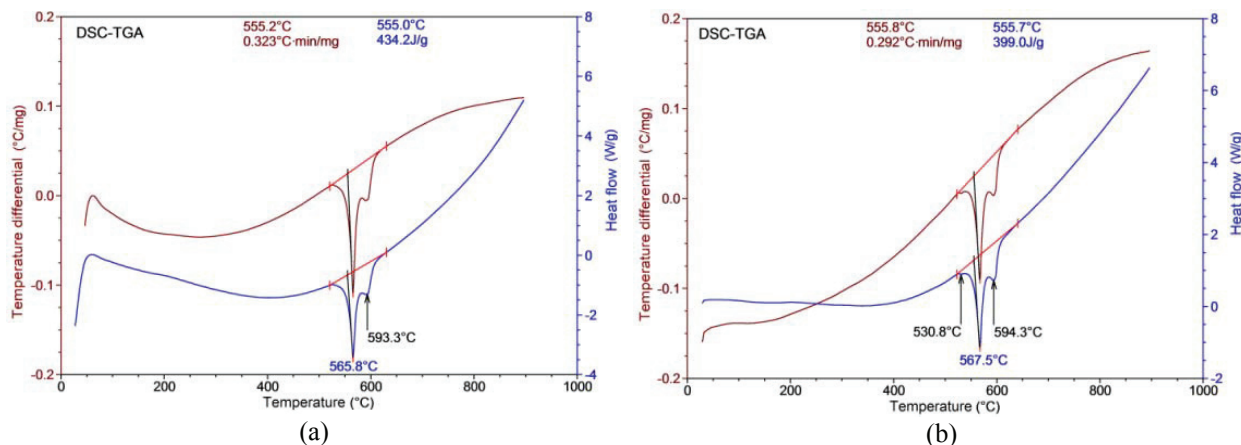


FIGURE 5. DSC pattern of the Al–7%Si alloy: a – initial state; b – after modification

Influence of Modification on the Mechanical Characteristics of the Al–7%Si Alloy

Silumins containing a macro-acicular eutectic point as a result of high friability and silicon material with Fe-containing phases are characterized by poor mechanical properties [12, 13]. Any changes in the size and location of the silicon inclusions can lead to significant changes in the mechanical properties of materials. Table 2 shows the results of the investigations of the mechanical properties of the Al–7%Si alloy for the initial state and after being injected with the MM. As observed in Table 2, the injection of the MM in the castings increases the ductility by a factor of 2, whereas the tensile strength is practically unchanged. Increased ductility in the modified castings is a result of the grinding of the silicon plates and Fe-containing phases (Fig. 4, c). Grinding of the acquired casting structure is connected to the high volume concentration of crystallization centres formed by the chemical processes during interactions of the MM with the melt. After the introduction of the MM, there is a slight increase in the density of the silumin castings. This may be associated with an increase in the fluidity of the alloy as a result of the presence of the MM salts including: K_2ZrF_6 , Na_3AlF_6 and $Na_5Al_3F_{14}$.

TABLE 2. Mechanical properties of the Al–7%Si alloy

Al–7%Si alloy	Tensile strength (σ_b), kgs/mm ²	Relative extension (δ), %	Density(ρ), g/cm ³	Hardness, HB
Initial	20.6±0.05	1.3±0.1	2.7±0.01	73±5%
After adding of modified mixture	20.0±0.05	2.0±0.1	2.8±0.01	72±5%

CONCLUSIONS

The injection of 0.4 wt. % MM containing ultrafine powders of TiO_2 , ZrO_2 , K_2ZrF_6 , Na_3AlF_6 and $Na_5Al_3F_{14}$ into the Al–7%Si melt leads to the formation of a multi-component system. A series of chemical reactions associated with the melting, decomposition and reduction of the fluoride salt mixture was used to modify the metallic oxides in the system. The thermodynamic characteristics of the reaction were studied. The presence of a large amount of dispersed particles in the melt, which act as crystallization centres, contributes to a finely structured crystal and the refinement of the structural components present in the material. The structural state of the acquired materials was studied in detail. The formation of α -(AlFeSi) and β -(Al_5FeSi) phases according to the phase

diagrams of the ternary system occurs. The injection of the MM into the Al–7%Si melt results in 1.5 times reduction of silicon plates, an average factor of 4 times reduction of sizes of Fe-containing phases and the equal distribution of the eutectic (α -Al + β -Si). It was observed increase in ductility in 2 times, whereas the tensile strength, hardness and density remained unchanged.

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