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EFFECT OF MICROALLOYING WITH NICKEL ALUMINIDES AND RARE-EARTH METALS ON THE STRUCTURE OF Al-5% Cu ALUMINUM ALLOY

The effect of the complex ligature with nickel and REM (Ce, La) aluminides on the structure formation, the nature of the distribution of the elements, and the microhardness of the structural constituents of Al-5 wt.% Cu aluminum alloy were investigated. On the example of microalloying of the Al-5 wt.% Cu alloy with a master alloy containing Ni and REM (Ce, La) aluminides it was shown that a redistribution of Al and Cu occurs in α-solid solution and eutectic. This is reflected in the refinement of α-solid solution and eutectic at 0.15 wt.% of the master alloy addition and, accordingly, increases the microhardness of α-solid solution by 100 MPa and eutectic by 125 MPa.

Keywords: aluminum alloys, master alloy, rare-earth metals, eutectic, α-solid solution

1. Introduction

Prospects for the creation of aircraft details operating under conditions of increased loads and temperatures, as well as the extended duration of their impact, determine tasks to improve the performance of structural materials, develop new alloy compositions and production technologies, including methods of alloying and modification [1-3]. Modern aluminum-based materials can acquire high performance due to microalloying [4-7]. Currently, one of the most effective alloying elements is scandium due to the formation of an anomalously supersaturated solid solution during crystallization and its subsequent disintegration with the precipitation of dispersed secondary intermetallides Al_3Sc [8]. Also discussed the creation and development of new master alloy types – complex master alloys containing nickel and rare-earth metals (REM) [9]. Intermetallic compounds such as nickel and REM (Ce, La) aluminides are proposed to be used as master alloys components for increasing the physical, mechanical and operational properties (heat resistance, corrosion resistance, high temperature oxidation resistance, wear resistance) of cast Al-Cu alloys.

This work is aimed at investigation the effect of microalloying by the synthesized ligature with nickel and REM (Ce, La) aluminides on the structure formation, elements distribution and microhardness of the structural constituents of Al-5% Cu aluminum alloy.

2. Materials and methods

Al-Cu ingot alloy (5.0 wt.% Cu) was used as an initial charge. To obtain the master alloy, aluminum grade A7 (>99.7 wt.% Al) and complex modifier Al-Ce (20 wt.% Al, 3 wt.% Ca, 25 wt.% REM, Ni bal.) were used. It consists of nickel aluminides (Al_3Ni) and REM ($Al_{11}Ce_3$, $Al_{11}La_3$) and eutectic Al + Al_3Ni + $Al_{11}REM_3$. The method of obtaining aluminum ligatures with intermetallic phases consisted in the saturation of aluminum grade A7 with the Al-Ce complex modifier in an amount of 60 wt.% at a temperature of 1400 °C. The synthesized ligature had the following chemical composition, wt.%: 65.84 Al; 20.67 Ni; 7.87 Ce; 3.65 La; 1.79 Ca; 0.343 Fe.

Fig. 1 shows the microstructure of the ligature and the points of the elements analysis in the structural components of the alloy A7 + 60 wt.% Al-Ce.

According to the results of metallographic and X-ray microanalysis of the structural components of the alloy A7 + 60

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wt.% Al-Ce, we have identified the following phases:

1. Intermetallic phase – nickel aluminide (Fig. 1, points 1, 2, 6, 8, 17, 18), having a dark color and an average elements content, at.%: 75.884 Al; 23.913 Ni; 0.104 REM (0.043 La; 0.0165 Ce; 0.0445 Nd). The estimated stoichiometric formula is Al_3Ni.
2. Nickel aluminide with REM (Fig. 1, points 4, 5, 9), containing in at. %: 73.13 Al; 17.05 Ni; 1.677 Ca; 7.396 REM. The stoichiometric formula is $Al_{73,13}Ni_{17,05}REM_{7,39}$ = $Al_{73,13}(Ni,REM)_{24,45}$ = $Al_{2,99}(Ni,REM)$ = $Al_3(Ni,REM)$.
3. REM aluminide (Fig. 1, points 11, 12, 13), containing in at. %: 74.66 Al; 18.01 REM; 0.24 Ni; 3.8 Ca; 1.13 Si. The stoichiometric formula is $Al_{74,66}$ (REM, Ni, Ca, Si)$_{23,18}$ = $Al_{3,23}$(REM, Ni, Ca, Si) ≈ $Al_{3,66}$(REM, Ni, Ca, Si) = Al_{11}(REM, Ni, Ca, Si)$_3$.
4. α-solid solution of nickel in the crystal lattice of aluminum (Fig. 1, points 3, 7, 10, 14, 16). Content of impurity elements, at. %: 0.053 Ca; 0.19 Ni.

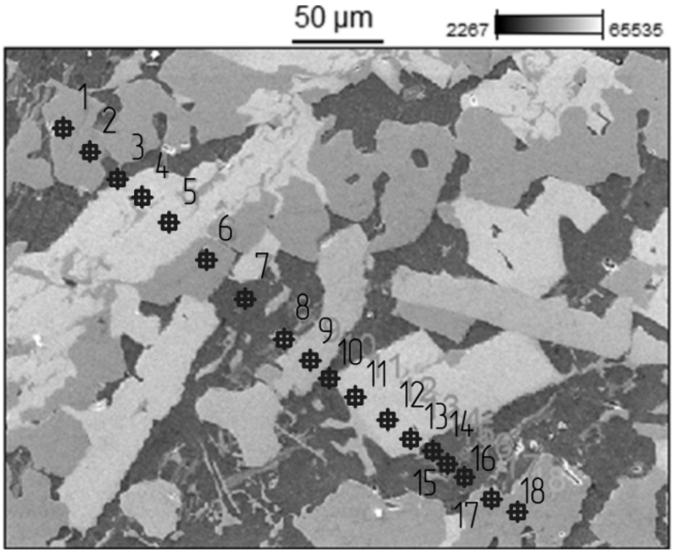

Fig. 1. Microstructure of the alloy A7 + 60 wt.% Al-Ce and the points of the elements analysis

The Al-5% Cu melt was superheated to a temperature of 900°C. After a melt holding during 5 min, a master alloy in amount of 0.05 to 0.3 wt.% was added through the variation range of the addition of 0.05 wt.%. The melt was cooled at a rate of 20°C/min.

Microhardness of the alloy structural constituents was determined on the PMT-3 tester. X-ray microanalysis was performed on the Hitachi SU-70 Analytical Field Emission SEM with the extensions Thermo Scientific UltraDry and Thermo Scientific MagnaRay.

3. Results and discussion

Fig. 2 shows the SEM image of the alloy A7 + 5.0 wt.% Cu microstructure: dark fields represent an α-solid solution of copper and silicon in aluminum, and light spherical inclusions represent eutectic consisting of α-solid solution + $CuAl_2$ with an insignificant content of iron ($FeAl_3$) and silicon, as in the original aluminum grade A7 contains up to 0.15 wt.% Fe and Si.

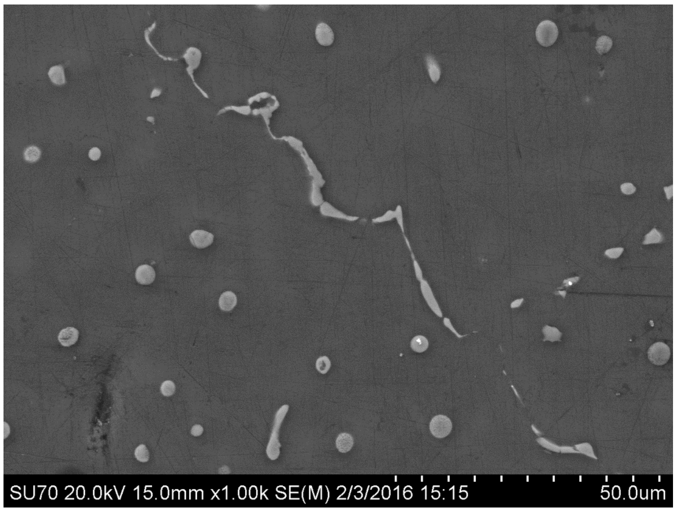

Fig. 2. Microstructure of A7 + 5.0 wt.% Cu alloy

In an α-solid solution, copper is dissolved in an amount of 3.01 wt.%, and silicon – 0.12 wt.%. Iron is not soluble in it. Two types of eutectics are observed in Fig. 2:

– in the eutectic of the spherical shape with a high copper content (>20 wt.% Cu) are dissolve, wt.%: 58.54 Al; 1.41 Si; 3.3 Fe; 36.76 Cu;
– in the eutectic of the elongated shape with a reduced copper content (from 10 to 20 wt.% Cu) are dissolve, wt.%: 64.96 Al; 3.85 Si; 12.86 Fe; 18.44 Cu.

Taking into account the content of nitrogen and oxygen, they are dissolved in an α-solid solution, wt.%: 0.127 N_2, 0.56 O_2, 96.14 Al, 0.119 Si, 3.01 Cu. In a eutectic with a high concentration of copper are dissolve, wt.%: 1.33 N_2, 1.44 O_2, 56.83 Al, 1.36 Si, 3.21 Fe, 35.85 Cu. In a eutectic with a lower copper content are dissolve, wt.%: 1.67 N_2, 1.42 O_2, 62.92 Al, 3.67 Si, 12.42 Fe, 17.89 Cu. Consequently, in this eutectic there is an increased content of iron and silicon in comparison with the eutectic of spherical shape.

The effect of the synthesized ligature on the structure formation, the nature of the distribution of the elements, and the microhardness of the A7 + 5.0 wt.% Cu alloy were investigated. From Fig. 3 it follows that with an increase in the addition of ligature to 0.1 wt.%, a sharp grinding of the eutectic component (α + $CuAl_2$ and α + $CuAl_2$ + $FeAl_3$) of the alloy was observed, and at 0.15 wt.% of the ligature in the structure eutectic inclusions with spherical shape are mostly observed.

Microhardness of the α-solid solution varies according to the extreme dependence with its maximum at 0.15 wt.% of the master alloy, increases from 825 MPa for the initial alloy to 950 MPa (Fig. 4a). In this case, microhardness of the eutectic also changes according to the extreme dependence with the

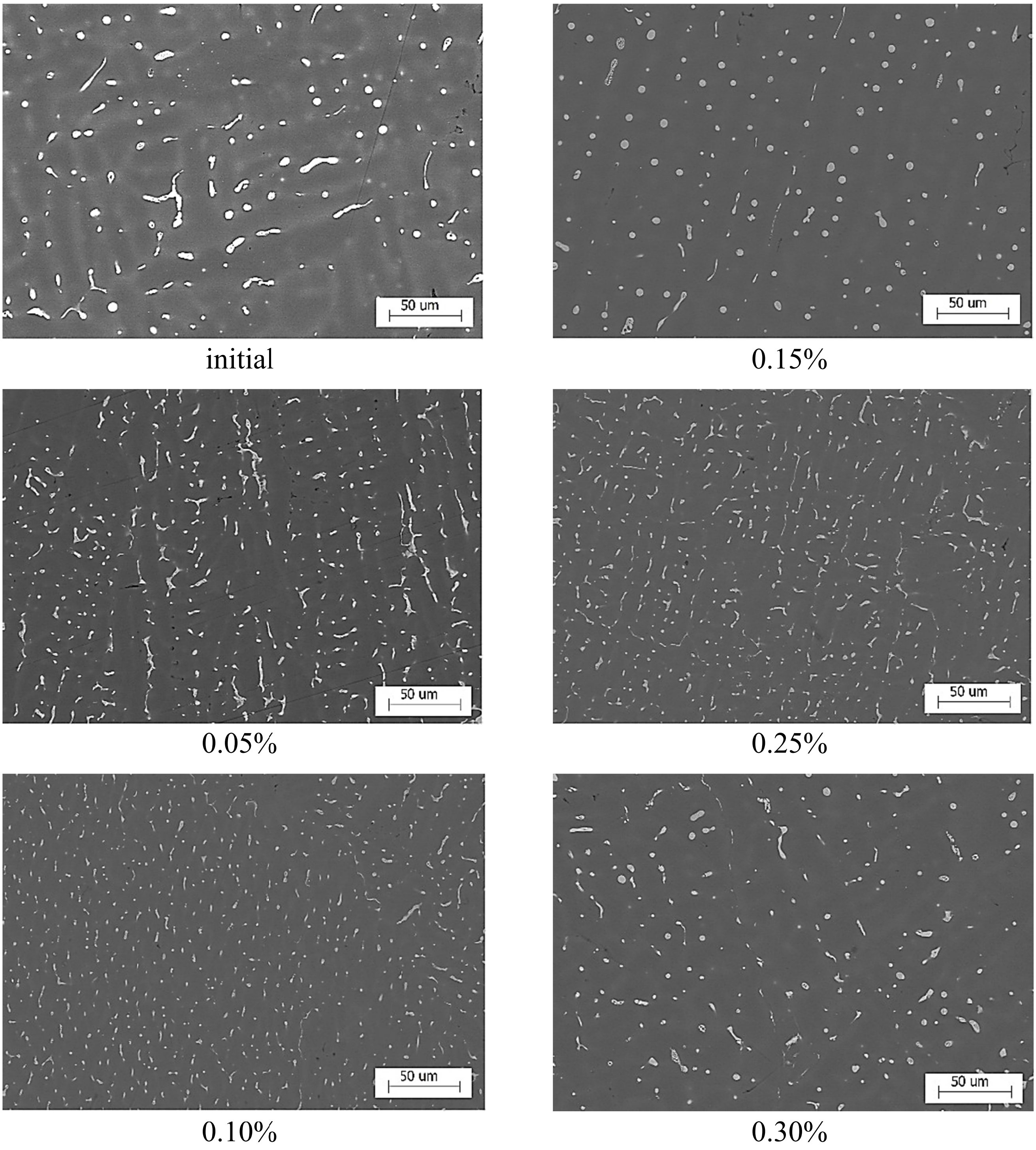

Fig. 3. Microstructure of A7+5.0 wt.% Cu at different amount of ligature

maximum at 0.15 wt.% of the master alloy, followed by a slight decrease at 0.3 wt.% of the master alloy.

From Fig. 4b it follows that the maximum solubility of Cu in the α-solid solution (3.5% Cu) was observed at the addition of 0.15 wt.% of the master alloy, and sharply decreases at 0.3 wt.% of the master alloy. The Al content varies inversely with its minimum in α-solid solution (95% Al). The maximum solubility of Cu in an α-solid solution contributes to its microhardness. In addition, under conditions of non-equilibrium crystallization, the formation of an α-solid solution supersaturated with copper and the manifestation of natural aging are possible. In a supersaturated α-solid solution, copper atoms form Guinier-Preston zones. Copper in the solid solution of aluminum reduces the lattice parameter, since the atomic radius of aluminum corresponds to 0.143 nm, and that of copper to 0.128 nm. This circumstance creates large stresses in the crystal lattice of the solid solution and crushes the mosaic blocks, which leads to an increase in its microhardness to 0.15 wt.% of the ligature.

With further increase in the addition of ligature, the copper content in the α-solid solution decreases and becomes lower than

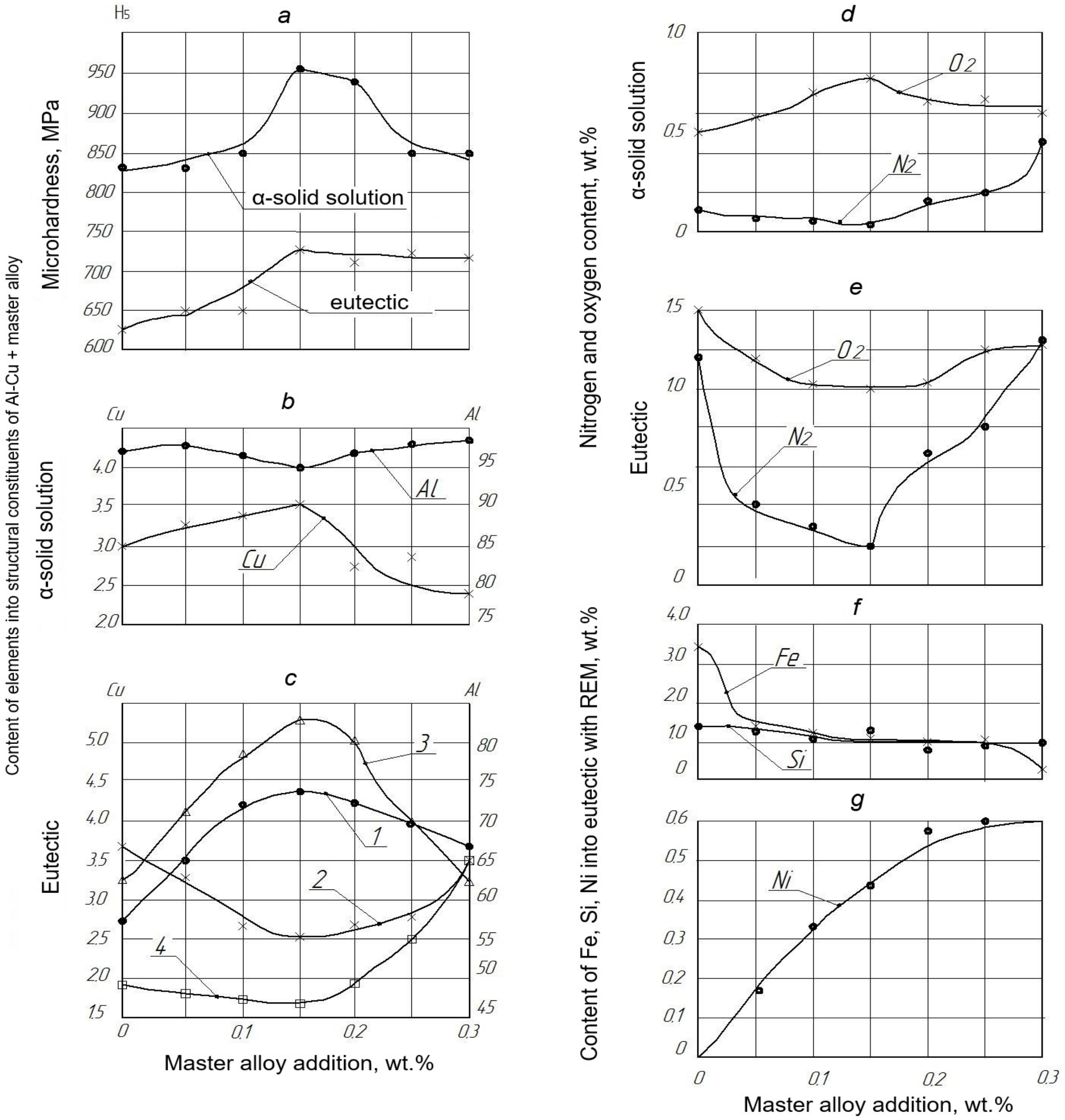

Fig. 4. Microhardness and distribution of elements in the structural components of the Al-Cu alloy at different amount of the ligature addition

the copper concentration in the initial alloy and the microhardness decreases due to the weakening of the natural aging effect.

Fig. 4c shows the distribution curves of Al and Cu in the eutectic. In it, copper is in a bound state in the form of an intermetallic compound $CuAl_2$. It is established that the eutectic is non-uniform in terms of Cu content:

- Cu-rich eutectics (> 20%), which correspond to curve 2 (Cu) and curve 1 (Al);
- eutectic, depleted with Cu (10 ... 20% Cu), which corresponds to curve 4 (Cu) and curve 3 (Al).

In these zones, the minimum copper content was observed with the addition of 0.15 wt.% of the master alloy, since it is intensively dissolved in the α-solid solution (Fig. 4b), which helps reduce the amount of the intermetallic $CuAl_2$, a solid but fragile component of the eutectic. For this reason, the microhardness of these types of eutectic should be reduced. On the other hand, the dispersion of the eutectic component should increase the microhardness of the eutectic. With a further increase in the addition of ligature, an increase in the concentration of Cu in the two indicated zones was observed, and with the addition of 0.3 wt.% ligature, the Cu content in eutectics is leveled. Accordingly, the Al content in the eutectic changes in the reverse order (curves 1 and 3 in Fig. 4c).

Therefore, due to an increase in the copper content in eutectics, the proportion of intermetallic phase $CuAl_2$ should increase and the microhardness should increase. However, the coarsening of the eutectic component with large additions of the master alloy (more than 0.15 wt.%) should contribute to the reduction of microhardness.

The microhardness of the structural components of the Al-Cu alloy should be affected by the content of gases (N_2, O_2) and the impurity elements Fe and Si, as well as the concentration of nickel and rare-earth metals, introduced with the ligature.

From Fig. 4d it follows that an increase in the addition of ligature to 0.15 wt.% contributes to an increase in the oxygen content and a decrease in the concentration of nitrogen in the α-solid solution. But the mechanism of the effect of gases on the microhardness of an α-solid solution has not yet been established.

Fig. 4e shows the curves of changes in the content of N_2 and O_2 in the eutectic from the value of the addition of ligature: up to 0.15 wt.% ligature the content of N_2 and O_2 decreases, and then with a further increase in the ligature addition to 0.3 wt.% the concentration of gases in oxides and nitrides, which should increase the microhardness of the eutectic.

An increase in the addition of a ligature helps to reduce the iron content in the modified eutectic, therefore, reducing the amount of $FeAl_3$ in the composition of the eutectic should contribute to the reduction of the microhardness of the eutectic. The Si content in the eutectic is almost unchanged, although there is a tendency of its decrease from the value of the ligature additive (Fig. 4f).

Starting with the addition of 0.1 wt.% of the ligature, the REM-containing eutectic crystallizes. In the composition of this eutectic, the following elements are concentrated, wt.%: 73.2 Al; 3.07 Si; 1.93 Fe; 0.35 Ni; 20.82 Cu; 0.17 La; 0.48 Ce. With the addition of 0.15 wt.% ligature in the eutectic the following elements are, wt.%: 64.2 Al; 5.19 Si; 0.9 Fe; 0.45 Ni; 22.94 Cu; 1.3 La; 4.0 Ce. With the addition of 0.25 wt.% ligature in the eutectic, the following elements are dissolved, wt.%: 59.07 Al; 5.71 Si; 3.02 Fe; 0.6 Ni; 25.67 Cu; 4.18 Ce; 1.56 La.

Therefore, in a modified eutectic:

- high content of Si and Fe is concentrated;
- with an increase in the addition of ligature, there is a tendency to increase the content of Ni, Cu and REM;
- an increase in the addition of ligatures contributes to a constant increase in the nickel content in the eutectic (Fig. 4g);
- calcium is often observed in an amount of 0.15-0.2 wt.%;
- probably highly solid aluminides Ni and REM crystallize.

4. Conclusion

On the example of microalloying of the Al-5% Cu alloy with a master alloy containing Ni and REM (Ce, La) aluminides it was shown that a redistribution of Al and Cu occurs in α-solid solution and eutectic. This is reflected in the refinement of α-solid solution and eutectic at 0.15% of the master alloy addition and, accordingly, increases the microhardness of α-solid solution by 100 MPa and eutectic by 125 MPa. At the next stage of this research, the results of the microalloying influence on the nature of distribution of Ni and Fe in the structural constituents, physical-mechanical and operational properties (heat resistance, corrosion resistance, high temperature oxidation resistance, wear resistance) of the Al-5% Cu cast alloy will be obtained.

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