Study of the structure and properties of Al-Cu alloys (up to 10 at.% Cu) produced at different cooling rates

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Abstract-In this study, we have used durametry, X-ray phase analysis and metallographic analysis to observe the morphological characteristics and microhardness of Al-Cu alloys (2, 5, 7 and 10 at.% Cu) cooled down from melt, at rates of 2 and 100 degrees/s and within a temperature range 973 to 1473 K. We have conducted a comparative study of structural and phase transformations in the castings. The study demonstrates that a growing Cu concentration and a growing cooling rate increase the microhardness of the groundmass metal (α-Al); the dendrite parameters of α-Al and the eutectic mixture volume ratio are also changed; the concentration dependence of the microhardness behaves similarly to the kinematic viscosity dependence.

I. INTRODUCTION

Aluminum-based alloys, such as Al-Cu, are of both scientific and technological importance. The phase diagram of Al-Cu system is rather complex, with eutectic as well as intermetallic compositions. The alloys of Al-Cu system (up to 10 at.% Cu), hypoeutectic in nature, constitute the groundmass of heatproof cast/wrought aluminum alloys. Besides low weight and high strength, aluminum-copper alloys are characterized by high plasticity and high corrosion resistance. Such alloys are widely used in various industries as components of turnery, aircraft bodies etc. Binary Al-Cu alloys have been observed in numerous researches, especially those devoted to the crystallization processes [1-6] etc. Their physical properties (viscosity, thermal conductivity, electrical resistivity, magnetic susceptibility, etc.) are mainly determined by the concentration ratio of their components, namely, Al and Cu atoms [7, 8].

The alloy properties can be improved when influenced in liquid and solid states. Sometimes the production process requires melting prepared compositions and, afterwards, ladling them in foundry moulds. The structural state of the melt and its cooling rate influence the morphology of the structures produced with hardening [8-11]. The theoretical and experimental studies of the phenomena observed in metal melts, such as structural transformations at certain temperatures and with certain compositions, relaxation processes and liquid-liquid phase transitions (LLPT), get more and more topical [12-14]. The liquid-phase states are often studied through indirect methods based on examination of the thermal and concentration correlations of the structure-sensitive properties, in particular, viscosity (ν) [15-21]. Viscosity is a unique thermophysical property which examination makes it possible to conclude on melt structure. Viscosity ratio is one of the principle characteristics to determine the glass-forming ability of the substance [7].

In our previous works, we held an viscometric experiment and modeled atomic dynamics of liquid Al-Cu alloys (up to 10 at.% Cu) near liquidus at T=973 K. The research found a peculiar segment at 5-7 at.% Cu on the concentration-kinematic viscosity diagram. With higher melts temperatures, this segment flattens - it was not observed in other authors’ works, in particular [20, 21]. The findings of the experiment and modeling show that a higher concentration of Cu atoms causes a higher melt viscosity.
A similar behavior of the concentration/kinematic dependency has been found for a binary eutectic system of Al-Ni: against growing ν-values, there is a local maximum near 1.5 at.% Ni and a local maximum near 2.7 at.% Ni [16]. The viscosimetric experiment also concludes that the temperature dependencies (from liquidus temperature to 1473 K) of the Al-Cu melt viscosity (up to 10 at.% Cu) deviate from Arrhenius plot. It can be explained by changing activation energy of viscous melt flow between 1183 and 1223 K. A similar deviation of temperature dependencies of kinematic viscosity has been found for liquid aluminum and Al-Co melts (up to 1.5 at.% Co) near 1223 K [18]. The structural and phase transformations in Al-Co alloys (up to 1.5 at.% Co), produced after various overheats of the melts as a result of cooling at rates from 2 to 10⁶ degrees/s, have been compared to prove the experimental data obtained from analysis of temperature dependencies of melts viscosity. The experiments evidence reversibility of the processes in the melt as it is heated from liquidus temperature to 1473 K and then cooled down [22].

Proceeding from the published studies on correlation of liquid and solid states [8, 9, 11, 22] etc., this paper has been intended to observe how the features found in Al-Cu melts (up to 10 at.% Cu) influence the structure and properties of their alloys produced from liquid state in a wide temperature range at different melt cooling rates¹.

II. OBJECTS AND EXPERIMENT PROCEDURE

The research object was Al-Cu alloys with 2, 5, 7 and 10 at.% Cu. The samples were produced through fusing metals in alumina crucibles in a Tamman furnace. The initial components were elements with the groundmass metal assay of 99.999 (Al) and 99.996% (Cu) (wt.). Chemical analysis showed that the groundmass component assay conformed with the selected compositions.

We observed a temperature range between 973 and 1473 K and cooling rates of ~ 2 and 100 degree/s. The cooling rate of 2 degrees/s was provided with a VTA-983 machine. The materials were cooled down in atmosphere of refined helium in alumina crucibles. The cooling rate of 100 degree/s was provided with water quenching of vacuum-protected quartz vessels containing the samples. Three different sample-acquisition modes were used: 1) "973 K→cooling", 2) "1473 K→cooling", 3) "1473 K→973 K→cooling". The hold time at each temperature was 10 minutes. The structure of the alloys with different Cu content produced at a cooling rate of 100 degrees/s was observed after only one temperature of melt heating, 973 K, since when heated up to 1473 K, the samples often reacted with the material of the vessel.

The metallographic studies involved etched (0.5%HF, Keller reactant, 5-10% NaOH) and unetched slices examined with a Neophot-32 optical microscope. The structural studies used the standard methods of metallographic analysis: Glagolev method - to find the eutectic mixture volume ratio – and intercept method - to find the dendrite parameter (thickness of secondary dendrite branches in the alloys). The durometric parameters were measured with a PMT-3M microhardness tester. The phase composition of the alloys was found through X-ray structural analysis with a Bruker Advance system in Cu-Kα-radiation.

III. RESULTS AND DISCUSSION

According to X-ray structural analysis, the structure of all the samples - regardless of their composition, temperature and cooling rate - includes two phases: α-Al and Al₂Cu. A growing cooling rate (increasing from 2 up to 100 degrees/s) reduces the α-Al lattice parameter. Meanwhile, the Al₂Cu phase lattice parameter remains constant and equal to the conventional reference data. The findings of the metallographic studies correspond with those of the X-ray structural analysis.

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Cooling rate of 2 degrees/s.

Figure 1(a-d) shows the microstructure of Al-Cu alloys cooled down from a melt of 973 K. According to the equilibrium state diagram, the Al-2%Cu alloy is in the segment of the αAl-solid solution. The structure is represented with α-phase primary dendrite crystals with round branch section and a eutectic mixture (α-Al+Al2Cu) of liquation origin with mutual dendrite penetration of its elements (Fig. 1a). The eutectic mixture is located along the borders of the α-phase crystals and looks like interlayers or ellipses. The eutectic mixture volume ratio in all three above modes remains almost constant, 7-8%. In the Al-5%Cu alloy structure, the α-phase dendrites are rounded, the eutectic mixture (α-Al+Al2Cu) of dendrite and laminar morphology is located along the borders of the α-phase (Fig. 1b). The eutectic mixture volume ratio in the alloy grows up to 20% against the Al-2%Cu composition and its amount is independent from the heat treatment mode of the melt. The Al-7%Cu alloy as compared with the previous composition crystallizes in a smaller crystallization interval but in the same manner (Fig. 1c). Depending on the melt heat treatment mode, the shape of the primary phase dendrites change: at the high temperature of the melt, 1473K, it is more spherulitic (Fig. 1e); in the "1473 K→973 K→cooling" mode, it is branched (Fig. 1f). Heating from 973 to 1473 K does not influence the eutectic mixture volume ratio: it remains 30%; in the "1473 K→973 K→cooling" mode it increases up to 40%. The Al-10%Cu alloy has the most narrow crystallization interval. In all the heat treatment modes, the structures are identical; they consist of α-phase dendrites and a eutectic mixture (Fig. 1d). The eutectic mixture volume ratio remains constant, ~ 50%.

Figure 1. Microstructure of Al-Cu alloys (Vcool= 2 degrees/s).

a-d-"973 K→cooling" mode, e-"1473 K→cooling" mode, f-"1473 K→973 K→cooling" mode. 1-α-Al, 2-eutectic (α-Al+Al2Cu)
Cooling rate of 100 degrees/s, the "973K→cooling" mode.

A higher cooling rate provides smaller structure components of the alloys. The Al-2%Cu alloy demonstrates apparent dendrite growth of the α-phase with rounded axes; there are also a globular eutectic mixture (α-Al+Al2Cu) of grain morphology in the form of ellipses located along the borders of the dendrites (Fig. 2a). Against the structure of the alloy produced at a cooling rate of 2 degrees/s, the thickness of the secondary dendrite stalks of α-phase decreases 5 times and the eutectic mixture amount grows twice. The Al-5, 7 and 10%Cu alloys form α-phase dendrites with thinner secondary branches (~ 5-6 µm thick), while the same compositions produced at a cooling rate of 2 degrees/sec are ~ 25-40 µm thick. The eutectic mixture in the Al-5 and 7%Cu alloys amounts to ~ 30%. In the Al-10%Cu alloy, this amount decreases twice against the slowly crystallized alloy.

Microhardness of the alloys.

The table shows the measurements of the α-phase microhardness depending on the alloy compositions, “973 K→cooling” mode. It is obvious that a higher Cu concentration in the alloy and a higher melt cooling rate result in a higher microhardness of the Al-Cu alloy groundmass. At T=973 K, the concentration correlation of the microhardness behaves similarly to the viscosity correlation that we have found [19].

At a cooling rate of 2 degrees/s in the Al-2%Cu alloy, the microhardness of the α-phase heated from 973 to 1473 K is constant, the "1473 K→973 K→cooling" mode results in a slight decrease of microhardness, Hv amounts to (550±20) MPa. The Al-5%Cu alloy demonstrates a similar situation; in the "1473 K→973 K→cooling" mode, the microhardness decreases and amounts to (550±30) MPa. In the Al-7%Cu alloy, the microhardness keeps decreasing when being heated from 973 to 1473K, while the "1473 K→973 K→cooling" mode, on the contrary, increases the α-phase microhardness up to (800±30) MPa. For the Al-10%Cu alloy, unlike other alloys: α-phase microhardness in the "973 K→cooling" and "1473 K→973 K→cooling" modes is constant, and in the "1473 K→cooling" mode, it grows up to (1000±20) MPa.

Figure 2. Microstructure of Al-Cu alloys
(Vcool= 100 degrees/s, "973 K→cooling" mode).
### Table

**Microhardness of Al-Cu samples (the "973K→quenching" mode)**

<table>
<thead>
<tr>
<th>Chemical composition, at.%</th>
<th>α-phase microhardness, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling rate 2 degrees/s</td>
<td></td>
</tr>
<tr>
<td>Al$_9$Cu$_2$</td>
<td>600±20</td>
</tr>
<tr>
<td>Al$_9$Cu$_5$</td>
<td>680±10</td>
</tr>
<tr>
<td>Al$_9$Cu$_7$</td>
<td>680±20</td>
</tr>
<tr>
<td>Al$_9$Cu$_10$</td>
<td>850±20</td>
</tr>
<tr>
<td>Cooling rate 100 degrees/s</td>
<td></td>
</tr>
<tr>
<td>Al$_9$Cu$_2$</td>
<td>700±30</td>
</tr>
<tr>
<td>Al$_9$Cu$_5$</td>
<td>800±20</td>
</tr>
<tr>
<td>Al$_9$Cu$_7$</td>
<td>1000±20</td>
</tr>
<tr>
<td>Al$_9$Cu$_10$</td>
<td>1070±20</td>
</tr>
</tbody>
</table>

### IV. Summary

The obtained data shows that overheating Al-Cu melts (up to 10 at.% Cu) to 100-500°C over the liquidus temperature and cooling them at cooling rates of 2 and 100 degrees/s result in crystallization that forms structures containing α-Al primary dendrites and a eutectic mixture (α-Al+Al$_2$Cu). It agrees with the phase equilibrium diagram. Increasing the cooling rate from 2 up to 100 degrees/s provides smaller structure elements of the alloys due to the changed distribution of the crystallization centers, their growth rate, the mass transfer moving force on the melt-crystal border and the overcooling value on the crystallization front. A higher cooling rate is also accompanied with a decreasing α-Al lattice parameter due to production of a solid solution Al(Cu) which is more supersaturated (solid solution hardening). It can explain the higher microhardness of the alloy groundmass with an increasing cooling rate.

We plan to (1) study the structure and properties of Al-Cu alloys in these compositions, produced in the environment of flash cooling of melts (cooling rate ~ 10$^5$-10$^6$ degrees/sec), and (2) compare the findings with the data of this study, with the concentration correlation of the viscosity of their melts. This work is partially described in [11].

### V. Conclusions

1. This study observes the influence of the melt heating temperature (from 973 to 1473 K) and the cooling rate (2 and 100 degrees/sec) on the structure, phase composition and microhardness of the groundmass matrix of Al alloys containing 2, 5, 7 and 10 at.% Cu.
2. We find that, in the observed cooling/overheating rate range for melts, the phase composition of the melts agrees with the state equilibrium diagram and that the alloy structure of all the compositions contains two phases: α-Al and Al$_2$Cu.
3. We show that a higher copper concentration in the alloy and a higher cooling rate result in a higher microhardness of the alloy groundmass, a lower α-Al dendrite parameters and a changed volume ratio of the eutectic mixture.
4. This study demonstrates that the concentration dependence of the microhardness behaves similarly to the kinematic viscosity dependence.

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