Microstructure Formation in Binary Al-TM Alloys under Non-equilibrium Solidification

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Abstract. The structure formation in hypereutectic Al-Sc and hyperperitectic Al-Zr, Al-Hf alloys with concentration of alloying element up to 1.3 at.% have been studied under conditions far from thermodynamical equilibrium depending on cooling rate and quenching temperature. The co-operative growth structures are solidified with cooling rate of \(10^{-2}-10^{-3}\) K/s regardless of overheating and under cooling rate of \(10^{-5}-10^{-6}\) K/s at small overheating. The phase compound of these structures is \(\text{Î}-\)solid solutions and phase with \(L_1^2\)-ordered structure or two solid solutions with different concentrations of alloying element. The large overheating leads to formation of \(\alpha\)-solid solution anomalously supersaturated under cooling rate of \(10^{-5}-10^{-6}\) K/s.

1. Introduction
During the recent years particular interest has been caused by modern technologies of melting and rapid solidification of metallic systems, which provides the crystallization conditions far from thermodynamical equilibrium and allows to reach deep undercooling of surface and high velocities of the phase transformation, large temperature and concentration gradients, high cooling rate. The microstructure formation in binary Al-alloys depending on cooling rate, quenching temperature (overheating above liquidus temperature) and nature of alloying element (Sc, Zr, Hf) have been studied in present work to determine conditions of formation of anomalous supersaturation by transition metals in Al.

2. Materials and methods of investigation
The hypereutectic Al-Sc and hyperperitectic Al-Zr, Al-Hf alloys with content of alloying element up to 1.3 at.% have been studied. The Sc, Zr and Hf are transition elements with unlimited solubility in each other. Their electronegativities and atomic radiuses are similar, their atomic weights \(A_{\text{Sc}}:A_{\text{Zr}}:A_{\text{Hf}}\) are related as 1:2:4.

Alloys were cast with cooling rate of \(10^{-3}-10^{-3}\) K/s in a copper mould on a plate and also with cooling rate of \(10^{-5}-10^{-5}\) K/s using melt-spinning technique. Two quenching temperatures of melt were chosen: 1000°C, which is higher than liquidus temperatures of studied alloys, and 1400°C, which is higher than the melting temperature of Al$_3$Sc intermetallic compound (1320°C) and lower than the melting temperatures of Al$_3$Zr (1560°C) and Al$_3$Hf (1590°C). The transmission electron microscopy JEM-2000FXII, conventional optic microscopy, resistometry and method of measuring kinematic viscosity of melt were used in researches.

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3. Results and discussion

The influence of cooling rate and quenching temperature of melt on the alloy microstructure has been studied for Al-Sc alloys. It has been established that the microstructure of Al-0.67 at.% Sc alloys solidified with cooling rate of $10^2$-$10^3$ K/s does not depend on the change of quenching temperature from 1000 to 1400 °C. The investigation of structural state of alloys has shown that the two-phase state ($\alpha$-solid solution and the stable Al$_3$Sc-phase) is formed in these alloys. The ingot thickness is 3-5 mm. The microstructures of free and contact sides of specimen are different (fig. 1a). The bright region is the region of free side of specimen. The dark region corresponds to the region of contact side of specimen. The structure containing the $\alpha$-solid solution and primary cube Al$_3$Sc particles with size of 15-20 μm in the center of grain have been observed in the region of free side of specimen (fig.1b). The co-operative growth structures containing the $\alpha$-solid solution and the stable Al$_3$Sc-phase are formed in the region of contact side of specimen (fig.1c). The thickness of branches of co-operative growth structures is about 0.2-0.5 μm. The equiaxed grains of 50-70 μm have been observed on contact and free sides, in cross and longitudinal sections of specimen.

### Figure 1. The structure of the Al-0.67 at.% Sc alloy quenched from 1000 °C with $10^2$-$10^3$ K/s:

- a) cross section; b) free side; c) contact side

After increasing cooling rate to $10^5$-$10^6$ K/s the thickness of the Al-0.67 at.% Sc and Al-1.32 at.% Sc ribbons decreases to 50-100 μm. The solidification structure is characterized by the presence of needle-shaped grains with a diameter of 1-2 μm (fig. 2a). The microstructures of free and contact sides of ribbons are different (fig. 2a). The TEM study has been shown the high volume fraction of grains of 100-200 nm in the region of contact side of ribbons in contrast to the free side of ribbons (fig.2b, c).

### Figure 2. The structure of Al-Sc alloy prepared by melt-spinning:

Al-1.32 at.% Sc alloy quenched from 1000 °C: a) cross section, b) contact side, c) free side; d) free side of Al-0.67 at. % Sc alloy quenched from 1400 °C

The TEM study of structural and phase states of Al-Sc alloys rapidly quenched with cooling rate of $10^5$-$10^6$ K/s has shown that the quenching temperature change from 1400 to 1000 °C results in the crystallization mechanism change (fig.2c, d). The formation of single-phase state and, accordingly, the $\alpha$-solid solution anomalously supersaturated have been observed in alloys rapidly quenched from 1400 °C (fig.2d), since particles of Al$_3$Sc-phase have not been determined. The rapid quenching from 1000 °C...
°C results in the solidification of two-phase state in alloys (fig.2c). Moreover, it has been established that the co-operative growth structures containing the α-solid solution and the stable Al$_3$Sc-phase are formed in Al-Sc alloys rapidly quenched from 1000 °C (fig.3a).

It should be pointed that similar influence of quenching temperature of melt on the microstructure of Al-Zr and Al-Hf alloys prepared by the melt-spinning was established [1-3]. The TEM study of the co-operative growth structures solidified with cooling rate of $10^5$-$10^6$ K/s has shown that these structures consist of α-solid solution and Al$_3$X-phase (X = Sc, Zr) with L1$_2$-ordered structure in Al-0.67at.% Sc, Al-1.32at.% Sc and Al-0.33at.% Zr, Al-0.89at.% Zr alloys quenched from 1000 °C (fig.3a, b). The Al$_3$Sc-phase is stable, while the Al$_3$Zr-phase is metastable. Moreover, two types of the co-operative growth structures have been observed in these alloys. The «vortex» structure covers several grains (fig.3a). The «fan» structure is inside a grain (fig.3b). In contrast to Al-Sc and Al-Zr alloys, the co-operative growth structure consists of two solid solutions for Al-1.1at.% Hf alloy (fig.3c). Branches of the «fan» structure are the solid solution enriched by Hf.

![Figure 3](image1.png)  
**Figure 3.** The co-operative growth structures of alloys prepared by melt-spinning from 1000 °C:  
a) Al-1.32 at.% Sc; b) Al-0.33 at.% Zr; c) Al-1.1 at.% Hf

Thus, for alloys prepared with cooling rate of $10^5$-$10^6$ K/s the solidification with suppression of diffusion processes at the crystallization front and subsequent formation of the α-solid solution anomalously supersaturated occurs under the rapid quenching from 1400 °C, while the co-operative growth structures are solidified under the rapid quenching from 1000 °C.

The temperature dependence of the kinematic viscosity of melt has been analyzed to understand the influence of quenching temperature (overheating above liquidus temperature) on microstructure of alloys solidified with cooling rate of $10^5$-$10^6$ K/s. The kinematic viscosity versus temperature dependence of the Al-0.67at.% Sc melt was investigated in ref. 4 and the results are shown in Fig. 4. One can notice the branching of heating and cooling curves near 1200 °C and the region of anomalous dependence of kinematic viscosity at cooling. The appearance of this region can be explained by the formation of microheterogeneous state of melt and presence of clusters enriched by alloying element.

![Figure 4](image2.png)  
**Figure 4.**  
**Figure 4.** The temperature dependence of the kinematic viscosity of Al-0.67at.% Sc melt during heating and subsequent cooling [4]
[4, 5]. It should be pointed that the correlation of microstructure of rapidly quenched alloys with behaviour of kinematic viscosity takes place. The quenching temperature of 1000 °C corresponds to the region of anomalous dependence of kinematic viscosity. The temperature of 1400 °C corresponds to the overheating above branching of v(T) and relates to the region of microhomogeneous melt without clusters. Taking into account the structural heredity under the non-equilibrium solidification, the different microstructures can be obtained quenching the melts from different temperature. Thus, the heating the melt up to 1000 °C (the region of anomalous dependence of kinematic viscosity) and subsequent rapid quenching result in the formation of co-operative growth structure. The heating the melt up to 1400°C (the region of microhomogeneous melt) and subsequent rapid quenching lead to the solidification of α-solid solution anomalously supersaturated.

The temperature dependence of electrical resistivity ρ(T) during the continuous heating of ribbon for Al-1.32at.%Sc, Al-0.33at.%Zr, Al-0.89at.%Zr and Al-0.94at.%Hf alloys rapidly quenched with cooling rate of 10^5-10^6 K/s was investigated in ref. 1-3. These results and data of structural and phase states of alloys obtained by TEM study have been analyzed to determine the degree of supersaturation of solid solution by alloying metal in rapidly quenched ribbons. The concentration of alloying element in solid solution C_{s.s}, the maximum solubility of alloying element in the aluminium

| Alloy (at.%) | T (°C) | C_{equal} (at.%) | C_{s.s} (at.%) |
|-------------|--------|----------------|---------------|
| Al-1.32 Sc  | 1400   | 0.15           | 1.32          |
| Al-1.32 Sc  | 1000   | 0.15           | 0.15          |
| Al-0.94 Hf  | 1400   | 0.18           | 0.94          |
| Al-0.33 Zr  | 1400   | 0.08           | 0.33          |
| Al-0.33 Zr  | 1000   | 0.08           | 0.25          |
| Al-0.89 Zr  | 1000   | 0.08           | 0.54          |

C_{equal} in accordance with the equilibrium diagram and the quenching temperature of melt T are summarized in tabl. 1. The high supersaturation of solid solution by alloying element is achieved under rapid solidification in all investigated alloys except the Al-1.32at.%Sc ribbon crystallized with forming the co-operative growth structures (1000 °C). It should be noted that the degree of supersaturation of solid solution depends on the conditions of alloy preparation and concentration of alloying element.

4. Conclusions
1. The Al-Sc, Al-Zr and Al-Hf alloys are solidified with the formation of anomalously supersaturated solid solution under cooling rate of 10^5-10^6 K/s at quenching temperature of 1400 °C.
2. The maximum supersaturation of solid solution is achieved in Al-Hf alloys, the minimum supersaturation of solid solution is achieved in Al-Sc alloys.
3. The co-operative growth structures are solidified under cooling rate of 10^2-10^3 K/s regardless of quenching temperature and under cooling rate of 10^2-10^6 K/s at quenching temperature of 1000 °C. These structures consist of α-solid solution and Al_{x}X (X = Sc, Zr) phase with L1_2-ordered structure in Al-Sc and Al-Zr alloys. These structures are the solid solution enriched by alloying element in Al-Hf alloys.

5. References
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