FORMATION AND DECOMPOSITION OF THE ANOMALOUS SUPERSATURATED SOLID SOLUTION OF ALUMINIUM ALLOYS ALLOYED WITH Sc AND Zr

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ABSTRACT

Decomposition processes of supersaturated solid solution of aluminium alloys alloyed with Sc and Zr have been studied in the work. Binary hypereutectic Al-Sc alloys, hyperperitectic Al-Zr alloys and triple Al-Sc-Zr alloys were chosen. Alloys were obtained by the melt-spinning. Melts were quenched from temperatures of T=1000 ºC and T=1400 ºC. The crystallization of anomalously supersaturated solid solution ($T_{quen.}$ 1400 ºC) or the crystallization with the formation of "fan" structure ($T_{quen.}$ 1000 ºC) are possible. The decomposition of anomalously supersaturated solid solution is continuous, with the precipitation of nano-sized spherical Al_3X (X - Sc, Zr) particles. The loss of thermal stability of Al-Sc alloys is due to the loss of coherence of the strengthening Al_3Sc phase. In Al-Zr alloys the loss of strength is due to the formation of a stable tetragonal DO_{23}-ordered $A1_3Zr$ phase. After co-alloying of Al by Sc and Zr a bimodal grained structure was observed for the hypereutectic ternary alloy ($T_{quen.}$ 1400ºC). Nano-sized grains of 50-60 nm were present on the boundaries of 1-2 μm large-sized grains. TEM shows the formation of composite Al_3Zr/Al_3Sc particles. The formation of Al_3Zr shell changes the nature of the interfacial fit of the particle with the matrix and slows down the decomposition during the coalescence.

Key words: Al-Sc, Al-Zr Al-Sc-Zr alloys, rapid quenching, decomposition of anomalously supersaturated solid solution, composite Al_3Zr/Al_3Sc particles

INTRODUCTION

The development of novel high-strength, heat-resistant aluminium alloys requires an increase in the volume fraction of particles of strengthening phase in aluminium matrix due to the formation of anomalous supersaturation with slightly soluble transition metals in Al. Conventional methods of quenching and aging the solid state are not effective in this case. The main task of the study is to examine the decomposition of anomalous supersaturated solutions by transition metals in Al obtained by quenching from the melt [1, 2]. To solve this problem it is necessary:

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- to study factors that determine the formation of anomalously supersaturated solid solutions in aluminium alloyed with slightly soluble refractory elements;
- to determine the kinetics and morphology of the decomposition of anomalously supersaturated solid solutions in rapidly quenched aluminium alloys;
- to study the thermal stability of structures obtained during decomposition and to assess the possibility of improving their thermal stability.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

The materials investigated had to be provided with: high volume fraction and high precipitation density of the streightnening phase, as well as high thermal stability of the structure produced [3]. It was supposed that the high volume fraction would be provided during the decomposition of anomalously supersaturated solid solution obtained by the melt-spinning method; high precipitation density would be formed during continuous decomposition with the precipitation of particles which had a low activation energy for nucleation; thermal stability would be ensured due to a low surface energy and low misfit parameter of the matrix with the phase formed, as well as low solubility and low diffusion coefficient of the alloying element in the matrix [4]. The formation of the $L1_2$-ordered phase, isomorphic to the matrix, during the decomposition meets the abovementioned requirements. Binary hypereutectic Al–Sc alloys, hyperperitectic Al–Zr alloys and triple Al–Sc–Zr alloys were chosen.

Table 1 – The composition of aluminium alloys and the processing parameters of ribbons

№	Al, at. %	Sc, at. %	Zr, at. %	T, ºC	V_L, m/s
1	base	0.67	-	1000	0
2	»	0.67	-	1400	0
3	»	0.67	-	1000	44
4	»	0.67	-	1400	44
5	»	1.2	-	1000	30
6	»	1.2	-	1000	44
7	»	1.32	-	1400	30
8	»	1.32	-	1400	44
9	»	-	0.33	1000	44
10	»	-	0.33	1400	44
11	»	-	1.2	1400	44
12	»	0.6	0.24	1000	30
13	»	0.6	0.24	1000	44
14	»	0.6	0.24	1400	30
15	»	0.6	0.24	1400	44

Alloys were cast with the cooling rate of $10^2 – 10^3$ ºC/s on a copper plate, and with the cooling rate of $10^5 – 10^6$ ºC/s, using melt-spinning method on the copper wheel with the rotation speed of V_L = 30 m/s and V_L = 44 m/s. Two quenching temperatures of the melt were chosen: 1000 ºC, which is higher than liquidus temperatures of the alloys studied, and 1400 ºC, which is higher than the melting temperature of Al_3Sc intermetallic compound (1320 ºC) but lower than the melting temperatures of Al_3Zr (1560 ºC). The composition of aluminium alloy ribbons, the quenching temperature of melt T and the copper wheel rotation speed V_L are summarized in *tabl 1*.

The transmission electron microscopy JEM-2000FXII, conventional light microscopy, and microhardness measurement were used in the studies.

RESULTS AND DISCUSSION

The effect of cooling rate on the structure of aluminuum alloys quenched from liquid state. The effect of cooling rate and quenching temperature of the melt on the alloy microstructure has been studied for Al–Sc alloys. It was established that the phase composition and morphology of phases of Al–0.67at.%Sc alloys solidified with the cooling rate of $10^2 – 10^3$ ºC/s does not depend on the change of quenching temperature from 1000 to 1400 ºC. The investigation of alloy structure proved that the two-phase state (α-solid solution and the stable Al_3Sc-phase) was formed in these alloys. Structural studies [5] demonstrated that the microstructures of free and contact sides of specimens were different. The change in the cooling rate of aluminium alloys from 10^2 ºC/s to 10^3 ºC/s led to a change in the excess phase morphology from the compact form (free side) to a branched "fan" structure (the side in contact with the copper plate).

The effect of quenching temperature of the melt on the structure of aluminuum alloys. The TEM study of structural and phase states of aluminium alloys rapidly quenched with the cooling rate of $10^5 – 10^6$ ºC/s showed that the quenching temperature change from 1400 to 1000 ºC resulted in the crystallization mechanism change. Examination of Al–Sc and Al–Zr alloys showed that regardless of the alloying element, the melt quenching from 1400 ºC led to the formation of single-phase state, i.e. anomalous supersaturated solid solution (*Fig.1*).

The highest concentration of the supersaturated solid solution was determined by the emergence of nano-sized grains. In Al–Sc alloys the increase in Sc concentration from 0.67 at.% to 1.3 at.% did not cause significant changes in the structure. In contrast, in Al–Zr ribbons quenched from 1400 ºC the increase in Zr concentration from 0.33 at.% to 1.2 at.% led to a large volume fraction of nanocrystalline structure. This state was characterized by a bimodal distribution of grain sizes. Nano-sized grains of 50 – 60 nm were present on the boundaries of 1–2 μm large-sized grains.

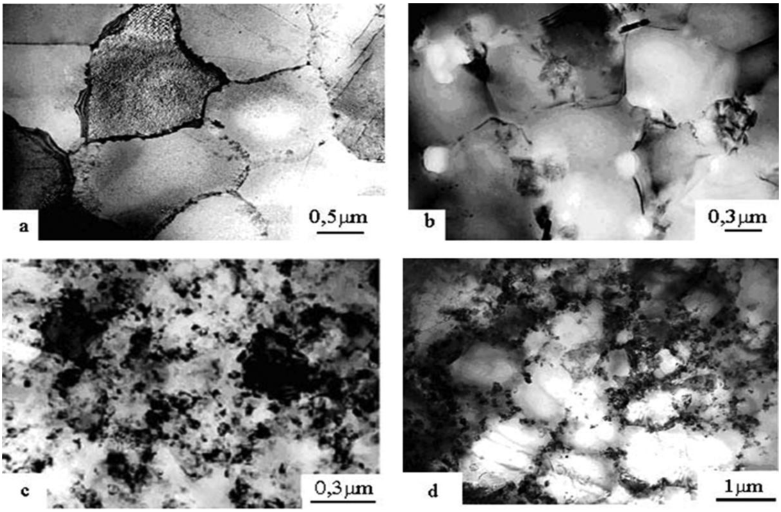

Fig.1 - The structure of the alloys quenched from 1400 ºC: a) Al–0.67at.%Sc; b) Al–0.33at.%Zr; c) Al–1.2at.%Zr; d) Al–0.6at.%Sc–0.24at.%Zr.

The presence of nanocrystalline grains accelerated the formation of metastable and stable phases during the decomposition of supersaturated solid solution.The structure had low thermal stability. The microhardness of the Al–1.2 at.%Zr alloy was 1300 MPa, which is twice as high as the hardness of the Al – 0.33at.%Zr alloy. The total supersaturation limit of triple Al–Sc–Zr alloys was lower as compared to binary Al–Zr and Al-Sc alloys. The formation of nano-sized grains was observed for triple Al – 0.6% Sc – 0.24% Zr alloy (*Fig.1 d*).

The melt quenching from 1000 ºC led to crystallization with the formation of "vortex" or "fan" structure (*Fig. 2*). The «vortex» structure covered several grains (*Fig.2a, c*). «Fan» structures were inside grains (*Fig.2b, d*). The thickness of the structure branches was about 10 nm.

The morphology of "fan" and "vortex" structures proves their crystallization origin. They grew directly from the melt and didn’t result from the transformation (cellular decomposition) in the solid state.

The effect of Zr on the structure and anomalous supersaturated solid solution of rapidly quenched Al-Sc alloys. The introduction of Zr in Al–Sc alloy brought about certain peculiarities in the structure of rapidly quenched alloys as compared to binary ones. The bimodal distribution of grains with the nanocrystalline component was observed in triple Al–Sc–Zr alloys after quenching from 1400 ºC, in contrast to the binary Al–Sc and Al–Zr alloys with the same degree of supersaturation. Consequently, the cumulative effect of these elements exceeded the effect of each component.

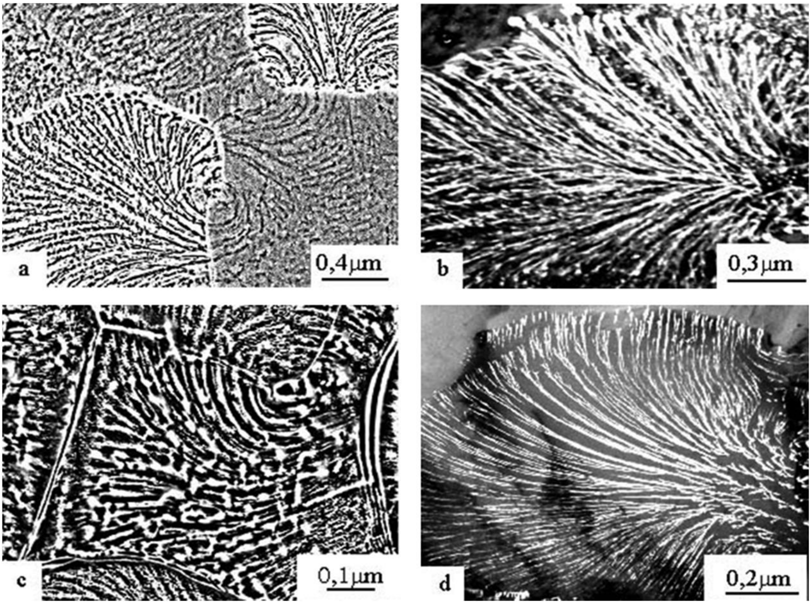

Fig.2 - The types of crystallized structures of alloys produced by melt-spinning from 1000 ºC: "Vortex" structure a) Al–0.67at.% Sc; c) Al–0.33 at.%Zr; "Fan" structure b) Al–0.67at.% Sc; d) Al–0.33 at.%Zr

A decrease in the quenching temperature to 1000 ºC (V_L = 44m/s) led to the formation of single-phase state, i.e. anomalous supersaturated solid solution. The mixed structure was formed after the reduction of V_L to 30 m/s. The grains crystallized to form a solid solution and "fan" - structured grains present in the alloy. Faceted primary Al_3Zr particles of the 400–500 nm were also observed. Thus, the introduction of Zr in Al–Sc alloys allowed us: to reduce the temperature of quenching for the formation of anomalously supersaturated solid solution, to reduce the total concentration of alloying elements for the formation of nano-sized grain structure.

Aging processes of rapidly quenched aluminium alloys. The TEM study showed that regardless of the nature of the alloying elements (Sc, Zr) in the initial stages of decomposition of the supersaturated solid solution the Al_3X (X = Sc, Zr) strengthening $L1_2$-ordered phase was formed. The Al_3Sc stable phase particles induced static distortions in the matrix as a result of misfit of lattice parameters. The Al_3Zr phase was metastable and did not induce static distortions in the matrix. It was established that the mechanism of decomposition and morphology of precipitated phase depended on the initial state of the alloy in accordance with the processing parameters. Ribbons crystallized with the formation of solid solutions (quenching from 1400 ºC) continuously decomposed with the precipitation of chaotically distributed particles. The variation of the temperature and aging time allowed us to obtain a highly dispersed structure containing nano-sized spherical Al_3X (X - Sc, Zr) particles of $L1_2$-ordered phase of about 2 nm size and the precipitation density ~ 10^{18} sm^{-3}.

Coherent Al_3Sc particles were observed in the Al – Sc alloy after aging at 450ºC for 2 hours. The average size *d*, the precipitation density *Nv* and the volume fraction *f* of particles are summarised in *Table 2*. The tendency of the particles being situated on dislocations was observed. When the particle sizes were about 30 nm they lost coherency due to the formation of misfit dislocations at the interphase boundary.

Table 2 – Characteristics of Al_3X particles after aging at 450ºC for 2 hours

Alloy, at. %	T, ºC	V_L, m/s	Phase type	d, nm	N_v, sm^{-3}	f, %
Al-0.67Sc	1400	44	$L1_2$	22	$4.5\cdot10^{15}$	2.5
Al-1.32Sc	1400	44	$L1_2$	15	$1.8\cdot10^{16}$	3.2
Al-1.32Sc	1400	30	$L1_2$	19	$1.1\cdot10^{16}$	4.6
Al-0.33Zr	1400	30	$L1_2/DO_{23}$	9	$2.3\cdot10^{16}$	1.2

Alloys which crystallized with the formation of "fan" structure (quenching from 1000 ºC) decomposed through thickening of the structure branches and formation of spherical precipitates of AL_3X (X = Sc, Zr) $L1_2$-ordered phase between the branches. Destruction of the "fans" occured during the aging process. Evolution of structure led to the formation of chaotically distributed particles of AL_3X (X = Sc, Zr) $L1_2$-ordered phase with the precipitation density ~ 10^{15} sm^{-3} (Al-Sc alloys) and ~ 10^{16} sm^{-3} (Al–Zr alloy). Further evolution of these structures was similar to that of alloys, crystallized with the formation of solid solutions.

Thermal stability of structures formed by rapid quenching of binary and triple Al–Sc, Al–Zr, Al–Sc–Zr alloys. The morphology of the decomposition after long-term aging at high temperatures was studied to determine the thermal stability of the structure obtained (*Fig. 3*). Comparison of structural changes during isothermal aging and changes in microhardness showed that the increase of hardness was due to the formation of $A1_3X$ (X = Sc, Zr) $L1_2$-ordered phase. The most high-strength state was achieved in the alloys, crystallized with the formation of solid solutions.

The decrease in microhardness below the initial value was found after aging of the Al-Sc alloys at T > 300 ºC, and the Al–Zr alloys at T > 350 ºC. Alloys, which crystallize with the formation of "fan" structure were thermally the most stable of the binary alloys. It was found that the loss of strength of Al–Sc alloys was due to the loss of coherence of the strengthening Al_3Sc phase particles (*Fig. 3 b, d*).

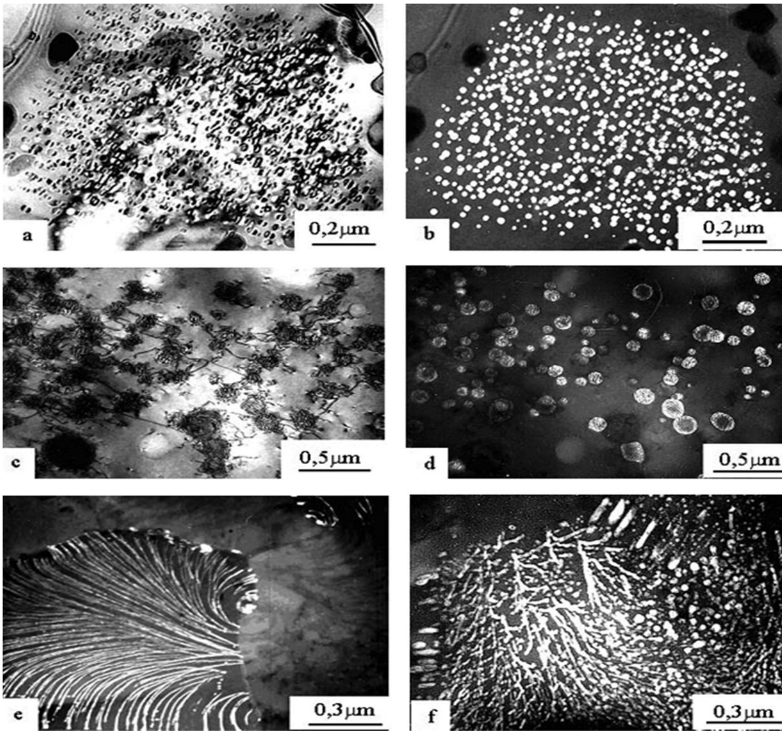

Fig. 3 - Decomposition processes in the Al–1.32 at.% Sc ribbons crystallized: 1) with the formation of solid solutions, quenching from 1400ºC at V_L=44m/s: a), b) aging at 450ºC for 2 hours, the particle size d≈15 nm, Nv≈10^{16} sm^{-3}; c), d) aging at 450ºC for 20 hours, the particle size d≈87,4±2,6 nm, Nv≈$10^{14}sm^{-3}$; 2) with the formation of "fan" structure, quenching from 1400ºC at V_L=44m/s: e) after quenching, the thickness of the "fan" branches ~5nm; f) aging at 450ºC for 2 hours, the particle size d ≈ 19,2 ± 2,4 nm; a), c), e) bright-field image, b), d), f) dark-field image in reflex (100) of the Al_3Sc-phase

In Al–Zr alloys the loss of strength was due to the formation of a stable tetragonal DO_{23}-ordered $A1_3Zr$ phase.

The Al_3Zr metastable phase particles were replaced by composite $L1_2/DO_{23}$ particles during aging at 450 ºC in Al–Zr alloys (*Fig. 4*). The plate-like stable phase was formed inside the metastable phase particle (the size ~10 nm) along <100>. Further aging resulted in complete dissolution of the metastable phase and the formation of a rod-like stable phase with the length of about 80 nm after 70 hours of aging (*Fig. 4*). The continuous decomposition of the anomalous supersaturated solid solution of Al–0,6%Sc–0,24% Zr triple alloy obtained by rapid quenching from 1000 °C at V_L=44м/c are most interesting.

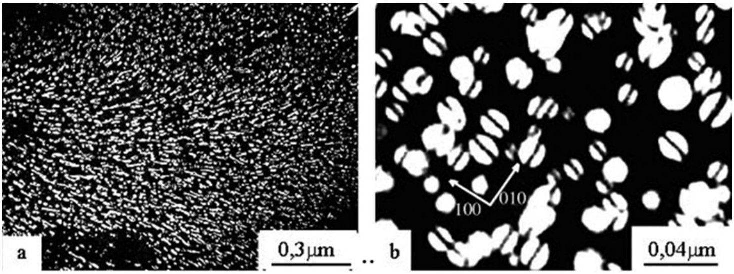

Fig. 4 - The structure of the Al–0.89 at.%Zr alloy quenched from 1000 ºC at V_L = 44m/s and aged at 450 ºC for 60 hours

Two alloying elements of the alloy have a considerable difference in diffusion mobility $D_{Sc}/D_{Zr} \sim 10^3$ and the difference in the misfit parameters of the matrix and the Al_3X intermetallic $\delta_{Al3Sc}/\delta_{Al3Zr} \sim 2$. Therefore one could expect that the nucleation processes of decomposition would be determined by the diffusion mobility of Sc, and the processes of growth and coalescence – by Zr diffusion. This facilitates the formation of composite Al_3Zr/Al_3Sc particles with Al_3Sc core and Al_3Zr shell.The morphology of such particles is shown in *Fig. 5*.

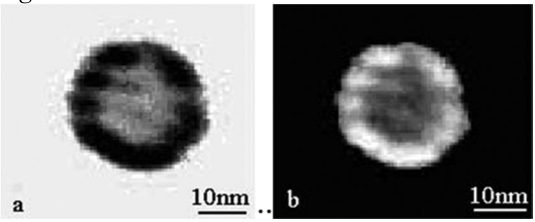

Fig. 5 - The morphology of Al_3Zr/Al_3Sc phase precipitate: a – bright-field image, b – dark-field image in superstructural reflex (100)

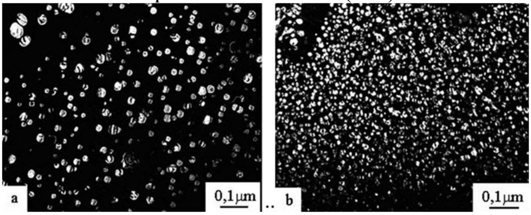

Fig. 6 – The dark-field image in superstructural reflex (110) of the Al_3X phase of the alloys: a) Al–0.6 at.% Sc, quenching from 1400 ºC at V_L = 44m/s, aging at 450ºC for 2 hours; b) Al–0.6 at.% Sc–0.24 at.%Zr, quenching from 1000 ºC at V_L = 44m/s, aging at 450 ºC for 40 hours

The formation of Al_3Zr shell changed the nature of the interfacial fit of the particle and the matrix and slowed down the decomposition during the coalescence stage. Reduction in size of particles formed after long-term aging due to the 0.24 at.%Zr addition in Al–0,6 at.% Sc alloy is shown in *Fig. 6*.

The microhardness change during isothermal aging at the temperatures 350 and 450 ºC for alloys rapidly quenched from 1000 ºC is shown in *Fig. 7*.

The data presented imply that triple Al–Sc–

Zr alloys have significantly higher thermal stability during aging at the temperatures 350 and 450 ºC as compared to binary Al–Sc and Al–Zr alloys.

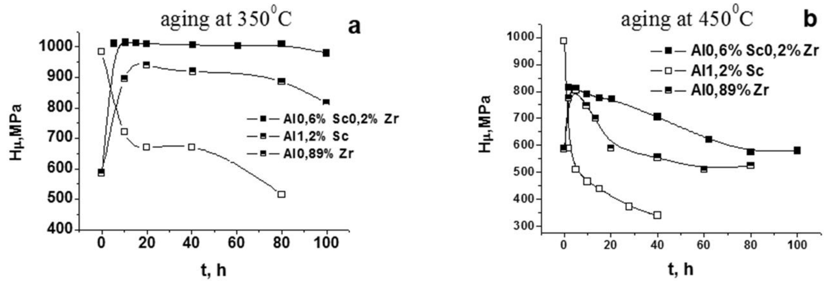

Fig. 7 – Microhardness change after isothermal aging

CONCLUSIONS

1. The Al–Sc and Al–Zr alloys are solidified with the formation of anomalously supersaturated solid solution at quenching temperature of 1400 ºC. The "fan" structures are solidified at quenching temperature of 1000 ºC.

2. The introduction of Zr in Al–Sc alloys allows one to reduce the temperature of melt quenching from 1400 ºC to 1000 ºC for the formation of anomalously supersaturated solid solution.

3. The loss of thermal stability of Al–Sc alloys is due to the loss of coherence of the strengthening Al_3Sc phase particles. In Al–Zr alloys the loss of thermal stability is due to the formation of a stable tetragonal DO_{23}-ordered $A1_3Zr$ phase.

4. The composite Al_3Zr/Al_3Sc particles with Al_3Sc core and Al_3Zr shell form in triple Al–Sc–Zr alloys during high temperature aging. The formation of Al_3Zr shell changes the nature of the interfacial fit of the particle and the matrix, slows down the decomposition during the coalescence stage, which improves the thermal stability of alloys.

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