Decomposition Processes in the Anomalous Supersaturated Solid Solution of Binary and Ternary Aluminium Alloys Alloyed with Sc and Zr

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Decomposition of supersaturated solid solution of aluminium alloys alloyed with Sc and Zr have been studied in the work. The binary hypereutectic Al–Sc alloys, hyperperitectic Al–Zr alloys and ternary Al–Sc–Zr alloys were chosen. Alloys were obtained by the melt-spinning. Melts were quenched from temperatures of $T = 1000^\circ\text{C}$ and $T = 1400^\circ\text{C}$. The crystallization of anomalously supersaturated solid solution ($T_{\text{quen.}} = 1400^\circ\text{C}$) or the crystallization with the formation of “fan” structure ($T_{\text{quen.}} = 1000^\circ\text{C}$) are possible. The decomposition of anomalously supersaturated solid solution is continuous, with the precipitation of nanosized spherical Al_3X ($\text{X} = \text{Sc}, \text{Zr}$) 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 Al_3Zr phase. After co-alloying of Al by Sc and Zr a bimodal grained structure was observed for the hypereutectic ternary alloy ($T_{\text{quen.}} = 1400^\circ\text{C}$). Nanosized grains of 50–60 nm were present on the boundaries of 1–2 μm large-sized grains. Transmission electron microscopy shows the formation of nanocomposite $\text{Al}_3\text{Zr}/\text{Al}_3\text{Sc}$ 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.

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1. 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:

- 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.

2. Experimental

The materials investigated had to be provided with: high volume fraction and high precipitation density of the strengthening 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 L_{12} -ordered phase, isomorphic to the matrix, during the decomposition meets the abovementioned requirements. Binary hypereutectic Al–Sc alloys, hyperperitectic Al–Zr alloys, and ternary Al–Sc–Zr alloys were chosen. The Sc and Zr are transition elements with unlimited solubility in each other. Alloys were cast with the cooling rate of 10^2 – 10^3°C/s on a copper plate, and with the cooling rate of 10^5 – 10^6°C/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°C , which is higher than liquidus temperatures of the alloys studied, and 1400°C , which is higher than the melting temperature of Al_3Sc inter-

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metallic compound (1320°C) but lower than the melting temperatures of Al_3Zr (1560°C). The composition of aluminium alloy ribbons, the quenching temperature of melt T and the copper wheel rotation speed V_L are summarized in Table I.

TABLE I

The composition of aluminium alloys and the processing parameters of ribbons.

No	Al [at.%]	Sc [at.%]	Zr [at.%]	T [$^{\circ}\text{C}$]	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

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

3. Results and discussion

3.1. The effect of quenching temperature of the melt on the structure of aluminum alloys

The TEM study of structural and phase states of aluminium alloys rapidly quenched with the cooling rate of 10^5 – 10^6 $^{\circ}\text{C}/\text{s}$ showed that the quenching temperature change from 1400 to 1000°C 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°C 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 nanosized 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°C 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. Nanosized grains of 50–60 nm were present on the boundaries of 1–2 μm large-sized grains. 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–1.2at.%Zr alloy was 1300 MPa, which

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

is twice as high as the hardness of the Al–0.33at.%Zr alloy. The total supersaturation limit of ternary 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 ternary Al–0.6%Sc–0.24%Zr alloy (Fig. 1d).

The melt quenching from 1000°C 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.

Fig. 2. The types of crystallized structures of alloys produced by melt-spinning from 1000°C : “vortex” structure (a) Al–0.67at.%Sc; (c) Al–0.33at.%Zr; “fan” structure (b) Al–0.67at.%Sc; (d) Al–0.33at.%Zr.

The morphology of “fan” and “vortex” structures proves their crystallization origin. They grew directly from the melt and did not result from the transformation (cellular decomposition) in the solid state.

3.2. The effect of Zr

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 ternary Al–Sc–Zr alloys after quenching from 1400 °C, 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. A decrease in the quenching temperature to 1000 °C ($V_L = 44$ m/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 nanosized grain structure.

3.3. 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 °C) 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 nanosized spherical Al_3X ($X = Sc, Zr$) particles of $L1_2$ -ordered phase of about 2 nm size and the precipitation density $\approx 10^{18}$ s m⁻³.

Coherent Al_3Sc particles were observed in the Al–Sc alloy after aging at 450 °C for 2 h. The average size d , the precipitation density N_v and the volume fraction f of particles are summarised in Table II.

TABLE II

Characteristics of Al_3X particles after aging at 450 °C for 2 hours.

Alloy [at.%]	T [°C]	V_L [m/s]	Phase type	d [nm]	N_v [s m ⁻³]	f [%]
Al–0.67Sc	1400	44	$L1_2$	22	4.5×10^{15}	2.5
Al–1.32Sc	1400	44	$L1_2$	15	1.8×10^{16}	3.2
Al–1.32Sc	1400	30	$L1_2$	19	1.1×10^{16}	4.6
Al–0.33Zr	1400	30	$L1_2/DO_{23}$	9	2.3×10^{16}	1.2

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.

Alloys which crystallized with the formation of “fan” structure (quenching from 1000 °C) 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” occurred 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 $\approx 10^{15}$ s m⁻³ (Al–Sc alloys) and $\approx 10^{16}$ s m⁻³ (Al–Zr alloy). Further evolution of these structures was similar to that of alloys, crystallized with the formation of solid solutions.

3.4. Thermal stability of structures formed by rapid quenching

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 ag-

Fig. 3. Decomposition processes in the Al–1.32at.% Sc ribbons crystallized: (1) with the formation of solid solutions, quenching from 1400 °C at $V_L = 44$ m/s: (a), (b) aging at 450 °C for 2 hours, the particle size $d \approx 15$ nm, $N_v \approx 10^{16}$ sm⁻³; (c), (d) aging at 450 °C for 20 h, the particle size $d \approx 87.4 \pm 2.6$ nm, $N_v \approx 10^{14}$ sm⁻³; (2) with the formation of “fan” structure, quenching from 1000 °C at $V_L = 44$ m/s: (e) after quenching, the thickness of the “fan” branches ≈ 5 nm; (f) aging at 450 °C for 2 hours, the particle size $d \approx 19.2 \pm 2.4$ nm. (a), (c), (e) bright-field image, (b), (d), (f) dark-field image in reflex (100) of the Al_3Sc -phase.

ing and changes in microhardness showed that the increase of hardness was due to the formation of Al_3X ($\text{X} = \text{Sc}, \text{Zr}$) $L1_2$ -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 $T > 300^\circ\text{C}$, and the Al–Zr alloys at $T > 350^\circ\text{C}$. 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. 3b,d). In Al–Zr alloys the loss of strength was due to the formation of a stable tetragonal DO_{23} -ordered Al_3Zr phase.

The Al_3Zr metastable phase particles were replaced by composite $L1_2/\text{DO}_{23}$ particles during aging at 450°C in Al–Zr alloys (Fig. 4). The plate-like stable phase was formed inside the metastable phase particle (the size ≈ 10 nm) along $\langle 100 \rangle$. 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 h of aging (Fig. 4).

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

Fig. 5. The morphology of $\text{Al}_3\text{Zr}/\text{Al}_3\text{Sc}$ phase precipitate: (a) bright-field image, (b) dark-field image in superstructural reflex (100).

The continuous decomposition of the anomalous supersaturated solid solution of Al–0.6%Sc–0.24%Zr ternary alloy obtained by rapid quenching from 1000°C at $V_L = 44$ m/s are most interesting. Two alloying elements of the alloy have a considerable difference in diffusion mobility $D_{\text{Sc}}/D_{\text{Zr}} \approx 10^3$ and the difference in the mis-

fit parameters of the matrix and the Al_3X intermetallic $\delta_{\text{Al}_3\text{Sc}}/\delta_{\text{Al}_3\text{Zr}} \approx 2$. 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 nanocomposite $\text{Al}_3\text{Zr}/\text{Al}_3\text{Sc}$ particles with Al_3Sc core and Al_3Zr shell. The morphology of such particles is shown in Fig. 5.

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.

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

Fig. 7. Microhardness change after isothermal aging.

The microhardness change during isothermal aging at the temperatures 350 and 450°C for alloys rapidly quenched from 1000°C is shown in Fig. 7. The data presented imply that ternary Al–Sc–Zr alloys have significantly higher thermal stability during aging at the temperatures 350 and 450°C as compared to binary Al–Sc and Al–Zr alloys.

4. Conclusions

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

2. The introduction of Zr in Al–Sc alloys allows one to reduce the temperature of melt quenching from 1400 °C to 1000 °C 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 Al_3Zr phase.
4. The nanocomposite $\text{Al}_3\text{Zr}/\text{Al}_3\text{Sc}$ particles with Al_3Sc core and Al_3Zr shell form in ternary 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 coales-

cence stage, which improves the thermal stability of alloys.

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