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Composite Particles Formation and Behaviour in Al–Li Alloys Alloyed by Sc (Zr) under Heat Treatment and Severe Plastic Deformation

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The mechanism and kinetics of Al₃Li/Al₃Sc composite particles formation during aging of triple Al-Li-Sc alloys were studied. The particles of such type consist of two isomorphic phases, ordered by $L1_2$ type. Composite particles in Al-Li-Sc are formed by epitaxial nucleation of $\delta'(Al_3Li)$ phase on pre-existing Al₃Sc precipitates at low temperature aging in the area of existence of Al₃Li phase, and form uniform shell around them. The motive force of such heterostructure formation is the minimization of total surface, elastic and chemical energy of the alloy. Dark-field transmission electron microscopy images of such composite particles taken from superlattice reflex 100 are composed of a dark core surrounded by a bright shell. The mutual diffusion of Li and Sc during the aging of Al-Li-Sc alloys is observed. The dark-field transmission electron microscopy image of the composite particle obtained from superlattice reflection became transparent after continuous natural aging of Al-Li-Sc alloys. The presence of the particle in Al matrix can be only seen due to decoration by secondary precipitations of δ' (Al₃Li) phase. Composition analysis of such transparent particles was carried out using two-beam kinematical theory of electron diffraction. Such composite particles with transparent cores remain in Al matrix even after severe plastic deformation of Al-Li-Sc alloy.

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1. Introduction

Currently, the formation of new types of strengthening particles is of great interest. Such heterophase nanocomposite particles are formed during aging and consist of two parts: the core and the shell. The shells of particles have structures that could not be interpreted as conventional heterogeneous formation of a new phase on the existing surface. Al₃Sc particles are known to be the preferred location for the nucleation of phases that are not isomorphic to the matrix, especially for additives with low solid solubility. Needle-phase precipitation of Fe compound on Al₃Sc particle is shown in Fig. 1a. In this



Fig. 1. Morphology of precipitates on Al3Sc particle: (a) heterogeneous Fe-containing needle-phase precipitate (bright field), (b) Al3Li-phase shell formation and nanocomposite Al3Li/Al3Sc particle generation (dark field in the superlattice reflection of $L1_2$ phase).

case the surface energy changes locally in the place where different phases are in contact. In Al–Li–Sc alloys the metastable δ' -phase (Al₃Li) produces a shell on Al₃Sc particles during aging (see Fig. 1b). This shell changes the value of the interface energy and elastic stress produced by strengthening particles in the matrix. The decomposition and properties of ternary Al–Sc–X alloys (where X — Zr, Hf, Ti and rare earth metals) and Al– Zr–Ti alloys, which are characterized by nanocomposite particles formation, were investigated giving the evidence about the increase of strength, fatigue properties and creep resistance [1–6].

The mechanism and kinetics of Al_3Li/Al_3Sc two-phase composite nanoparticles formation in the process of aging of ternary Al-(2-3)%Li-(0.1-0.6)%Sc alloys were studied [2, 3]. The particles of this type consist of two isomorphic phases with $L1_2$ type order. Constituents of Al_3Sc and Al_3Li phases precipitate at different aging temperatures.

Spherical high-strength coherent particles of Al₃Sc phase appear during crystallization, homogenization and high-temperature technological annealing. Composite particles Al–Li–Sc are formed by epitaxial nucleation of δ' (Al₃Li) phase on pre-existing Al₃Sc precipitates during further low-temperature aging in the range of Al₃Li phase existence, and produce uniform shells around them.

The cause of composite nanoparticle formation are the processes of solid phase heteroepitaxy during which the interface of Al_3Sc particles is enriched with Li, followed by nucleation of particles of the new Al_3Li phase. In the process of their coalescence, a continuous single-crystal epitaxial film is formed (due to full

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structural-geometrical match of phases forming the composite particle). The driving force of such heterostructure formation is the minimization of the total surface, elastic and chemical energy of the alloy. Formation kinetics is given by the degree of solid solution supersaturation and aging temperature.

The subject of this study is to examine and identify structural changes in nanocomposite particles caused by complex multistage aging modes: artificial aging + natural long-term aging (for more than 25 years) + dynamic aging of Al–Li–Sc alloys at temperatures ranging from 20 to 460 °C.

2. Experimental

The investigation was carried out using the electricalresistivity, metallography and electron microscopy methods.

Al-3Li-0.3Sc alloy (alloy 1) and Al-3Li-0.7Sc alloy (alloy 2) were studied. Alloys were homogenized at 580 °C, quenched and aged at 175 °C for 16 h [2].

Besides, the structure and properties of Al–2.3%Li– 3%Cu–0.1%Sc–0.1%Zr (commercial 1460 alloy) were studied after friction-stir welding (FSW) of thin coldrolled sheets 2 mm thick. Before FSW, sheets were aged in the T8 mode and then continuously naturally aged at room temperature. During FSW, severe plastic deformation and material flow occurs at temperatures lower than melting temperature. Welding was performed at the tool rotation speed of 2880 rps. The tool moves along the weld joint at constant speed of 16 m/h.

Metallographic studies were carried out on polished and etched cross-section. Etching was done using the Keller reagent at room temperature. Four different etching zones were observed: A — stirred zone (SZ) B and C — thermo-mechanically affected zone (TMAZ), D heat affected zone (HAZ), E — base metal (BM). The location of HAZ can be recognized from hardness measurements (Fig. 2).

The half-plate where the direction of tool rotation is the same as the direction of half-plate motion is called the *retreating* side (marked as C), with the other side designated as the *advancing* side (marked as B). Extrusion phenomena were observed on the retreating side. This gives the proof that material flows from the advancing to the retreating side during FSW [7].

The phase composition as well as dislocations and grain sizes were observed in the base material and FSW sample using transmission electronic microscopy (TEM). Disc specimens (3 mm in diameter) were prepared by mechanical grinding to 250 μ m thickness and electropolishing using a 30% nitric acid solution in methanol with 60 V × 1 A at 20 °C. Material for these specimens was taken from different weld zones at four different sites along the midthickness of the cross-section of the FSW sample (marked by rectangles in Fig. 2).

Resistance measurements were performed using a fourprobe dc method. The temperature coefficient of electrical resistivity $\alpha_{\rm T} = 1/R_0 \times dR/dT$ was monitored during



Fig. 2. The Vickers hardness plot scaled to the weld macrostructure picture. Four different zones were observed: A — stirred zone (SZ), B and C — thermomechanically affected zone (TMAZ), D — heat affected zone (HAZ), E — base metal (BM).

continuous heating at the heating rate of $3 \,^{\circ}C/min$ in the temperature range from room temperature up to $600 \,^{\circ}C$.

3. Results and discussion

3.1. Structure of nanocomposite particles after long-term natural aging

Curves $\alpha_{\rm T} = f(T)$ show that the supersaturated solid solution after quenching decomposes in the lowtemperature minimum range by the precipitation of a metastable phase (Fig. 3a). In this temperature range 130–200 nm nanocomposite Al₃Li/Al₃Sc particles are formed and they have characteristic TEM dark field contrast with decreasing intensity in the center of the particle (see Fig. 1b, 3c). The precipitated δ' -phase particles have homogeneous dark field contrast and theirs size is significantly smaller (5–15 nm) than the size of composite particles (Fig. 3c).

The low-temperature minimum disappears on the $\alpha_{\rm T} = f(T)$ curves after long-term natural aging. A diffuse maximum replaces the low-temperature minimum (see Fig. 3b). The matrix is fully depleted from Li atoms and Ostwald ripening occurs at higher temperature; it is accompanied with the growth of metastable δ' -phase particles and the decrease of their density in the matrix about 300 °C a stable δ (AlLi) is formed.

The temperature coefficient of electrical resistivity of the commercial 1460 alloy is shown in Fig. 4. Two temperature regions are present in all curves (Fig. 4). There is a positive peak in the low-temperature region indicating δ' -phase dissolution and there is the negative peak in the high-temperature region related to T_1 -phase and



Fig. 3. Changes in the temperature coefficient of electrical resistivity $\alpha_{\rm T} = (1/R_0 \times dR/dT)$ of alloys 1 (**II**) and 2 (**D**) during continuous heating at the rate of 3 °C/min after quenching from 580 °C (a), 175 °C × 16 h + natural aging for about 25 years at room temperature (b), structural state of alloy Al-2%Li-0.3%Sc after artificial aging 175 °C × 16 h (c).



Fig. 4. Changes in the temperature coefficient of electrical resistivity $\alpha_{\rm T}$ of the commercial 1460 alloy during continuous heating at the rate 3 °C/min in 20–600 °C temperature range.

stable δ -phase formation. A small negative peak on the "SZ" curve (welded joint zone) in Fig. 4 located before the δ' -phase dissolution peak shows that the material of the joint core has been partially transformed into solid solution under intensive plastic deformation during FSW. There is no negative peak in other curves in Fig. 4 like as in Fig. 3b. This is due to the fact that half-sheets of 1460 alloy have been naturally aged for a long time before FSW (as alloys in Fig. 3b).

TEM studies have shown that long-term natural aging has completely changed the dark field contrast of composite particles (see Fig. 3c, 5b).

Al₃Sc particles of 130-200 nm size have different type of interface with matrix, i.e. coherent, incoherent and semicoherent (Fig. 5a) and the characteristic dark field contrast with a small intensity in the center of the particle disappears (Fig. 5b) and the composite particle core becomes "transparent".

The composite Al₃Li/Al₃Sc nanoparticles with characteristic dark field (DF) contrast of Al₃Sc core were



Fig. 5. The structure of Al-3Li-0.3Sc alloy after longterm natural ageing of pre-aged specimens (a, b), natural aging + continuous heating to 230 °C (c,d,e), natural aging + continuous heating to 460 °C (f), (a,c,e) bright field, (b,d,f) dark field in the superlattice reflection (100) of δ -phase.

observed after continuous natural aging for 25 years. $L1_2$ -ordered Al₃Sc core gives zero intensity on DF TEM images in 100 superstructural reflection (Fig. 5b). This proves that the nanoparticle consists of Al₃Sc_xLi_{1-x} core and the shell of Al₃Li with L1₂ order in the disordered matrix. Modelling of theoretical electron images (TEI) of such composite nano-particles has been made [8, 9]. The calculation of the intensity of scattered electrons was done within the kinematic approach of the electron scattering theory. Scattering in the direction of superlattice reflections occurs only in the ordered particle and does not occur in the disordered matrix. The amplitude of electron scattering in the kinematic approach is as follows:

$$\Phi(x,y) = \frac{\mathrm{i}\lambda}{V_c \cos \Theta} \int F_g \exp(-2\mathrm{i}\pi sz) \,\mathrm{d}z$$

where $F_{\rm g}$ is the structural factor equal to $F_{\rm core}$ value in the core of the composite particle, $F_{\rm shell}$ — in the shell and 0 — in the matrix. Integration is carried out through the thickness of the composite particle within the column approximation [10].

"Transparency" of the composite particle core observed in the dark field images in superlattice reflection implies zero structural factor. If Li solubility in the core is taken into account [11, 12], the core structure factor with variable composition $Al_3Li_xSc_{1-x}$ is described as

$$F_{hkl} = xf_{\mathrm{Li}} + (1-x)f_{\mathrm{Sc}} - f_{\mathrm{Al}},$$

where F is the resulting structure factor; f_{Li} , f_{Sc} , f_{Al} are electron scattering factors for atoms of Li, Sc, and Al, respectively [8].



Fig. 6. Structure factors and their squares for the superlattice 100, 110 reflections as a function of core composition. Image intensity is proportional to F^2 .

The structure factor F_{100} changes from 1.814 for Al₃Scphase to -2.217 for Al₃Li phase [9] when x changes from 0 to 1 (Fig. 6). It means that the structure factor of the reflection changes its sign in the region of interphase of the composite Al₃Li/Al₃Sc particle.



Fig. 7. The dependence of the dark field image "transparency" of the composite $Al_3Li/Al_3Sc_xLi_1 - x$ particle in superlattice reflection g = 100 on the ratio of core diameter (d) to that of the whole particle (D) d/D and on Li concentration in the composite particle core C_{Li} .



Fig. 8. Dark field contrast from the composite particle in 100 reflection: (a) TEI, (b) 3D intensity distribution; (c) intensity profile.

The dependence of the dark field image "transparency" of the composite Al₃Li/Al₃(Li_x,Sc_{1-x}) particle on d/D (the ratio of the core diameter d to the whole particle diameter D) in the superlattice reflection g = 100 was calculated by Beresina et al. (see Fig. 7 and Fig. 8) [9].

Using this dependence Li content in the core can be determined. For example, to get "transparency" for Al₃Sc particle without shell (d/D = 1) the content of Li must be 11.35 at.%.

After long-term natural aging all composite particles become transparent irrespective of the type of interface with the matrix (see Fig. 5b). The shell is absent $(d/D = 1 \text{ and } C_{\text{Li}} \approx 11.35 \text{ at.}\%$ Li for particles with D > 170 nm. For particles with D < 170 nm, d/D changes in the interval of 0.75–0.9; this corresponds to Li content variation in the particle core in the range of 8.5–10 at.%.

3.2. Thermal stability of the composite particles under dynamic ageing

To understand the thermal stability of composite particles their structures were investigated after dynamic aging during continuous heating up to the selected points in the $\alpha_{\rm T} = f(T)$ curve (see Fig. 3b): 230, 325, 395, and 460 °C (correspond to extrema in $\alpha_{\rm T} = f(T)$).

After heating to 230 °C the composite particles retain their "transparency", they have shells and $C_{\text{Li}} \approx 10$ at.%. The presence of dislocations in the Al₃Li/Al₃Sc interface (semicoherent particle in Fig. 5c) changes the contrast and the discontinuous shell in the dark field images and non-transparent stripes in places where dislocations emerge on the surface of the core are observed (see Fig. 5d). The loss of coherence between α -solid solution and Al₃Li on the interphase is caused by the ejection of the dislocation into the matrix and the formation of complex dislocation structure near the particle (Fig. 5e). Screw dislocations move in the matrix bend around the composite particles but they can cut δ' -phase particles. The evidence of δ' -phase particles cutting intersection is the splitting of the whole dislocation into two partial ones $(a/2)\langle 110 \rangle$ with oscillating distance between them (see Fig. 5e) [13].

When the temperature rises from 325 to 395 °C (above the region of the existing δ' -phase) Al₃Li phase dissolves, the shell disappears and the equilibrium δ -phase forms. After heating of the alloy up to 460 °C (the region of homogeneous Li solid solution in Al) Al₃Sc particles produce deformation contrast and a pore of ≈ 12 nm in size is observed in these interior (see Fig. 5f). The pore formation is due to the vacancy supersaturation of Al₃Sc phase as Li diffuses from the particle into the matrix.

3.3. Structural state of nanocomposite particles in Al-2.3%Li-3%Cu-0.1%Sc-0.1%Zr (commercial 1460 alloy) after FSW

The respective dependence for $Al_3Li_xZr_{1-x}$ looks similar but the amount of lithium dissolved in the particle core is higher. The maximum of dissolved Li corresponds to $Al_3Li_xZr_{1-x}$ particle without shell and is equal to $\approx 14.5\%$.

Low-temperature heat treatment of the alloy results in a very low Zr content in the composite particle cores due to the fact that Zr diffusion coefficient is by an order of magnitude lower than that of Sc and therefore Zr generally segregates at the core/shell interface [14, 15]. Therefore, the curve shown in Fig. 7 can be also used for the estimation of Li content in the composite particle cores.

The maximum of lithium content in $\delta'/Al_3(Sc,Zr)$ composite particles is ≈ 8 -10 at.%. Most probably, Li content in the composite particle core remains constant after friction stir welding in spite of significant temperature increase (up to ≈ 450 °C) in the welded joint zone during welding, because $\delta'/Al_3(Sc,Zr)$ composite particles with "transparent" cores are observed in the stirred zone as well (Fig. 9a).



Fig. 9. Dark field image of composite $Al_3Li_xSc_{1-x}$ particles in superlattice reflection g = 100: (a) in the joint core after friction stir welding; (b) in the joint core after artificial aging in T8 mode (160 °C × 10 h + 120 °C × 20 h).

After treatment in T8 mode $(160 \text{ °C} \times 10 \text{ h} + 120 \text{ °C} \times 20 \text{ h})$ of the welded joint core, composite particles do not lose their "transparency" so Li content in their cores should correspond to values in Fig. 7.

The increase of annealing temperature up to $350 \,^{\circ}\text{C}$ (above the region of δ' -phase existence) leads to the shell disappearance and the equilibrium δ -phase formation. The following Al₃(Sc,Zr) particle evolution differs depending on the welded position inside the zone. Pores of ≈ 10 nm size are observed (see Fig. 10) in centers of particles located in zone B (Fig. 2) after artificial aging of $350 \,^{\circ}\text{C}$ for 24 h.



Fig. 10. Dark field image of $Al_3Li_xSc_{1-x}$ particles in superlattice reflection g = 100 after artificial aging $350 \,^{\circ}C \times 24$ h (*advancing* side B).



Fig. 11. Dark field image of $Al_3Li_xSc_{1-x}$ particles in superlattice reflection g = 100 after artificial aging $350 \,^{\circ}C \times 24$ h (*retreating* side C).

The pore in the $Al_3(Sc,Zr)$ particle is generated due to the Frenkel effect, when the stream of vacancies from the matrix and their accumulation in the center of the particle compensates the diffuse flow of lithium from the particle to matrix [16]. The particles of $Al_3(Sc,Zr)$ phase located in the zone C (Fig. 11) also lose lithium and become "non-transparent" after artificial aging 350 °C for 24 h. But inside they do not contain pores. Moreover, they transform into cubes.

During friction stir welding not only material mass transfer occurs from the *advancing* side to the *retreating* side of the joint. There is also compression present in the thermo-mechanically affected zone of the *retreating* side of the joint, which induces material extrusion. This compression is sufficient to suppress the Frenkel sinks of vacancies, so the pore neither nucleates nor grows (the compression of about 5–10 MPa is sufficient) [17].

The particle shape changes from spherical to cubic because of an excessive compressive stress in this region of the joint [18]. The energy of coherent deformation in the particle decreases by more than 30% after such particle shape change [19].

4. Conclusions

- 1. The shells from Al₃Li-phase form in the region of the existing metastable δ' -phase on all Al₃Sc particles regardless of the type of interface with the matrix.
- 2. After long-term natural aging the dark field contrast in the superlattice reflection of the composite particle changes: beginning with the intensity extinction in the composite particle core (before natural aging) and ending with "transparency" formation after natural aging. The effect of "transparency" is explained by modelling the TEM contrast. This method is used for the determination of Li concentration in the "transparent" particle core. The lithium enrichment of Al₃Sc phase is shown to be 8–11 at.% Li during natural aging.

- 3. Dislocations do not intersect composite particles. Their precipitation with sufficient density can prevent the localization of deformation in Al–Li alloys.
- 4. The Al₃Li shell on the Al₃Sc particle reduces elastic distortions at the interface with the matrix and therefore the critical size of Al₃Sc particles is twice as large as the size of particles without shells.
- 5. Al₃Sc-phase is depleted of Li and is saturated by vacancies at temperatures which are above the solvus of δ' -phase.
- 6. The increase of temperature up to 350 °C (above the region of δ' -phase existence) leads to the shell disappearance and the formation of equilibrium δ phase. The following $Al_3(Sc,Zr)$ particle evolution differs, depending on the position of particles in the welded joint zone. Pores of ≈ 10 nm size are observed in centers of particles located in *advancing* side B. The pore in the particle of $Al_3(Sc,Zr)$ -phase is generated owing to the Frenkel effect, when the stream of vacancies from the matrix and their accumulation in the particle center compensates the diffuse Li flow from the particle to matrix. Particles of $Al_3(Sc,Zr)$ phase located in *retreating* side C also lose lithium and become "non-transparent" after artificial aging. But they do not contain vacancy pores inside. Moreover, they transform into cubes due to excessive compressive stress in this region of the joint.

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