



Determination of Er and Yb solvuses and trialuminide nucleation in Al–Er and Al–Yb alloys



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ABSTRACT

The solubilities of Er and Yb in Al at high temperature were evaluated from the electrical resistivity measurement, from which the ΔS and ΔH were estimated to be 3.0 ± 0.1 k and -0.86 ± 0.01 eV for Al–Er alloys, 3.7 ± 1.0 k and -0.93 ± 0.07 eV for Al–Yb alloys, respectively. The solubility curves of Er and Yb therefore could be obtained. According to the solubility curves of Er and Yb, on the one hand, the largest volume fractions of Al_3Er , Al_3Yb at room temperature were calculated to be 0.18%, 0.10%, respectively, which were obviously less than that of Al_3Sc , i.e., 0.92%. On the other hand, the free energy per unit volume for the nucleation of trialuminides was evaluated with the consideration of Gibbs–Thomson effect. According to the obtained chemical driving force, the corresponding critical radius, critical nucleation energy and the steady state nucleation rate could be further calculated. The results indicated that in the binary alloys with the same concentration at the same temperature, comparing with Al_3Sc , Al_3Yb and Al_3Er showed smaller critical radius and larger steady state nucleation rate, which implied that in Al–Yb and Al–Er alloys, higher number density of fine precipitates would be possibly existed.

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1. Introduction

The comprehensive performance of Al alloy could be improved by small addition of transitional or rare-earth elements [1–21]. Among them, Sc was the most effective element so far [22]. The hardness of the pure Al could be increased from about 240 MPa to almost 668 MPa by a mere addition of 0.1 at.% Sc when isochronal aged to 325 °C [23]. The benefit resulted from the large volume fraction of Al_3Sc and coherent nano-sized Al_3Sc with $L1_2$ crystal structure. But the high cost hinders its industrial applications. Actually, lots of work have been done to find other elements to replace or partially replace Sc [4]. In the periodic table of elements, similar with Sc, Er and Yb can form thermodynamically stable $L1_2$ structure trialuminides as well [22]. Various studies have showed that Sc could be partially replaced by them to form $Al_3(-X,Sc)$ [4,15,24], and in $Al_3(Er,Sc)$, 30% of Sc could be replaced [24]. It should be noted that, except for the former simple replacement, the addition of Er and Yb exhibits some other unique characteristics, especially for Er. Such as in Al–0.06Sc–0.06Zr alloys, upon annealing at 400 °C, the micro-hardness did not increase significantly during the whole aging times, but only by a trace addition of 0.01 at.%Er, the micro-hardness did increase from the 250 MPa

to 450 MPa [25]. In another good example, the isochronal aging curve of Al–Er–Zr [26] was obviously different from that of Al–Sc–Zr [23,27]. In Al–Er–Zr alloys, the first peaks (isochronal aged to 300 °C) decreased and the second peaks (isochronal aged to 450 °C) increased with the increasing of Zr concentration, which called synergetic strengthening, and in Al–0.04Er–0.08Zr, the second peak hardness of ternary alloy was much higher than the sum of corresponding binary alloy [26]. While in Al–Sc–Zr alloy, the first peak (isochronal aged to 325 °C) did not decreased by the addition of Zr, and it was just a superposition of the binary alloys [23,27]. These phenomena stimulate an insight into the corresponding mechanism from the view of nucleation. Therefore, the study of the nucleation of Al_3Er , Al_3Yb and Al_3Sc was not only of application potential, but also of scientific significance.

According to the classical nucleation theory [28], the chemical driving force was very important which determines the occurrence of the nucleation, and was one of the key factors for the calculation of critical radius, critical nucleation energy and the static nucleation rate. In dilute alloys, the chemical driving force was calculated from the actual composition and the solubility of solute [28]. Therefore, an accurate complete solvus was the prerequisite for the study of the nucleation behavior. As for Sc, from the point view of experiment, the solvus was evaluated from the heat of mixing ΔH and excess entropy of mixing ΔS which were based on the fitting of the solubility data at 743–913 K determined by the measurement of resistivity [29]. Theoretically, ΔH and ΔS could be calculated

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by the first-principle theory, and the calculated solvuses were in good agreement with the experimental data [30–33]. In the case of Er and Yb, due to the extremely low solubilities, the solvuses of Er [34] and Yb [35] have not been reported yet. Experimentally, the solubilities of Er and Yb in Al at 913 K and 898 K were measured to be 0.0461 ± 0.0006 at.% and 0.0248 ± 0.0007 at.% respectively by 3DAP [36] whose sensitivity could achieve 10 ppm or better (that is 10^{-3} at.%) [37]. The solubility of Er and Yb at 573 K were estimated to be $(4 \pm 3) \times 10^{-4}$ at.% and $(2.9 \pm 0.5) \times 10^{-4}$ at.% according to the modified LSW model [36]. But the accuracy of the latter cannot be guaranteed. Meanwhile, theoretically, the ΔH and ΔS in Al–Er and Al–Yb alloys [38] were also calculated by the first principles. But the obtained solubilities of Er and Yb in aluminum at 913 K and 898 K were 0.056 at.% and 0.04 at.% respectively, which are larger than the experimental values [36]. In a word, a systematic study on the solubilities of Er and Yb is needed. Then the related nucleation behavior of Al_3Er , Al_3Yb could be studied further.

In present work, the solubility curves of Er and Yb were determined by the measurement of resistivity which had been used to obtain the solubilities of Sc [29] and Zr [39]. And then according to the obtained solubility curves of Er, Yb and that of Sc [29], the temperature and composition dependence of chemical driving force for nucleation of Al_3Er , Al_3Yb and Al_3Sc were calculated, and the corresponding critical radius, critical nucleation energy and steady state nucleation were also calculated and discussed.

2. Experiment

The Al–Er and Al–Yb alloys were prepared in crucible furnace with the high purity aluminum (99.99 wt.%) and the Al–6Er or Al–5Yb (wt.%) master alloys at 983 K. After melting, the melt was stirred and stood for 20 min, and was poured into an iron mold to get a 10 mm \times 100 mm \times 100 mm plate. The concentrations of Er and Yb were verified using X-ray fluorescence spectrometry as listed in Table 1. The impurities of Fe and Si were verified by Inductively Coupled Plasma fluorescence spectrometry to be about 0.0025 at.% and 0.0036 at.%, respectively.

The prepared ingots were cold rolled to 3 mm, and then cut into cubes by electrical discharge machining whose size were 3 mm \times 3 mm \times 250 mm. These specimens were annealed thereafter. For studying the relationship between resistivity and the concentration of Er and Yb, the Al–Er and Al–Yb alloys were homogenized at 913 K and 893 K for 24 h, respectively, and then water quenched. To get the solubilities of Er and Yb at different temperatures, the Al–0.035 \pm 0.006 at.%Er and Al–0.026 \pm 0.004 at.%Yb were annealed at 863–903 K and 863–883 K for 24 h, and terminated by water quench.

Table 1

The composition of Al–Er and Al–Yb binary alloys.

No.	Er (at.%)	Yb (at.%)
1	0.002 \pm 0.001	0.011 \pm 0.002
2	0.004 \pm 0.001	0.016 \pm 0.003
3	0.009 \pm 0.002	0.020 \pm 0.005
4	0.012 \pm 0.003	0.023 \pm 0.002
5	0.021 \pm 0.005	0.026 \pm 0.004
6	0.028 \pm 0.004	0.033 \pm 0.007
7	0.035 \pm 0.006	
8	0.044 \pm 0.005	
9	0.051 \pm 0.004	

Table 2

The excess entropy ΔS and solubility enthalpy ΔH for Al–Er, Al–Yb and Al–Sc alloys.

	ΔS (k)		ΔH (eV/atom)	
	Calculated	EXP.	Calculated	EXP.
Al–Er	3.528 [38]	3.0 \pm 0.1	–0.867 [38]	–0.86 \pm 0.01
Al–Yb	3.986 [38]	3.7 \pm 1.0	–0.913 [38]	–0.93 \pm 0.07
Al–Sc				–0.61 [29]
		1.4 [29]	–0.75 [30]	–0.72 [60]
	3.3 [43]	2.3 [42]	–0.72 [33]	–0.65 [42]
	2.66 [33]	2.3 [41]	–0.77 [32]	–0.67 [41]
		2.1 \pm 0.2		–0.66 \pm 0.01

The resistance measurements were performed using digital low resistance ohmmeter (Megger DLRO 10), whose accuracy was $\pm 0.2\%$. Two parallel samples were prepared for each composition of alloy, which was mechanically polished to a 1 μ m surface finish after annealing. During the measurement of the resistance, the temperature was monitored by a thermometer and kept at 26 ± 1 °C in an air-conditioned laboratory. Each sample was measured for 5 times from which the error was determined. A measurement time of 3 s was chosen in order to avoid the overheating of the samples and equipment caused by the large current (10 A) during test.

3. Results and discussions

3.1. The relationships between resistivity and concentration in Al–Er and Al–Yb alloys

According to the Nordheim law [40], the resistivity depends linearly upon the concentration of the impurity in solid solution state. With the increase of concentration, the second phase would be precipitated which has little effect on the resistivity comparing to the solid solution state [29,39]. Therefore, there would be a knee point on the resistivity versus concentration curve accordingly, which was regarded as the solubility limit at the corresponding temperature.

The Al–Er (0.002 \pm 0.001–0.051 \pm 0.004 at.%) and Al–Yb (0.0011 \pm 0.002–0.033 \pm 0.007 at.%) alloys were homogenized at 913 K and 893 K for 24 h respectively, and then water quenched. The measured resistivities of Al–Er and Al–Yb alloys as a function of concentration were shown in Fig. 1. It could be seen that the resistivity curves of these two kinds of alloys consist of two regions. When the concentration was smaller than 0.035 \pm 0.006 at.% for Er and 0.023 \pm 0.002 at.% for Yb respectively, the resistivities increased linearly, which was in accordance with the Nordheim law [40]. When the concentration increased further, the resistivity curve showed a flat plateau. The linear relationships between resistivity and concentration in Al–Er alloys at 913 K and Al–Yb alloys at 893 K were

$$\rho_{Er} = (27.85 \pm 0.02) + (54 \pm 1)C_{Er} \quad (1)$$

$$\rho_{Yb} = (27.83 \pm 0.04) + (64 \pm 2)C_{Yb} \quad (2)$$

where ρ_{Er} , C_{Er} and ρ_{Yb} , C_{Yb} were the resistivity and the composition of Al–Er alloy and Al–Yb alloy, respectively. From Eqs. (1) and (2), the intercepts are 27.85 ± 0.03 and 27.83 ± 0.03 $\mu\Omega$ mm, which indicated an accuracy measurement of the resistivity compared with that of high purity Al 27.85 ± 0.09 $\mu\Omega$ mm, and the residual resistivities per 1 at.%Er and Yb are 54 ± 1 and 64 ± 2 $\mu\Omega$ mm, respectively. When the concentrations of Er and Yb exceeded 0.035 \pm 0.006 at.% and 0.023 \pm 0.002 at.%, the Er and Yb remained in the matrix would be unchanged, so there were two knee points

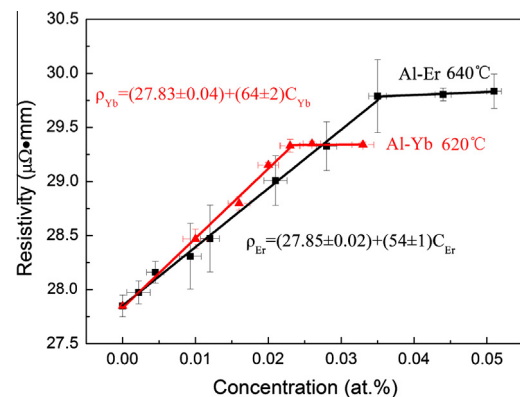


Fig. 1. Resistivities of Al–Er (homogenized at 913 K for 24 h) and Al–Yb (homogenized at 893 K for 24 h) alloys as the function of concentration.

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