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A study of precipitation strengthening and recrystallization behavior in dilute Al–Er–Hf–Zr alloys

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ABSTRACT

A study on the precipitation hardening and recrystallization behavior of dilute Al–Er–Hf and Al–Er–Hf–Zr alloys has been carried out. The results show that both Al–0.045Er–0.18Hf and Al–0.045Er–0.08Zr–0.1Hf alloys can obtain remarkable age strengthening effect and recrystallization resistance. The precipitation hardening rate of Al–0.045Er–0.08Zr–0.1Hf is accelerated compared with that of the Al–0.045Er–0.18Hf alloy due to substituting 0.08 at% Zr for Hf, which can be ascribed to the sequential precipitation of solute elements on the basis of the disparity in their intrinsic diffusivities ($D_{Er} > D_{Zr} > D_{Hf}$). The peak hardness values for the Al–0.045Er–0.08Zr–0.1Hf are 644 MPa and 662 MPa after isochronal aging to 450 °C and isothermal aging at 350 °C for 84 h, respectively, which are higher than those of the Al–0.045Er–0.18Hf alloy. The recrystallization temperature of Al–Er–Hf–Zr alloy is 450 °C, about 25 °C higher than that of the Al–Er–Hf alloy due to the larger *f*/*r* ratio of precipitates in Al–Er–Hf–Zr alloys.

1. Introduction

Dispersoid phases, especially the thermally stable $L1_2$-structured precipitates are effective to stabilize the sub-grain structure, inhibit recrystallization and the corresponding strength loss by exerting a retarding force on migrating dislocation and grain boundaries during thermo-mechanical processing and subsequent annealing [1]. However, only a limited number of alloying elements, such as Er, Sc, Yb, Zr and Hf, have the capability to crystallize to form the coherent strengthening phases (Al_3M) with ordered $L1_2$-structured in Al-based alloys [2]. Furthermore, both fast precipitation and high thermal stability of the precipitates cannot be obtained by a single addition of these elements, because both precipitation and coarsening are closely related to the diffusivity of these elements in aluminum. The nucleation kinetics of $L1_2$-structured Al_3Hf in Al–Hf alloys is very slow at relatively low temperature, but the low diffusivity of Hf ensures that Al_3Hf particles coarsen slowly at elevated temperature, and so does in the binary Al–Zr alloys [3–8]. The addition of other elements, such as Sc [5,9,10], Er [4,9,11,12] and Yb [9,13–15] leads to rapid nucleation of coherent $L1_2$-structured Al_3M (M=Er,Yb and Sc) precipitates, but the relatively higher diffusivity of these element limits the thermal stability of the precipitates at elevated temperature.

Fortunately, it has been reported that the coherent ordered $L1_2$-structured precipitates with both rapid precipitation kinetics and high thermal stability are relatively easy to obtain in aluminum alloys with joint addition of the above mentioned elements. For example, Al–Er–Hf and Al–Er–Zr ternary alloys have a pronounced strengthening effect and recrystallization resistance due to the higher number density of thermal stable precipitation compared with that of the binary Al–Zr, Al–Er and Al–Hf alloys [4,8,11,16]. The synergy effects of joint addition of elements in Al–Sc–Hf [17,18] and Al–Sc–Zr [5,19–21] alloys are similar to that of Al–Er–Zr/Hf alloys. Furthermore, Hallam's investigations have shown that an even higher precipitation strengthening and recrystallization resistance can be obtained in Al–Sc–Zr–Hf quaternary alloy than that in ternary Al–Sc–Hf alloys [18,22]. In our previous investigation, the Al–Er–Hf alloy has shown an outstanding precipitation hardening [8]. It is expected to further enhance the strength of this alloy by addition of quaternary elements. Moreover, substitution of more expensive Hf by other elements, such as Zr, will reduce the alloy cost. Therefore, in this article, isochronal and isothermal annealing treatments for Al–Er–Hf–(Zr) alloys have been carried out in order to describe the precipitation strengthening effect of Al–Er–Hf–Zr alloys. In addition, the subsequent effect of the precipitates on recrystallization behavior of the cold rolled alloy has also been examined.

2. Experimental methods

A ternary and a quaternary alloys with nominal compositions of Al–0.045Er–0.18Hf and Al–0.045Er–0.1Hf–0.08Zr (with the same

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total solute concentration), respectively, were prepared by ingot metallurgy. Their compositions in the as-cast state are given in Table 1 (all compositions are in at% unless otherwise noted), as verified by inductively coupled plasma-atomic emission spectroscopy. The alloy were dilution casted from the commercially pure aluminum (Fe: 0.04 wt%; Si: 0.03 wt%), with Al–6 wt% Er, Al–4 wt% Hf and Al–4 wt% Zr master alloys. Appropriate amounts of the starting materials were melted in a crucible furnace in a resistively heated furnace to 790 °C. After thorough stirring, the melt was poured into an iron mold and quickly cooled to ambient temperature. In order to minimize or eliminate dendrite segregation during solidification, the castings were homogenized in air at 640 °C for 24 h and followed by water quenching. The as-solution alloys were immediately aged isochronally from 150 to 600 °C with increments of 25 °C, lasting for 3 h at each temperature. Some samples were isothermally aged at 350 °C for different times ranging from 0.1 to 500 h. In order to evaluate the effect of precipitates on recrystallization resistance of alloys, the isothermally peak aged samples were cold rolled 60% to a thickness of approximately 6 mm. The cold rolled samples were cut parallel to the RD/ND plane (longitudinal section) of the rolled plate and annealed in the temperature range of 175–600 °C with increment of 25 °C, and at each temperature point the samples were isothermally aged for 1 h. After each aging step, the samples were water quenched to ambient temperature.

Vickers microhardness measurements were performed on polished samples using a load of 200 gf and a dwell time of 10 s. At least 10 independent indentations were made per sample across different grains. The microstructural evolution was investigated by transmission electron microscopy (TEM) using a JEOL 2100 with an operating voltage of 200 kV. TEM foils were cut from the aged specimens, subsequently ground to less than 100 μm and punched into 3 mm diameter disks. Then the thin foils were prepared by twin-jet polishing with an electrolyte solution consisting of 30% nitric acid and 70% methanol at voltage ~15 V DC and temperature below −25 °C. The size of precipitates and particle size distribution (PSD) of every condition was analyzed using Image-Pro Plus software and by selecting more than 500 particles.

3. Results and discussion

Fig. 1 displays the age hardening behavior of Al–0.045Er–0.18Hf, and Al–0.045Er–0.08Zr–0.1Hf during isochronal aging as determined by microhardness. Data for the ternary Al–0.04Er–0.08Zr alloy [4] are plotted for comparison. In Al–0.045Er–0.18Hf alloy, visible age hardening commences at 200 °C, and increases slightly between 200 and 400 °C, then sharply increases at temperature ranging from 400 to 475 °C as reflected by the variation in the microhardness. The microhardness achieves a maximum value of 609 MPa at 475 °C. Above 475 °C, the microhardness continuously decrease as a result of the coarsening or dissolution of the precipitates.

For Al–0.045Er–0.08Zr–0.1Hf alloy, the initial precipitation hardening at temperature below 300 °C is similar to that of the Al–0.045Er–0.18Hf and Al–0.04Er–0.08Zr alloys. However, the precipitation hardening rate of Al–0.045Er–0.08Zr–0.1Hf is much faster than that of Al–0.045–0.18Hf at temperature ranging from 300 °C to 400 °C. The hardness of Al–0.045Er–0.08Zr–0.1Hf approaches 525 MPa at 400 °C, which is significantly larger than that of the Al–0.045–0.18Hf alloy at the same temperature. Then Al–0.045Er–0.08Zr–0.1Hf alloy keep the same precipitation hardening rate as that of the Al–0.045Er–0.18Hf alloy, and obtain a peak hardness value of 644 MPa at 450 °C. It can be found that the value of peak hardness is about 140 MPa and 40 MPa higher than that of the Al–0.04Er–0.08Zr and Al–0.045Er–0.18Hf alloys, respectively. The temperature to obtain the peak hardness is about 25 °C lower and higher than that of the Al–0.045Er–0.18Hf and the Al–0.04Er–0.08Zr alloys, respectively.

Vickers microhardness evolutions of the experimental alloys during isothermal aging at 350 °C are displayed in Fig. 2. Data for Al–0.04Er–0.08Zr [4] alloy are presented for comparison. The peak hardness of the Al–0.04Er–0.08Zr, Al–0.045Er–0.18Hf and Al–0.045Er–0.08Zr–0.1Hf is 560 MPa, 640 MPa and 660 MPa, respectively. The time to obtain the peak hardness of the Al–0.04Er–0.08Zr, Al–0.045Er–0.18Hf and Al–0.045Er–0.08Zr–0.1Hf is 64 h, 84 h and 100 h, respectively. From these results, it can be found that addition of 0.1Hf in Al–0.04Er–0.08Zr alloy leads to an

Table 1
Compositions of the experimental alloys (at%).

Samples	Nominal composition			Verified composition		
	Er	Zr	Hf	Er	Zr	Hf
Al–0.045Er–0.18Hf	0.045	–	0.18	0.045	–	0.185
Al–0.045Er–0.08Zr–0.1Hf	0.045	0.08	0.1	0.04	0.08	0.1

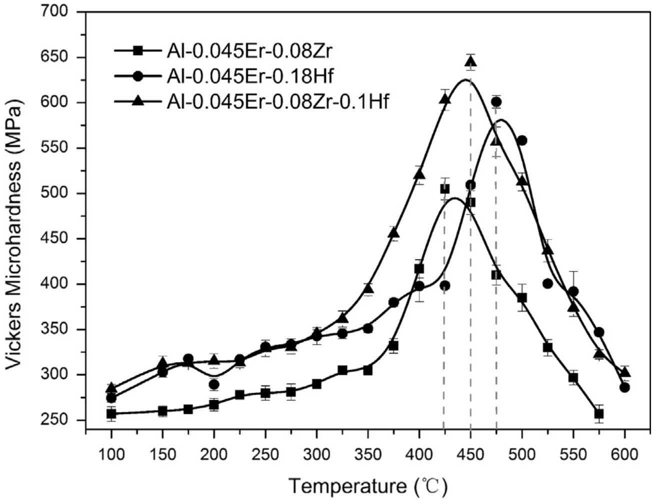

Fig. 1. Vickers microhardness evolution of Al–0.045E–0.08Zr [4], Al–0.045Er–0.18Hf and Al–0.045E–0.1Hf–0.08Zr alloys during isochronal aging.

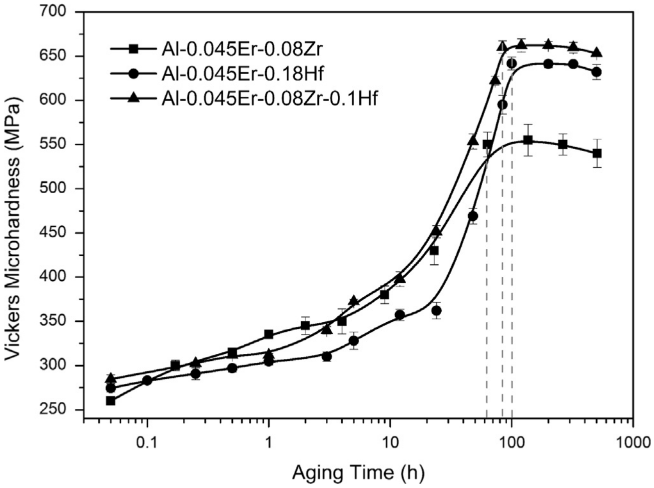

Fig. 2. Vickers microhardness evolution of Al–0.045E–0.08Zr [4], Al–0.045Er–0.18Hf and Al–0.045E–0.1Hf–0.08Zr alloys during isothermal aging at 350 °C.