Journal of Alloys and Compounds 352 (2003) 84–88

Effect of rare earth Ce addition on the microstructure and mechanical properties of an Al–Cu–Mg–Ag alloy

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Received 5 August 2002; received in revised form 9 October 2002; accepted 17 October 2002

Abstract

The precipitation hardening response, microstructure and mechanical properties of three Al–Cu–Mg–Ag based alloys containing 0, 0.20 and 0.45 (wt%) Ce were investigated by transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It is shown that increasing Ce content from 0 to 0.45 wt% increased the tensile strength at all test temperatures up to 350 °C. The high strength of the alloys with Ce is attributed to the high density and high thermal stability of fine Ω precipitates.

Keywords: Aluminum alloys; Cerium; Mechanical properties; Microstructure

1. Introduction

For many applications in the aerospace and automobile industries, aluminum alloys are required to be able to operate at higher and higher temperatures. For example, aluminum aircraft wheels, including those for future high-speed civil transport (HSCT) aircraft, must not catastrophically fail on a rejected take-off during which temperatures may reach 327 °C. As advanced braking systems are developed, such temperatures are expected to increase. Thus, developing high temperature (H/T) aluminum has been an important task in the light-alloys community.

Microalloying has been used to improve the H/T strength of selected age hardenable Al alloys throughout the years [1–3]. Wrought Al–Cu–Mg alloys with additions of Fe and Ni were developed for operating temperatures up to 150 °C (alloy 2618). Since such alloys suffer a comparatively pronounced decrease in strength above 150 °C, they cannot be regarded as H/T Al alloys in the present sense.

Rare earth elements in conventional casting aluminum alloys have shown beneficial effects on melting and solidification. These elements reduce the contents of gases and some impurities and the spacing between secondary dendrite arms. The use of rare earth Ce as a micro-alloying element in Al has been studied for several years. It was reported [4] that the Ce content affected the grain size of a binary Al–Li alloy and the mechanical properties of Al–Li–Mg casting alloys containing impurity Fe. The number of grains per unit area in the binary alloy linearly increases with raising the Ce content up to 1.1%. The mechanical properties of the Al–Li–Mg casting alloys were improved and the negative effect of impurity Fe was controlled by Ce addition. The Ce addition was also reported to affect the ductility and fracture toughness of 8090 alloy sheets rich in impurities of Fe, Si and alkali metals [5–9].

The addition of Ag has proved to have a more marked effect than Fe and Ni on the H/T strength of Al–Cu–Mg alloys with high Cu:Mg ratios (e.g. 10:1) [10,11]. The addition not only enhanced the hardening response but also totally changed the precipitation processes. In particular, it promoted the formation of a fine and uniform dispersion of hexagonal-shaped plate-like precipitates on $\{111\}_\alpha$ planes of the matrix, but at the expense of the precipitation of θ′ (Al_2Cu) usually observed in the Al–Cu–Mg alloys [12,13]. It is the fine and uniform distribution of the new precipitate (designated as Ω) and its good thermal stability that led the alloys to have superior strength at temperatures up to 250 °C [14].

The structure of the Ω phase has been a subject of some studies. At first, it was proposed to be a θ-Al_2Cu phase, with a monoclinic unit cell [15]. Later, it was described as being hexagonal [16], and subsequently as being orthorhombic [17]. More recently, it was suggested that the structure of Ω is tetragonal with $a = b = 0.6066$ nm and

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0925-8388/02/$ – see front matter
doi:10.1016/S0925-8388(02)01162-3

$c = 0.496$ nm based on convergent beam electron diffraction results [18]. It should be mentioned that although several models were proposed for the structure of Ω, the differences among them are not significant [18].

Based on the Al–Cu–Mg–Ag system, several alloy elements were individually or simultaneously added, attempting to further improve the mechanical properties. The transition metals Mn, Zr, and V were intended for grain refinement and for the formation of intermetallic phases which affected dispersion-hardening and above all contributed to an increase in high temperature strength. The addition of Fe, Ni and Cr had similar effects on the claimed alloys. However, these elements have the disadvantage that they form additional intermetallic compounds with copper, so that the content of these latter elements available for the precipitation hardening and the strengthening of the matrix is reduced. For the Al–Cu–Mg–Ag alloys modified by transition metals, the tensile strength is typically ~300 MPa at 250 °C [19].

Compared to that for transition metals, there is little information available for the effect of rare earth Ce addition on precipitation hardening and strengthening in Al–Cu–Mg–Ag alloys. The present research was thus designed to examine such an effect with a view of establishing the potential for enhancing the mechanical properties of these alloys.

2. Experimental

Table 1 shows the chemical compositions of the present alloys with Ce additions of 0.0, 0.20, and 0.45% (wt%). The alloys were melted by induction heating, and then cast into iron moulds to produce billets of 300–700 mm in length and 85 mm in diameter. The billets were homogenized at 500 °C for 10 h, followed by air cooling to room temperature, and then hot extruded to bars at 420 °C. Subsequently, the bars were solution treated at 525 °C for 2 h, water quenched, and finally aged for different periods of time between room temperature and 185 °C.

Tensile tests were performed at 25, 200, 300, and 350 °C at a strain rate of about 10^{-4} s^{-1} on a Shimadzu AG-100KN machine. The specimens used were those peak-aged and had a gauge diameter of 5 mm and a gauge length of 25 mm. In the tests at high temperatures, the specimens were held at the temperatures for about 20 min before loading. This was for achieving thermal equilibration in the furnace. The mechanical results reported in this study are the mean values of at least two specimens.

Table 1
The chemical compositions of the present alloys (wt%)

Alloy	Cu	Mg	Ag	Mn	Zr	Ce	Al
1	5.30	0.79	0.61	0.38	0.20	0.0	Balance
2	5.36	0.84	0.60	0.40	0.17	0.20	Balance
3	5.35	0.80	0.62	0.37	0.19	0.45	Balance

Differential scanning calorimetry (DSC) was performed on disc specimens of 3 mm in diameter and 1–2 mm in thickness. These specimens were the first solution treated at 525 °C for 60 min and quenched in water. They were then analyzed immediately in a DSC-SP instrument from room temperature to 400 °C at a rate of 10 °C/min. Measurements were performed in nitrogen atmosphere using pure Al as a reference.

Transmission electron microscopy (TEM) was applied to characterize the microstructures of the alloys with different Ce additions. TEM samples were electro-polished, in a 70% ethanol and 30% nitric acid solution at −35 °C, by using a twin-jet equipment operated at 30 V.

3. Results

3.1. Precipitation hardening response

Fig. 1a and b shows the variation of hardness with aging time at room temperature and 185 °C for present alloys containing Ce additions up to 0.45%. Different behavior was observed in the effect of Ce addition on the aging response when compared with the Ce-free alloy. For the aging at room temperature, the rate of age hardening and the Vickers hardness were increased with the Ce addition (Fig. 1a). For the aging at 185 °C, the hardening response of the alloy was also enhanced by the addition of Ce. In particular, the maximum hardness increased from ~160 VHN for the Ce-free alloy to 181 VHN for that containing 0.2% Ce (Fig. 1b). However, the maximum hardness was reduced to ~175 VHN, when the Ce content was further increased to 0.45% (Fig. 1b). Meanwhile, the peak-aging time for the Ce-free alloy was ~12 h, but those for Ce containing alloys were ~8 h. Furthermore, alloy 1 showed two aging stages before reaching the maximum hardness, but with Ce addition, there was only one hardening stage.

3.2. Tensile properties

Tensile testing was made at temperatures up to 350 °C. The results are shown in Table 2. At room temperature, the tensile strength was increased from 516 to 556 MPa when the Ce content was increased up to 0.20%. However, it was increased only slightly when the Ce content was increased from 0.20 to 0.45%. The changing tendency of tensile strength with Ce content at high temperatures up to 350 °C is similar to that at room temperature. At 300 °C, the tensile strength of alloys 2 and 3 was over 260 MPa, but that for alloy 1 was only 205 MPa. And at 350 °C, the tensile strength of alloys with Ce was over 150 MPa, that of alloy 1 below 100 MPa.

Meanwhile, with increasing Ce content in the present alloys, the elongation was decreased. The elongation of

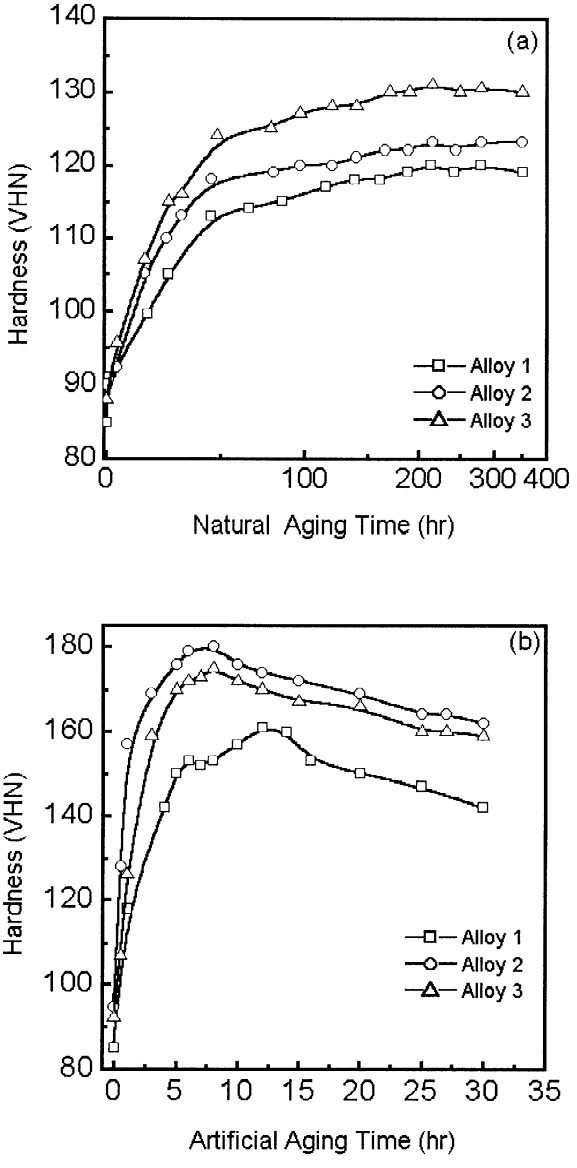

Fig. 1. Hardness curves of present alloys. (a) Natural aging at room temperature, (b) artificial aging at 185 °C.

alloys 2 and 3 was generally lower than that of alloy 1. In the testing range between room temperature and 350 °C, the elongation of alloy 1 was increased from 9 to 18.2%, that for alloy 2 was increased from 7.6 to 17.5%, and that of alloy 3 from 7.3 to 16.3%. Since these data are the mean values of at least two specimens, and the error associated with the measurement is generally low, it could be concluded that increasing Ce content increased the elevated temperature strength but slightly decreased the elongation of Al–Cu–Mg–Ag alloys.

3.3. Microstructure

The microstructures of the present alloys in different conditions were investigated by TEM. Fig. 2 shows the TEM images of alloys 1, 2 and 3 after peak aging at

Table 2
Mechanical properties of the present alloys tested at different temperatures

Alloy	Testing temperature (°C)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
1 (0% Ce)	25	482	516	9.5
	200	390	410	12.0
	300	200	205	15.3
	350	89	99	18.2
2 (0.20% Ce)	25	523	556	7.6
	200	420	425	11.2
	300	260	265	14.9
	350	165	170	17.5
3 (0.45% Ce)	25	528	562	7.3
	200	415	423	10.5
	300	269	271	12.1
	350	154	156	16.3

185 °C. It was confirmed that the lath- or needle-shaped Ω phase which formed on the $\{111\}_\alpha$ planes was the dominant precipitate in the present alloys. Meanwhile, a certain amount of θ′ phase as platelets on the $\{001\}_\alpha$ plane was also observed. Nevertheless, the densities of Ω and θ′ phases in alloys 2 and 3 were higher than in alloy 1. The Ω precipitate in alloy 2 was about 2–6 nm thick with aspect ratios of up to 100, but was about 5–20 nm thick with aspect ratios of up to 200 in alloy 1.

To further understand the difference in intrinsic feature of the Ω phase at high temperatures, alloys 1, 2 and 3 were thermally exposed at 300 °C for 100 h. TEM results (Fig. 3) show that in alloys 2 and 3, the Ω and θ′ precipitates coarsened. However, the Ω precipitates in alloy 1 were all transformed to the θ phase. This observation indicates that the thermal stability of the Ω phase in alloys with Ce is better than that without Ce.

3.4. Differential scanning calorimetry

Fig. 4 represents differential scanning calorimetry (DSC) traces for alloys 1, 2 and 3 after solution treatment. As can be seen, the Ce addition shifted the trace (peak B) position such that the exotherm associated with precipitation of Ω occurred at different temperatures for different alloys. When the Ce addition was from 0 to 0.45%, the peak B was shifted to a lower temperature. This suggests that adding Ce up to 0.45% might have promoted the precipitation reaction.

The DSC traces also indicate a weak endothermic reaction (peak A) at low temperatures. This peak was shifted to a lower temperature with the Ce addition from 0 to 0.45%. The occurrence of the endothermic peak A was attributed to the dissolution of GP zones [12] or the dissolution of an Al–Cu–Mg phase θ′ as a precursor of the Ω phase [19]. Since inconsistencies exist [20], more studies are required to clarify the origin of peak A.

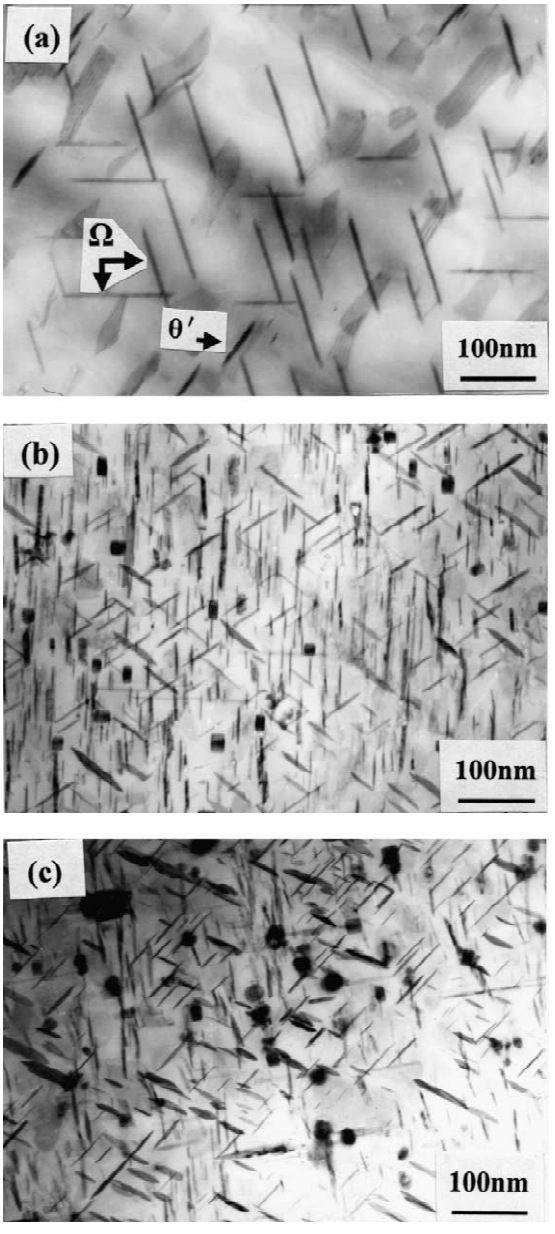

Fig. 2. TEM micrographs of alloys 1 (a), 2 (b) and 3 (c) after peak-aging at 185 °C.

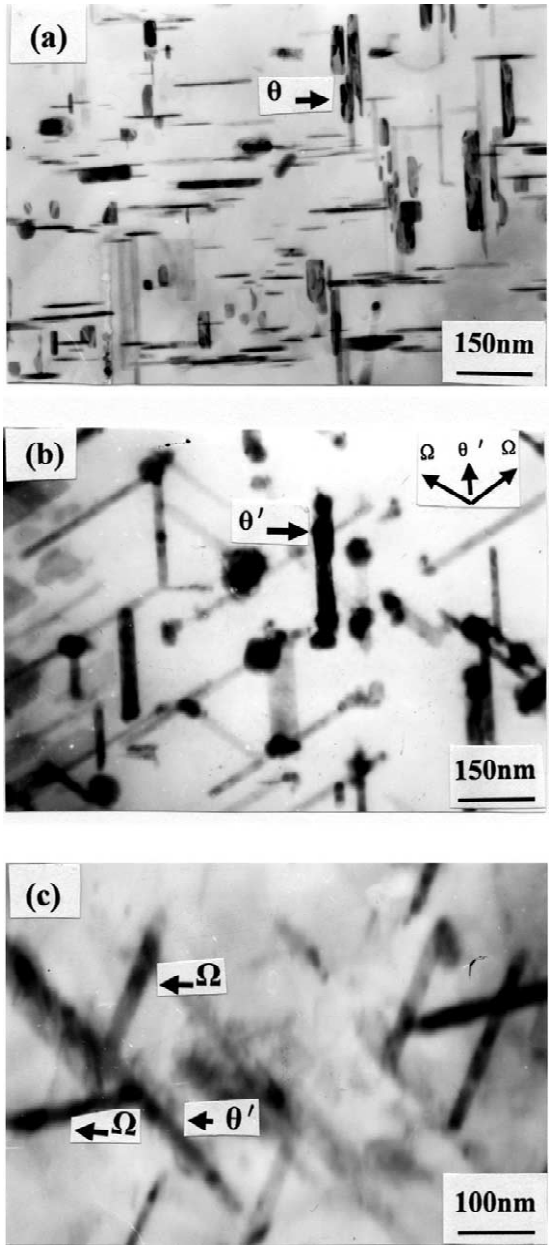

Fig. 3. TEM micrographs of alloys 1 (a), 2 (b) and 3 (c) after aging at 300 °C for 100 h.

4. Discussion

The present study shows that the addition of Ce affected the microstructure development in the Al–Cu–Mg–Ag alloy in various ways. Firstly, with the addition of Ce, the size and density of the predominant hardening phases of Ω and θ′ were changed in the present alloys after peak-aging at 185 °C. Referring to Fig. 2, the density of these phases is higher and the size is smaller in alloys 2 and 3 with Ce than in alloy 1 without Ce. Secondly, with the addition of Ce, the hardening process was somehow altered. This is shown by the existence of a short period during which the hardness remained almost unchanged before reaching the peak for the Ce-free alloy. But such a period was absent for the Ce-containing alloy (Fig. 1b). Thirdly, with the addition of 0.2% Ce, the precipitation temperature of the Ω phase was shifted to a lower temperature, as shown by the DSC results (Fig. 4). This may be due to the fact that Ce addition tends to retard the GP zone stage, and enhance the Ω formation. Fourthly, the Ce addition affected the thermal stability of the Ω phase (Fig. 3). This is evidenced by the observation that after lengthy exposure at 300 °C, there were Ω, θ′ phases in alloys 2 and 3, but there was only the θ phase in alloy 1.

The present study also shows that the addition of Ce affected the mechanical behavior of the Al–Cu–Mg–Ag

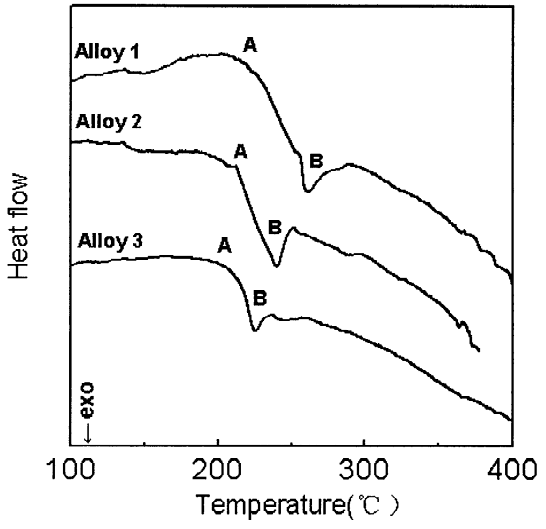

Fig. 4. DSC traces for alloys 1, 2 and 3 (scanning rate 10 ℃ min^{-1}).

alloy. For example, both the hardness and tensile strength were increased with Ce addition (Fig. 1 and Table 2). This may be a result of the enhanced precipitate strengthening of the finer and denser Ω and θ′ phases with Ce addition. Additionally, this may also be due to Ce solid solution strengthening and grain refinement as similar effects were found in Al–Li alloys with 0.25% Ce [4]. Finally, the higher strength at high temperatures may further be related to higher thermal stability of the Ω phase with the addition of Ce (Fig. 3).

The dominant strengthening phases of the present alloys are Ω and the small amount of θ′ phases (Fig. 2), and their composition is Al_2Cu [21]. The Ω phase shows thermal stability at temperatures up to 200 ℃ [13]. However, this phase coarsens, and its thermal stability decreases due to the redistribution of Ag and Mg and the diffusion of Cu over 200° [22]. With the Ce addition in the Al–Cu–Mg–Ag alloy, the diffusion of Cu may be decreased, the coarsening rate of the Ω phase may be reduced, and the elevated temperature strength may thus be increased at high temperature (e.g. 300 ℃).

With the addition of Ce, the tensile strength is apparently increased for the present Al–Cu–Mg–Ag alloy. Although having not been tested, with such addition, the creep resistance of the alloy could also be improved. This is because there is indication for the increase of thermal stability of the Ω phase in the presence of Ce. Thus, the present alloys containing Ce may be used at higher temperatures than conventional Ce-free Al–Cu–Mg–Ag alloys.

5. Conclusions

Addition of Ce up to 0.45% to an Al–Cu–Mg–Ag alloy induced the precipitation of finer and denser Ω and θ′ phases when compared to the Ce-free case. It may be such precipitation that improved the tensile strength both at room temperature and at high temperatures. Besides, the addition of Ce up to 0.45% also improved the thermal stability of the Ω phase. These factors may promote the service temperature of the conventional Al–Cu–Mg–Ag base alloys.

Acknowledgements

This work was supported by the National Key Fundamental Research Project on Al (1999064900-9-02) and the National Outstanding Youth Fund of China (598251110).

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