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Trans. Nonferrous Met. Soc. China 17(2007) 340−345
Transactions of Nonferrous Metals Society of China
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Effect of minor Sc and Zr addition on microstructures and mechanical properties of Al-Zn-Mg-Cu alloys

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Received 10 May 2006; accepted 9 November 2006

Abstract: Three kinds of Al-Zn-Mg-Cu based alloys with 0.22%, 0.36%(Sc+Zr) (mass fraction, %), and without Sc, Zr addition were prepared by ingot metallurgy. By using optical microscopy, transmission electronic microscopy and scanning electron microscopy, the effects of microalloying elements of Sc, Zr on the microstructure of super-high-strength Al-Zn-Mg-Cu alloys related to mechanical properties were investigated. The tensile properties and microstructures of the studied alloys under different heat treatment conditions were studied. The addition of minor Sc, Zr results in the formation of Al_3(Sc,Zr) particles. These particles are highly effective in refining the microstructures, retarding recrystallization, pinning dislocations and subboundaries. The strength of Al-Zn-Mg-Cu alloys was greatly improved by simultaneously adding minor Sc, Zr, meanwhile the ductility of the studied alloys remains at a higher level. The 0.36%(Sc+Zr) alloys gain the optimal properties after 465 ℃/h solution and 120 ℃/24 h aging. The increment of strength is mainly due to strengthening of fine grain and substructure and precipitation of Al_3(Sc, Zr) particles.

Key words: Al-Zn-Mg-Cu alloy; Sc; Zr; microstructure; tensile properties

1 Introduction

Compared with higher cost Al-Li alloys and powder metallurgy(PM) aluminum alloys, Al-Zn-Mg-Cu alloys made by using the ingot approach are mainly applied in aerospace industry[1−3]. Due to their high strength, low density, good hot workability, weldability and more cost-effective enhancement of materials performance, a lot of research on Al-Zn-Mg-Cu based alloys with Zr, Ag, Ce addition by microalloying treatment has been made, but there are few reports on Al-Zn-Mg-Cu alloys with Sc and Zr simultaneous adding[4−7]. When Sc and Zr are both used in Al-Zn-Mg-Cu alloys, Al_3(Sc,Zr) dispersoids occur. These dispersoids are more effective recrystallization inhibitors than Al_3Sc and Al_3Zr, and the distribution of Al_3(Sc,Zr) is more homogeneous than Al_3Zr in Al-Zn-Mg-Cu alloys[8]. In this paper, the effects of minor Sc and Zr addition on the microstructures and tensile properties of Al-Zn-Mg-Cu alloys are studied, the strengthening mechanism of minor Sc and Zr simultaneously added to Al-Zn-Mg-Cu based alloys was discussed and different modes of fracture of the studied alloys after 120 ℃ aging for different time are also investigated.

2 Experimental

Three kinds of Al-Zn-Mg-Cu based alloys, produced by pure Al, pure Mg, pure Zn and Al-Cu, Al-Sc, Al-Zr master alloys, were prepared and made into alloys containing different compositions of Sc and Zr by ingot-metallurgy. The chemical compositions of the three kinds of alloys are listed in Table 1.

After homogenization of these castings, the ingots were hot-rolled and then cold-rolled to 2.5 mm-thick

Table 1 Chemical compositions of studied alloys (mass fraction, %)

Alloy	Zn	Mg	Cu	Sc+Zr	Al
A	6.2	2.3	1.0	−	Bal.
B	6.2	2.3	1.0	0.22	Bal.
C	6.2	2.3	1.0	0.36	Bal.

Foundation item: Project(2002AA305104) supported by the National High-Tech Research and Development Program of China
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plates. Tensile samples were taken along the rolling direction of the plates. After 465 ℃/h solution treatment, and then water quenching and aging for different times at 120 ℃, tensile mechanical tests were taken at a tensile ratio of 1.2 mm/min. Metallography specimens were examined on POLYVER-MET after electrolytic polishing and anodizing with water solution of HF and H_3BO_3, thin foils for TEM observation were prepared by twin-jet polishing with an electrolyte solution consisting of 30% HNO_3 and 70% methanol (volume fraction, %) below −20 ℃. The foils were examined on Hitachi-800 electron microscope. Fractured samples for SEM were observed on KYKY2800 electron microscope.

3 Experimental results

3.1 Microstructure

The microstructures of the studied alloys are shown in Fig.1. Coarsening as-cast grains, dendritic structures (as shown in Fig.1(a)) and serious segregation can be obviously observed in alloy A. Simultaneous adding of minor Sc and Zr can greatly refine the as-cast grain and abate the dendritic structures. The most effective refining appears in alloy C, the average size is 35 μm, and the dendritic structures vanish completely (as shown in Fig.1(e)). After solution treatment, the alloy without Sc and Zr addition exhibits slight recrystallization microstructure, but the microstructure of the alloy with Sc and Zr addition remains fibrous (as shown in Figs.1(d) and (f)).

TEM microstructures of all the studied alloys are shown in Fig.2. The tenuous dispersoids of second phase have precipitated from matrix of alloy C after 120 ℃, 24 h aging treatment (as shown in Figs.2(a) and (c)). The Al_3Sc particles appear in the studied alloys, which are coherent to the matrix (as shown in Fig.2(a)), strongly

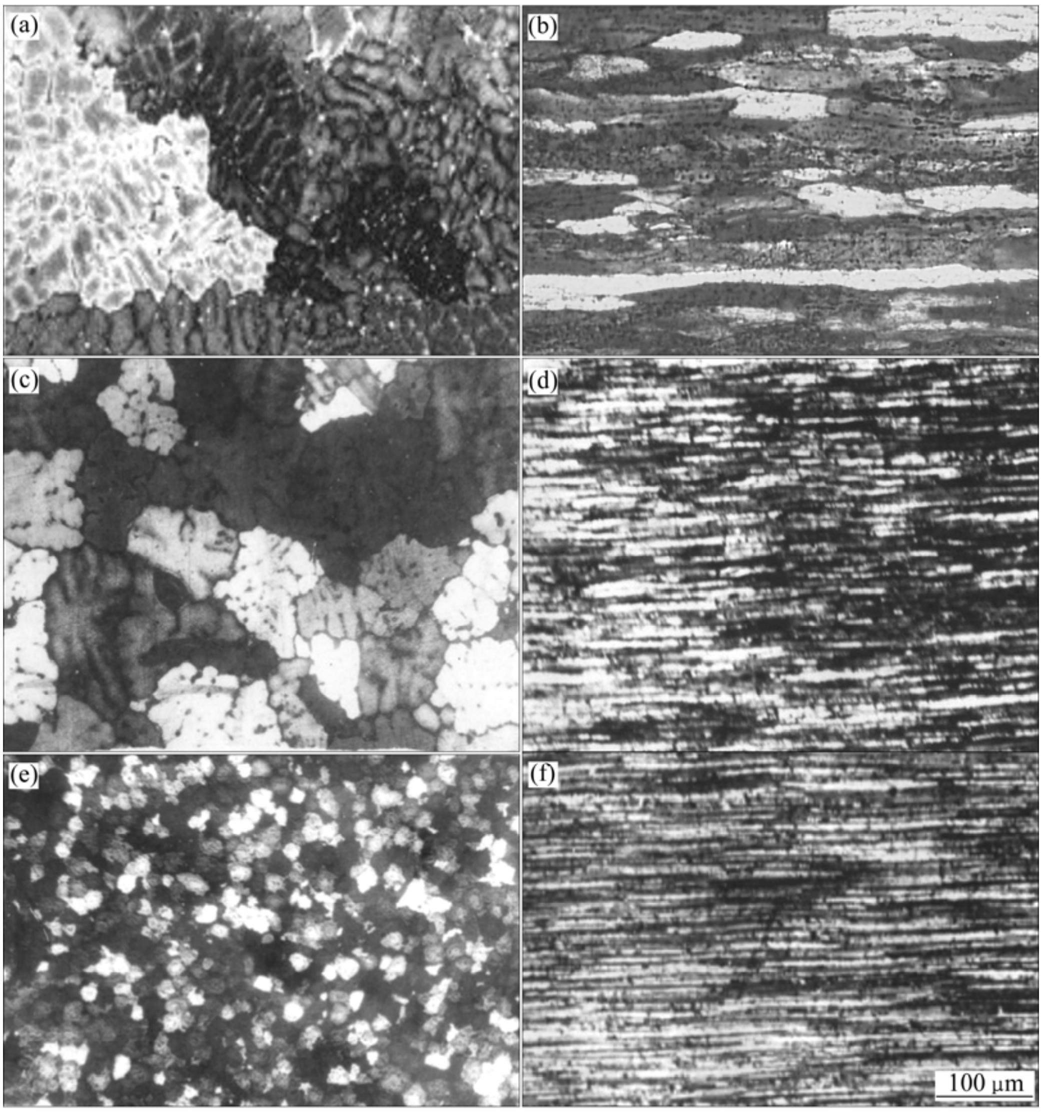

Fig.1 Optical microstructures of studied alloys: (a) Alloy A, as-cast; (b) Alloy A, as-solution; (c) Alloy B, as-cast; (d) Alloy B, as-solution; (e) Alloy C, as-cast; (f) Alloy C, as-solution

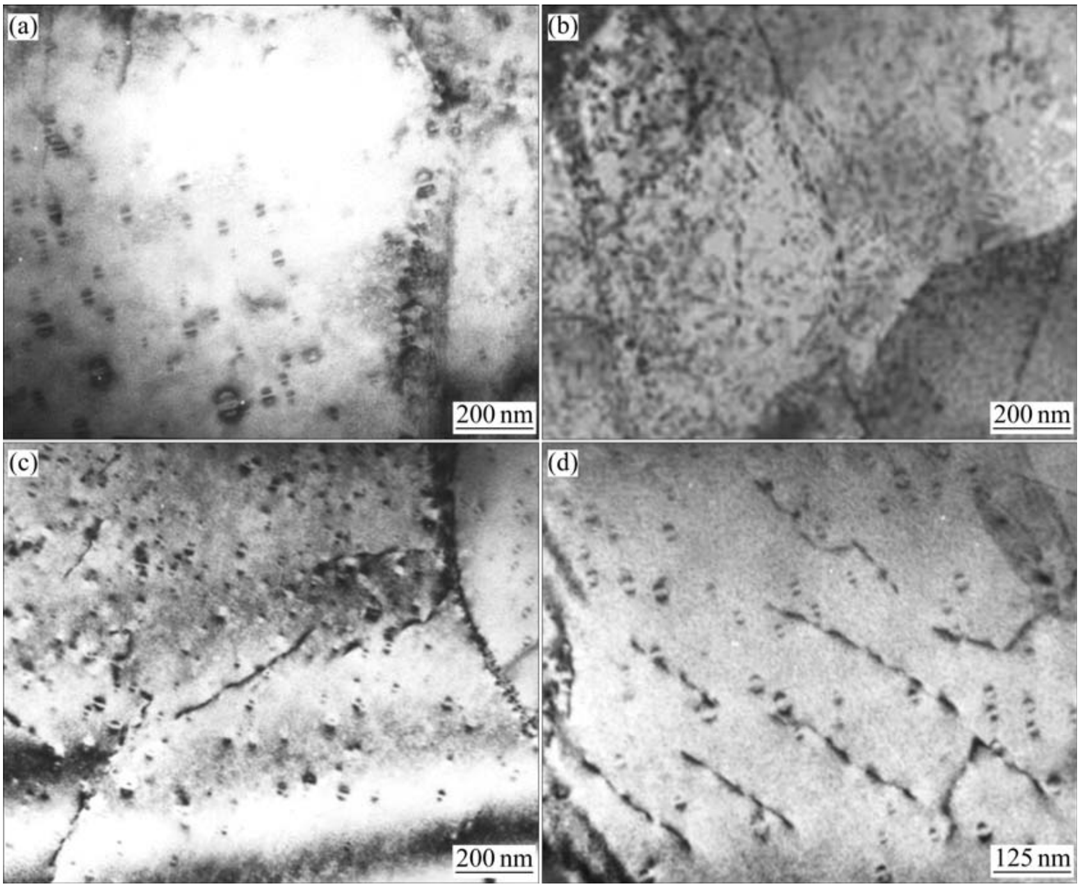

Fig.2 TEM images of alloy C at 120 ℃ ageing for 24 h: (a), (b) Dispersed particles; (c), (d) Pinned dislocations

pin dislocations and grain boundaries (as shown in Figs.2(c) and (d))[9]. Thus these particles block the movement of dislocations and boundaries. A majority of needle precipitations, that is η' ($MgZn_2$) phase, are also observed (as shown in Fig.2(b)).

3.2 Mechanical properties

After 465 ℃/h solution treatment, water quenching and 120 ℃ aging for different times, the tensile mechanical properties of the studied alloys were tested and the results are shown in Fig.3.

Fig.3 indicates that the aging strengthening properties of these studied alloys were obviously improved with prolonging aging time. Alloy A reaches the ultimate tensile strength(UTS) after 120 ℃/32 h aging treatment, alloy B and alloy C reach UTS after aging 120 ℃/18 h and 120 ℃/24 h, respectively. The tensile strength increases by 64 MPa and 92 MPa compared with alloy A, which indicates that the minor Sc and Zr combined addition can make the peak aging arriving earlier, and improve the strength obviously. The strength of the studied alloys increases with the increase of Sc addition. The plasticity of the studied alloys declines with prolonging aging time, but remains at a higher level.

3.3 Fractography analysis

The samples were fractured by ductility at room temperature, and photomicrographs of fracture surfaces of the studied alloy C are shown in Fig.4. Although the elongation of alloy C is lower than other two kinds of studied alloys, very developed dimples as an evidence of ductile fracture are observed(as shown in Figs.4(a) and (b)), and the ductile dimples dominate in peak aging. The fracture surface also appears in a transgranular fracture by cleavage (as shown in Fig.4(c)).

4 Discussion

Minor Sc and Zr added to the Al-Zn-Mg-Cu based alloys is divided into two parts after non-equilibrium freezing process. The one is to solve into α(Al), and the other exists as primary $Al_3(Sc,Zr)$ particles[9−14]. Minor Sc and Zr is mainly to solve into α(Al) when concentration of Sc is 0.1%. When the concentration of Sc reaches 0.25%, Sc and Zr mainly precipitate with primary $Al_3(Sc,Zr)$ particles, which own fcc structure, high melting point, good heat endurance and homogeneous distribution. Therefore adding 0.25% Sc can obviously refine the grains, due to its meeting the need for heteropical nucleation[9]. The most effective

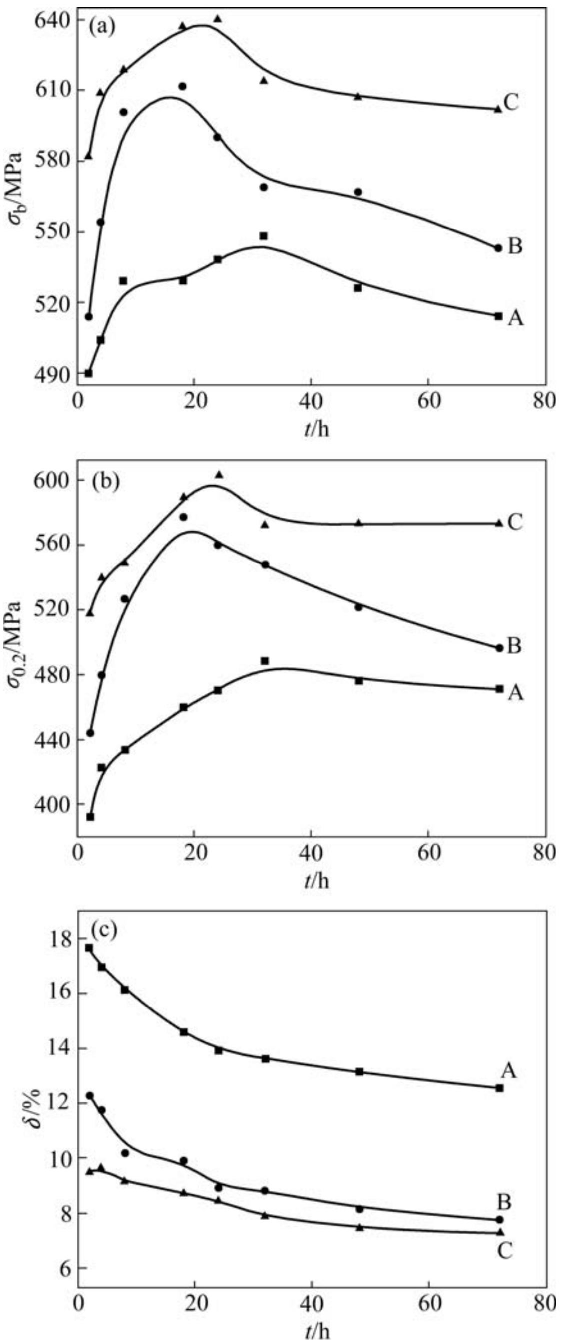

Fig.3 Mechanical properties of studied alloys aged at 120 ℃ for various times: (a) σ_b—t; (b) $\sigma_{0.2}$—t; (c) δ—t

grain refinement occurs in alloy C, because more primary Al_3(Sc,Zr) particles are formed during the freezing process.

Fig.1 indicates the alloy without Sc and Zr is slightly recrystallized after solution treatment, but the microstructure remains fibrous[19]. It represents that a majority of secondary Al_3(Sc,Zr) particles precipitate from saturated solid solution (as shown in Figs.2(a) and (b)) [10]. Secondary Al_3(Sc,Zr) particles have small size and dispersedly distribute, also adhere to matrix. These

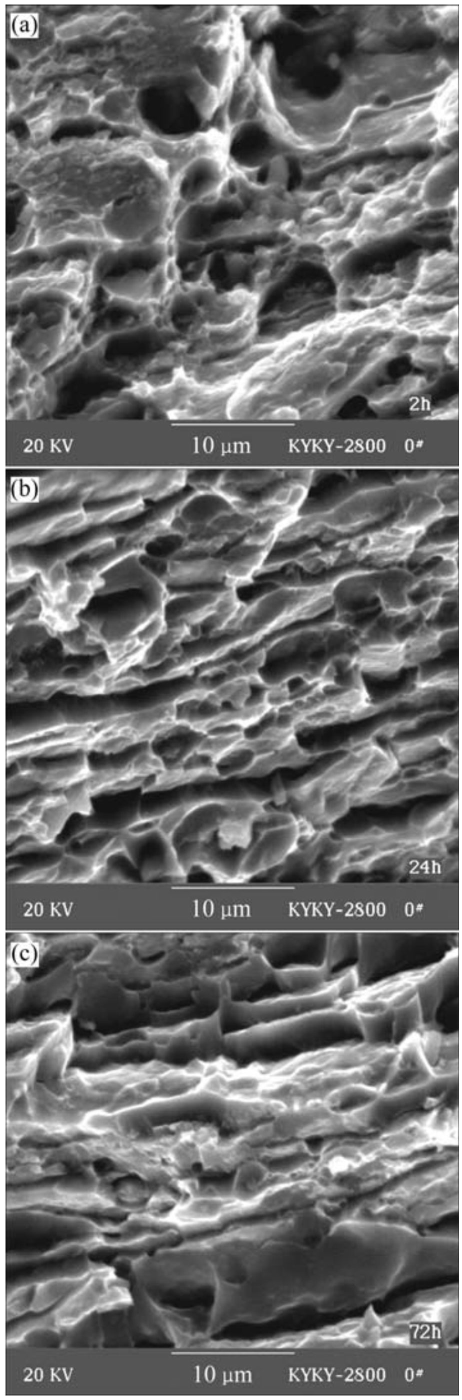

Fig.4 SEM images of fracture surfaces of alloy C aged for various times: (a) Aging 120 ℃, 2 h; (b) Aging 120 ℃, 24 h; (c) Aging 120 ℃, 72 h

particles can keep subboundaries from emerging and growing up[11].

In Al-Zn-Mg-Cu alloy, the addition of minor Sc, Zr results in the formation of secondary Al_3(Sc,Zr) particles after homogenization and subsequent heat treatment. Secondary Al_3(Sc,Zr) particles strongly pin subboundaries and retard emergence and growth of subgrains, namely substructure strengthening. These particles also obviously pin dislocations and keep them from moving. According to Orowan mechanism, dislocations consume energy to cross secondary $Al_3(Sc,Zr)$ particles, more energy is for particles which are smaller and much dispersed. So alloy containing Sc owns higher tensile properties. In addition, primary $Al_3(Sc,Zr)$ particles occur in casting ingots, so the strength of the studied alloy is improved.

A lot of research on Al-Mg and Al-Zn-Mg modified with Sc, Zr has been reported[15−16]. In Al-Zn-Mg-Cu-Sc-Zr alloys, element Cu played a role as primary alloying element, which greatly improved the tensile strength and led to a dispersive precipitates in the studied alloys[17]. Compared with Al-Zn-Mg-Sc-Zr alloys, the corrosion behavior of the studied alloys was depressed due to a tendency of intergranular corrosion and pitting corrosion. The potential difference decreases among grain boundaries, and intracrystalline leads to a lower stress corrosion cracking(SCC) sensitivity because element Cu can dissolve in η' and η phase. GAO et al[18] pointed out that the strongest covalent bond n_A is the Al—Zr bond in Al_3(Sc, Zr) dispersoids, n_A=0.322 8, which is stronger than that in Al_3Sc and Al_3Zr. So the thermal-stability of Al_3 (Sc, Zr) is better than that of Al_3Sc and Al_3Zr at high temperature, and furthermore, Al_3(Sc, Zr) particles hinder the migrating of subgrain boundary and restraining recrystallization of grain are the most notable. So the tensile strength and thermal-stability of the studied alloys with Sc and Zr are improved.

The mainly strengthened phase in Al-Zn-Mg-Cu alloy is $\eta'(MgZn_2)$, and the general precipitation sequence is as follows: α sosoloid→G.P. zones→$\eta'(MgZn_2)$→η phase. Two effects of Sc and Zr can be observed in Al-Zn-Mg-Cu alloys. One is minor Sc addition can improve the concentration of Zn and Mg into α sosoloid, therefore the driving force of phase transition is enhanced from G.P. zones to $\eta'(MgZn_2)$ phase[4]; the other is $Al_3(Sc,Zr)$ particles can come into being nucleation core during aging when these particles do not melt back after solution treatment and distribute dispersively in the matrix alloy. Thus minor Sc and Zr addition can make the peak aging arriving earlier for Al-Zn-Mg-Cu alloys.

The ductile fracture is decided by the size of dimples, meaning more homogenous and deeper dimples producing a higher ductility for the alloys. The biggest dimples (as shown in Fig.4(a)) occur after 120 ℃, 2 h, which leads to the highest ductility but a very low strength. The big homogeneous dimples appear in T_6 condition, thus the best property is obtained for the studied alloy. After 120 ℃, 72 h over-aging, the fracture is prevailed in transgranular fracture by cleavage[19−20]. A sufficient fracture toughness produced in alloy C is due to no tendency for the intergranular fracture.

5 Conclusions

1) Simultaneous addition of Sc and Zr can greatly improve the tensile property and make the peak aging arrive earlier for Al-Zn-Mg-Cu alloys. The tensile property is increased by adding Sc.

2) Simultaneous addition of Sc and Zr can refine as-cast grain structures and strongly depress recrystallization. The effect of refinement on as-cast grain is highly improves with the increase of Sc addition.

3) Sc and Zr elements in Al-Zn-Mg-Cu alloys mainly exist as $Al_3(Sc,Zr)$ particles. Primary $Al_3(Sc,Zr)$ particles can refine the casting structures, which leads to fine grain. Secondary $Al_3(Sc,Zr)$ particles can produce substructure strengthening and precipitation strengthening.

4) Alloys containing 0.36% (Sc+Zr) show mixed fracture modes after 120 ℃ aging for different times. The ductile dimples dominate in samples under aging and peak aging condition. After over-aging, a very low ductility appears due to transgranular fracture by cleavage and prevails in the studied alloy.

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(Edited by YANG Hua)