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Effect of Minor Cr Additions on Dispersed Phase and Properties of Al-Zn-Mg-Cu-Zr Alloys

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Abstract

The influences of Cr on dispersed phase and properties of Al-Zn-Mg-Cu-Zr alloys were investigated by mechanical testing, slow strain rate stress corrosion, intergranular corrosion, combined with optical microscope, scanning electronic microscope, transmission electronic microscopy (OM, SEM, TEM). Research shows that: with the increase of element Cr, the recrystallization and grain growth had been inhibited, the strength, toughness and corrosion resistance of the alloy increased first and then decreased; when added 0.1 wt% Cr element, the properties of the alloy are the best. The main reasons of that were as below: when added 0.1 wt% Cr element, $(Al,Cr)_3(Zr,Yb)$ appeared, that cohered with the matrix. When added 0.18 wt% Cr element, $(Al,Cr)_3(Zr,Yb)$ and $Al_{18}Mg_3Cr_2$ had been found, making adverse effects on alloys. This work studied the effect of Cr content on recrystallization and grain growth in order to get a new super high strength aluminum alloy.

Keywords

Al-Zn-Mg-Cu-Zr Alloys, Chromium, Dispersed Phase, Property

1. Introduction

Al-Zn-Mg-Cu super high strength aluminum alloys have high specific strength, specific stiffness and good processability, which are widely used in aerospace and civil industry [1] [2] [3]. It is an important way to improve the strength of the alloy to control the size and quantity of the precipitated strengthening phase [4] [5]. With the development of modern Aeronautics and Astronautics, the requirements of new generation aluminum alloy for reducing weight and increasing life are further improved. It is required to maintain the alloy strength and improve its corrosion resistance and toughness. Therefore, its corrosion resistance becomes an important research direction at present [6] [7]. At present, many scholars use the method of adding trace elements to form multicomponent coherent dispersion phase in aluminum alloy to inhibit recrystallization and improve the toughness and corrosion resistance of ultra-high strength aluminum alloy. Adding Cr to Al-Zn-Mg-Cu-Zr alloys can produce $Al_{18}Mg_3Cr_2$ dispersion phase, which has no obvious coherent relationship with the matrix. Although it can inhibit recrystallization, the effect is limited and the quenching sensitivity of the alloy is improved, so it should be restrained as much as possible [8]; The addition of Zr to Al-Zn-Mg-Cu-Zr alloys alone will form Al_3Zr dispersion phase which is coherent with the matrix, and the effect of inhibiting recrystallization is better than that of adding Cr alone [9] [10]. However, the L_{12} type Al_3Zr dispersion phase is unstable, and it is easy to transform into DO_{23} type Al_3Zr dispersion phase under high temperature, which is not coherent with the matrix, thus reducing its effect of inhibiting recrystallization [11]. Adding Sc or adding Sc and Zr in combination can form L_{12} dispersion phase Al_3Sc and Al_3(Sc, Zr) which are coherent with the matrix, which can significantly inhibit recrystallization, but Sc is expensive, so large-scale application is almost impossible [12] [13] [14] [15]. The preliminary work of the research group shows that the addition of Zr, Cr and Yb can inhibit recrystallization and improve the strength, toughness and corrosion resistance of the alloy. However, the effect of Cr content on the microstructure and properties of Al-Zn-Mg-Cu-Zr-Yb alloys is rarely studied. Therefore, the effect of Cr on the structure and properties of Al-Zn-Mg-Cu-Zr-Yb was further studied by adjusting Cr content, which laid a foundation for the development of new super aluminum alloy.

2. Experimental

In the experiment, high-purity aluminum, industrial pure magnesium and industrial pure zinc (the purity of Al, Zn and Mg is 99.9%) are used as raw materials. Cu, Zr, Cr and Yb are all added in the form of intermediate alloy. See **Table 1** for the nominal composition of experimental aluminum alloys while **Table 2** is the actual composition of experimental aluminum alloys. Alloy ingots are melted at 700˚C - 740˚C. Adding 0.2 - 0.4 wt% C_2Cl_6 into the melting metal alloy to achieve the purpose of degassing and slag removal. Homogenization was carried out in a 45 mm diameter cylindrical mold preheated to 270˚C: ingot was homogenized and annealed at 460˚C for 24 hours. Before hot extrusion, the preheating temperature is 410˚C - 430˚C, and the extrusion deformation is carried out on a

Table 1. Nominal composition of experimental aluminum alloys (mass fraction, %).

Alloys	Zn	Mg	Cu	Zr	Yb	Cr	Al
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb	8.54	2.41	1.30	0.16	0.30	0	Bal
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr	8.54	2.41	1.30	0.16	0.30	0.10	Bal
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr	8.54	2.41	1.30	0.16	0.30	0.18	Bal

Table 2. Actual composition of experimental aluminum alloys by ICP conversion (mass fraction, %).

Alloys	Zn	Mg	Cu	Zr	Yb	Cr	Fe	Si	Al
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr	8.96	2.16	1.34	0.183	0.24	0.12	0.03	0.12	Bal

500 t press, and the extrusion ratio is 9. The extruded sample was kept in a 480˚C resistance furnace for 1 hour, and the aging treatment was carried out at 120˚C after water quenching for 24 hours.

After solution aging, the alloy sample was polished and etched with Graff Sargent reagent (3 g CrO_3 + 0.5 ml HF + 84 ml H_2O_2 + 15.5 ml HNO_3). The recrystallization was observed at low magnification by optical microscope. The microstructures (second phase morphology, size, distribution, etc.) of the alloys were observed by TECNAI G2 20 and JEOL-2100F high resolution transmission electron microscopy. TEM samples were prepared by double jet electrolysis. After the sample thickness is reduced to 100 - 150 μm by grinding the sample, the sample is cut into a Φ 3 mm disc, and the double jet electrolytic thinning is carried out on the Struers TenuPol-2 thinning instrument. The mixed solution of 30% nitric acid and 70% methanol solution (volume fraction) is used as electrolyte, the voltage is 20 V, the current is 80 - 100 mA, and the temperature is controlled at −30˚C.

Intergranular corrosion test was carried out according to GB7998-87 standard. 57 g/L NaCl and 10 ml H_2O_2 (30%, chemically pure) were used. The intergranular corrosion solution was prepared at the ratio of 50 cm^2/L (the ratio of corrosion surface area to corrosion medium volume). The test temperature was 35˚C ± 1˚C, and then placed in the air for 6 hours. Wash the corroded sample with distilled water and dry it. Grind the sample on the grinding machine for about 5 mm (select the cross section perpendicular to the extrusion deformation direction) to make the metallographic sample. The intergranular corrosion of polished samples was observed under metallographic microscope.

Stress corrosion test shall be conducted according to GB/T 15970.7-2000. The samples were taken in the direction of L-T on the Xi'an Rio Tinto slow strain rate corrosion tensile machine. Slow tensile test (SSRT) test working gauge is 25 mm and plate sample is 2 mm thick. After the sample is installed, a certain load is applied to reduce the gap as much as possible. The strain rate is 6.67×10^{-6} s^{-1}, and the corrosion solution is 57 g/L NaCl + 10 ml/L H_2O_2.

3. Results and Discussions

3.1. Metallographic Analysis

Figure 1 shows the microstructure of Al-Zn-Mg-Cu-Zr-Yb alloys with adding different Cr content. It can be seen from Figure 1(a) that when Cr is not added, the recrystallization area of the alloy is large and the recrystallization degree of the alloy is serious (the white area is the recrystallization area); when Cr content reaches 0.1 wt%, as shown in Figure 1(b), there are a large number of submicron

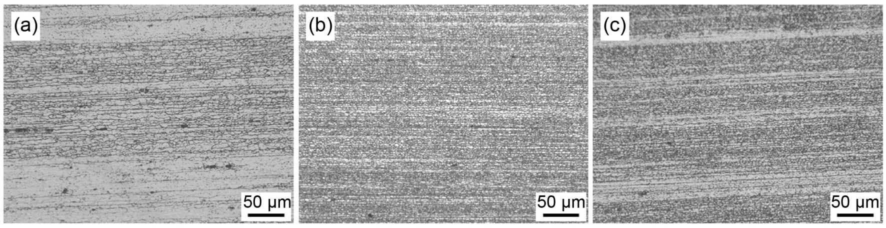

Figure 1. Optical microstructures of Al-Zn-Mg-Cu-Zr-Yb alloys with different Cr addition. (a) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb;
(b) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr;
(c) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr.

fine sub grains in the alloy, and the black sub grain boundary in the figure is obvious, and these sub grains are still in the form of variable fibrous structure distribution; when Cr content increases to 0.18. As shown in **Figure 1(c)**, there is no obvious difference in the fibrous sub crystal structure of the alloy compared with the previous Cr = 1.0 wt%. The results show that the addition of trace Cr improves the recrystallization resistance of the alloy with intact deformation recovery substructure. When the Cr content reaches a certain value, the Cr content (0.18 wt%) will continue to increase, and the recrystallization resistance of the alloy will not be significantly improved.

3.2. TEM Microstructure Analysis of Alloy

Figure 2 shows the morphology, size and distribution of dispersion phase in Al-Zn-Mg-Cu-Zr-Yb alloy with adding different Cr amount; **Figure 3** shows the selected area diffraction pattern of Al-Zn-Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr. It can be seen from the figure that in the case of no Cr addition, a fine dispersed Al_3(Zr, Yb) phase is formed in the alloy. Compared with the case of no Cr addition and 0.1 wt% Cr addition, the number of the second phase with fine dispersion distribution in the alloy is significantly increased. The second phase is (Al, $Cr)_3$(Zr, Yb) particle by energy spectrum analysis [16]-[23]. When the Cr content increases to 0.18 wt%, there are two kinds of dispersed phases, one is spherical (Al, $Cr)_3$(Zr, Yb) phase, the other is coarse rod-shaped $Al_{18}Mg_3Cr_2$ phase.

3.3. Analysis of Mechanical Properties of Alloy

Table 3 shows the mechanical properties and fracture toughness of Al-Zn-Mg-Cu-Zr-Yb alloy with different Cr content after peak aging. When the Cr content increases from 0 wt% to 0.1 wt%, the strength and fracture toughness of the alloy increase, and when the Cr content increases further, the strength and toughness decrease. When Cr content is 0.1 wt%, the strength of the alloy reaches the peak value, and the corresponding strength and toughness are 731.5 Mpa, 710.9 Mpa and 37.2 Mpa·$m^{1/2}$ respectively.

Figure 4 shows the tensile fracture morphology of alloys with different Cr content. When Cr is not added, the tensile fracture of the alloy is mainly coarse dimple transgranular fracture; when 0.1 wt% Cr is added, the tensile fracture of

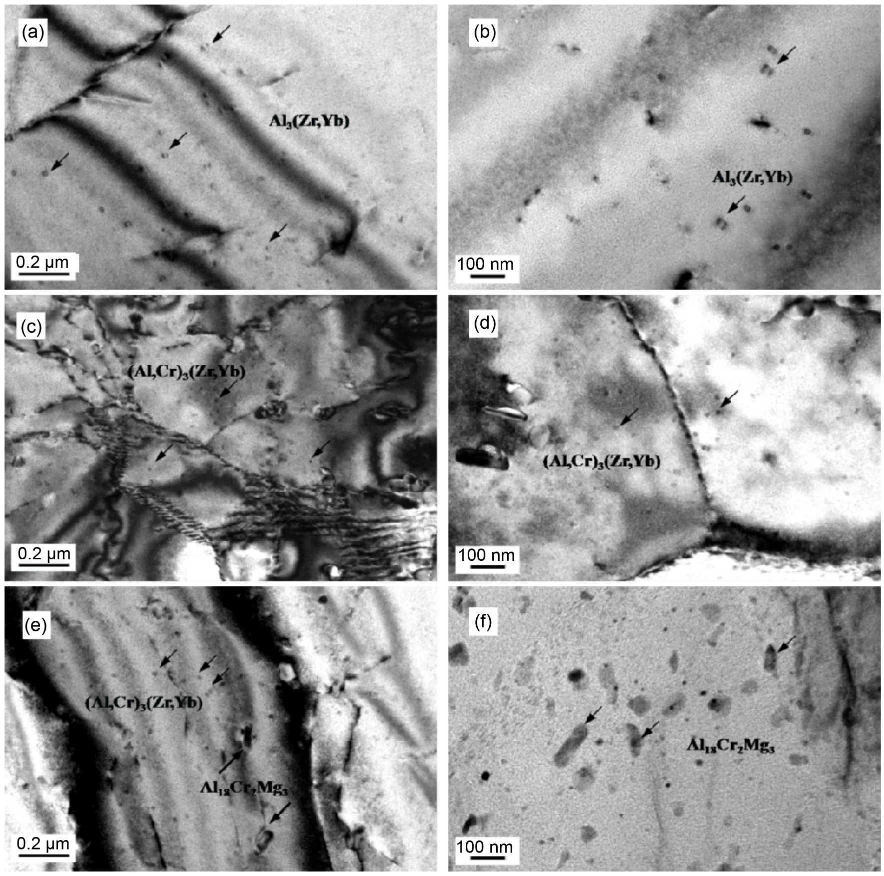

Figure 2. The effect of Cr to the dispersed phase of the Al-Zn-Mg-Cu alloys.
(a) (b) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb;
(c) (d) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr;
(e) (f) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr.

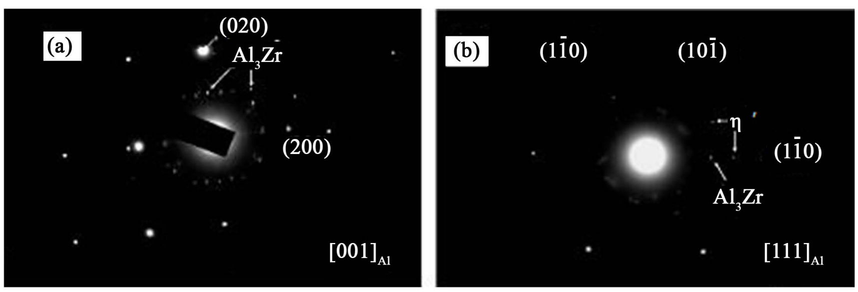

Figure 3. The selected area diffraction of Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr.

the alloy is evenly distributed with fine dimples with obvious ductile fracture characteristics; when the Cr content is increased to 0.18 wt%, the alloy is mainly composed of uniformly distributed fine fracture dimples.

3.4. Analysis of Intergranular Corrosion Properties

Figure 5 shows the corrosion depth of cross section (T-S) of Al-Zn-Mg-Cu-Zr-Yb alloy with different Cr content after intergranular corrosion along its L-T surface. It can be seen from the intergranular corrosion depth that the corrosion

Table 3. Tensile strength, yield strength and mechanical properties of experimental alloys of different Cr element.

Alloys	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	K_{IC}/MPa·m$^{1/2}$
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb	683.80	660.50	9.60	34.30
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr	731.50	710.90	8.50	37.20
Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr	706.80	685.00	8.70	35.60

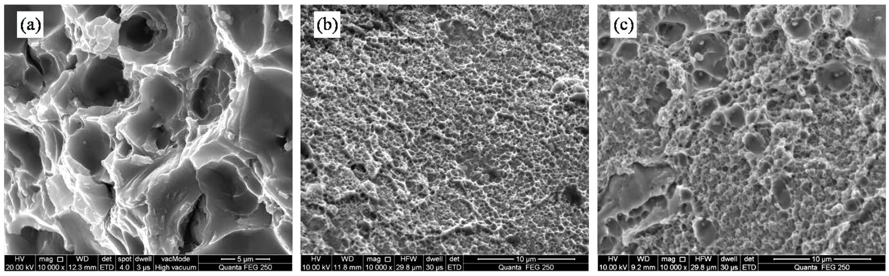

Figure 4. The effect of Cr element to the tensile fracture morphology of the alloys.
(a) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb;
(b) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr;
(c) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr.

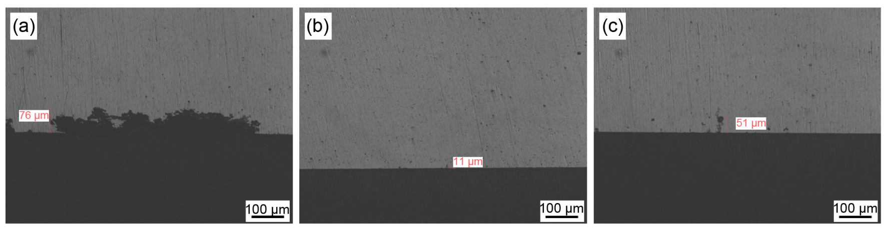

Figure 5. The corrosion cross section of the alloys was determined by different Cr content. (a) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb;
(b) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.1Cr;
(c) Al-8.54Zn-2.41Mg-1.3Cu-0.16Zr-0.3Yb-0.18Cr.

depth of the alloy with Cr content of 0 wt%, 0.1 wt%, 0.18 wt% is 76 μm, 11 μm and 51 μm respectively.

3.5. Analysis of Stress Corrosion Resistance

Figure 6 shows the slow drawing curve of alloy with different Cr content. It can be seen from the figure that with the increase of Cr content, the stress corrosion cracking time and yield strength of the alloy increase first and then decrease. The results show that the stress corrosion resistance of the alloy is the best when Cr content is 0.1 wt%.

With the increase of Cr (0 - 0.1 wt), the recrystallization resistance of the alloy is improved, and the deformation recovery substructure of the alloy with low Cr content is retained completely. With the increase of Cr content (0.1 - 0.18 wt), the recrystallization resistance of the alloy did not change significantly. The main reason is that when Cr is not added, the size of precipitated particles is 30 - 50 nm. These particles are Al_3(Zr, Yb) phase (**Figure 2(a)**, **Figure 2(b)**) which is

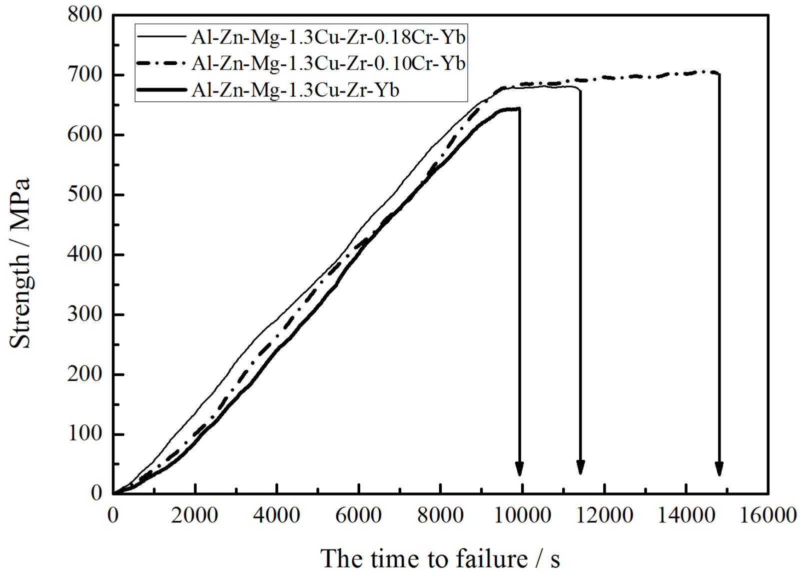

Figure 6. Different Cr content alloys slow stretch curve.

co lattice with the matrix. After high temperature treatment, most of the Al_3(Zr, Yb) phase which is co lattice with the matrix changes to Al_3(Zr, Yb) phase which is not co lattice, leading to the increase of recrystallization tendency. The addition of trace Cr results in the formation of (Al, Cr)$_3$(Zr, Yb) phase with a small amount of Cr whose particle size is 10 - 20 nm, which increases the stability of Al_3(Zr, Yb) phase and improves the recrystallization resistance of the alloy. When Cr content is 0.18 wt%, except for L_{12} type dispersion phase, there is also a coarse phase $Al_{18}Mg_3Cr_2$ with the size of 50 - 150 nm in the alloy matrix, which will not be dissolved after solution heat treatment. As a heterogeneous phase, this phase can inhibit the formation of recrystallization to some extent, but its coarse size and coherent relationship with the matrix are not obvious, which can inhibit the recrystallization nucleation and growth process. The effect ratio (Al, Zr)$_3$(Zr, Yb) is different.

When Cr content is 0.1 wt%, the fine dispersion can play a strong role in pinning relative to dislocation and sub grain boundary, hindering the transformation from sub grain boundary to large angle grain boundary, and greatly improving the stability of deformation recovery structure (**Figure 1(b)**). The energy difference between small angle grain boundary and in crystal is much smaller than that between large angle grain boundary and in crystal, which hinders the enrichment of precipitated phase particles in grain boundary and reduces the recrystallization tendency of alloy. Moreover, the dispersion distribution of the precipitates in the crystal makes the dislocations only bypass the coherent dispersion phase, thus inhibiting the coplanar slip of dislocations and improving the deformation uniformity of the alloy. This is helpful to restrain the grain boundary fracture tendency and improve the stress corrosion resistance of the alloy.

As Cr containing dispersion phase can significantly inhibit matrix recrystallization (**Figures 1(a)-(c)**), maintain deformation recovery structure and small angle grain boundary, it can significantly improve the fracture toughness of the alloy. Due to the low energy of small angle grain boundary, the possibility of aging precipitates enriching on it is very low. In addition, a large number of Cr containing dispersed phases are evenly distributed in the crystal, which makes grain growth difficult, promotes even deformation of the alloy, reduces the coplanar slip trend, avoids the grain boundary stress concentration caused by dislocation plugging at the grain boundary, thus reduces the tendency of grain boundary cracking caused by local stress concentration, and greatly improves the fracture toughness of the alloy.

4. Conclusions

1) With the increase of Cr content, the recrystallization and grain growth are inhibited, the strength, toughness and corrosion resistance of the alloy increase first and then decrease. When the Cr content is 0.1 wt%, the performance of the alloy is the best.

2) The main reason is that $(Al, Cr)_3(Zr, Yb)$ phase containing trace Cr is formed when Cr content is 0.1 wt%; when Cr content is increased to 0.18 wt%, $Al_{18}Mg_3Cr_2$ and $(Al, Cr)_3(Zr, Yb)$ phases are formed.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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