Effects of Minor Zirconium on Microstructure and Mechanical Properties of Al-Mg-Mn-Sc Alloys

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Abstract: Al-5.8Mg-0.4Mn-0.25Sc and Al−5.8Mg−0.4Mn−0.25Sc−0.1Zr (mass fraction, %) alloys were prepared by water chilling copper mould ingot metallurgy processing which was protected by active flux. The effects of Zr on microstructure and mechanical properties were studied by means of observations of optical microscopy and transmission electron microscopy. The results show that after adding Zr into Al-5.8Mg-0.4Mn-0.25Sc alloy the grains are obviously refined. Tensile properties increase significantly; under the condition that ductility(δ) is similar, tensile strength(σb) increases by nearly 20%, and the yield strength(σ0.2) increases by more than 30%. Zirconium in the alloy leads to the formation of more heterogeneous nucleation core during casting process, and more primary Al3(Sc,Zr) particles precipitate, thus refining the grain. In the same time the supersaturated solid solubility in the alloy can be improved. After stabilizing annealing，there is a higher degree of dispersion, and smaller and more secondary Al3(Sc,Zr) particles come to distribute in the matrix, improving the comprehensive mechanical properties of alloy with functions of strong pinning dislocations and sub-grain boundaries, and stabilizing sub-structures.

1 INTRODUCTION

Al-Mg-Mn belongs to the moderately strong, corrosion-resistant, weldable aluminum alloy. Because of their excellent comprehensive performance, they have been widely used in aerospace, transportation, electronic appliances, instruments and meters, armed ships, etc[1]. With the development of technology and increasingly diverse application requirements, higher requirements on the performance of these alloys have put forward. This kind of alloy cannot be strengthened by heat treatment. One way to increase the properties is by improving the deformation process; the other way is through micro alloying. The studies show that in improving Al-Mg-Mn alloy performance effect is prominent[2-4]. In all of the adding elements, the most significant element is Sc. Therefore in Russia a series of scandium aluminum alloy have been researched and developed depend on Sc, such as 01570 and 01571 alloys. Adding Sc into Al-Mg-Mn alloy, the primary Al_3Sc phase will precipitate during casting process, dendritic structure will be removed; and the grain size will be refined. And in the process of cold and hot deformation and stabilizing treatment, secondary Al_3Sc particles will precipitate, improving the performance of the alloy greatly with pinning dislocation, sub-grain boundary, and stable sub-structure.

In order to excavate the potential of Sc as much as possible, and to improve the performance of alloy more significantly, the research is focused on the composite micro alloying in recent, such as Sc and Zr[5-6], Sc and Ti[7-8], Sc and Er[9-10], Sc, Zr and Ti[11]. The study finds out that the effect of adding Sc and Zr together into Al-Mg-Mn alloy is better than that of adding single Sc. meanwhile, the strength properties and the recrystallization temperature are higher[1]. But the research of composite micro alloying about Sc and Zr is more focused on the role of the Sc, and the work about Zr may not be enough. In this work, both Al-5.8Mg-0.4Mn-0.25Sc and Al-5.8Mg-0.4Mn-0.25Sc-0.1Zr alloys are used as the research objects. The aim of this work is to investigate the role and the effecting rule of Zr to Al-Mg-Mn-Sc alloy.

2 EXPERIMENTAL

Two alloys for the study (marked A, B) are prepared by ingot metallurgy, using as the starting materials pure Al, pure Mg and Al-2.23%Sc, Al-4.48%Zr, Al-8.5%Mn master alloys. Their nominal compositions are listed in Table 1. After homogenization at 460°C for 24h, the ingots are cut head and milled surface to 25mm thickness. Then a hot-rolling process is applied to 6mm after heat preservation for 3h at 470 °C, which is followed by intermediate annealing at 400 °C for 2h. Subsequently, the hot-rolled sheets are cold-rolled to a thickness of 2.0 mm. The total deformation rate is up to 92%. The cold-rolled sheets are annealed at 340 °C or 150°C for 1h. Homogenization; intermediate annealing and stabilizing annealing processing are made in SPC box-type resistance furnace, and the error is ±2 ℃.

The microstructures of the alloys are examined using a POLYVER-Met optical microscope, with the specimens first mechanical polished, then electro-polished, followed by anodizing in a water solution of HF and H_3BO_3(30mlHF+11gH_3BO_3+970mlH_2O). Electrolytic polishing voltage is 20~28V, about 1~3 min, and anodizing voltage is 15~25, about 1~2min. TEM thin foils are prepared by twin-jet polishing with an electrolyte solution composed of 30%HNO_3 and 70%CH_3OH(volume fraction) at the temperature below -25°C. The foils are examined using HITACHI-800 and TECNAI G220 transmission electron microscope at an accelerating voltage of 200kV. Tensile specimens are cut along the rolling direction of the plates and tested on a MTS-858 tensile testing machine according to GB/T 228-2002 standard.

Table 1: Chemical composition of the studied alloys.

Specimen No.	Chemical composition (mass fraction, %)				
	Al	Mg	Mn	Sc	Zr
A	Bal.	5.8	0.4	0.25	
B	Bal.	5.8	0.4	0.25	0.1

3 RESULTS

3.1 Effect of Minor Zr on the Tensile Properties of Al-Mg-Mn-Sc Alloys

Table 2: Tensile properties of two studied alloys

Heat treatments	σb , MPa	
	A	B
130℃/1h	396	472
340℃/1h	336	395
Heat treatments	σ0.2 , MPa	
	A	B
130℃/1h	304	406
340℃/1h	191	268
Heat treatments	δ,%	
	A	B
130℃/1h	11.4	9.7
340℃/1h	15.5	16.5

Table2 lists tensile properties of the 2 alloys annealed at 130 °C or 340°C for 1h. It is clear that co-addition of small amounts of Sc and Zr can have higher tensile strength(σ_b) and higher yield strength($\sigma_{0.2}$) than that of adding single Sc. Under the condition that ductility(δ) is similar, tensile strength increases by nearly 20%, and the yield strength increases by more than 30%. It can also be seen in the table 2 that two kinds of alloy mechanical properties and annealing system have close relations. In order to maintain higher ductility, 340℃/1h annealing system is a better choice. The experimental results show that Zr plays a great role in improving the mechanical properties of Al-Mg-Mn-Sc alloy.

3.2 Effects of Trace Zr on the Optical Microstructure

Figure1 illustrates the optical microstructures of the 2 alloys in different states. It is shown that in 2 alloys dendritic structures haven't been found(Figure.1a, b). These observations indicate that addition of 0.2%Sc alone, or co-addition of 0.25%Sc and 0.1%Zr into the Al-Mg-Mn alloys could bring about an inoculation effect of the cast

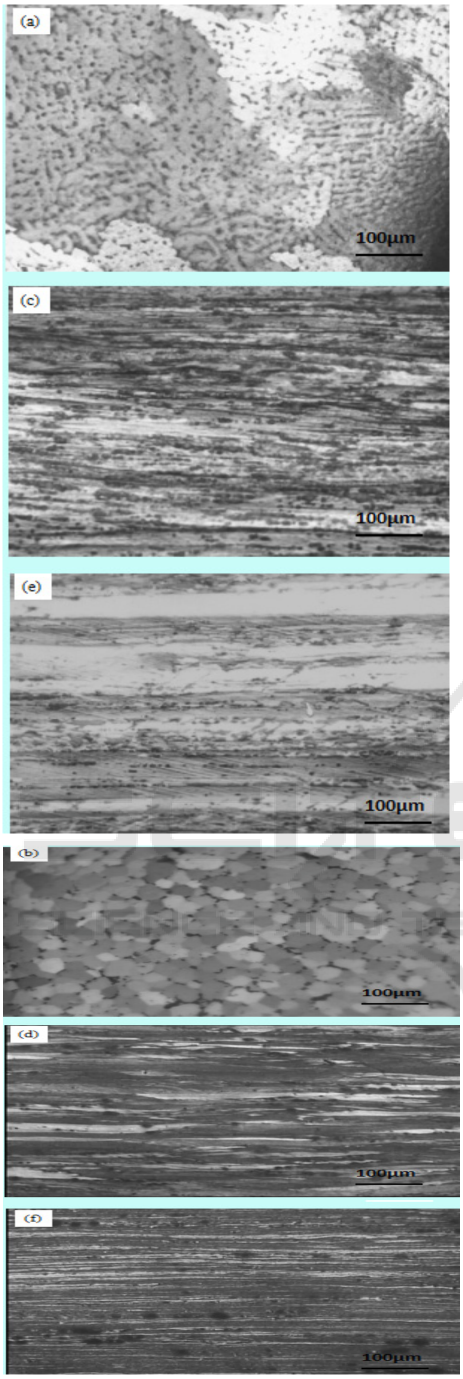
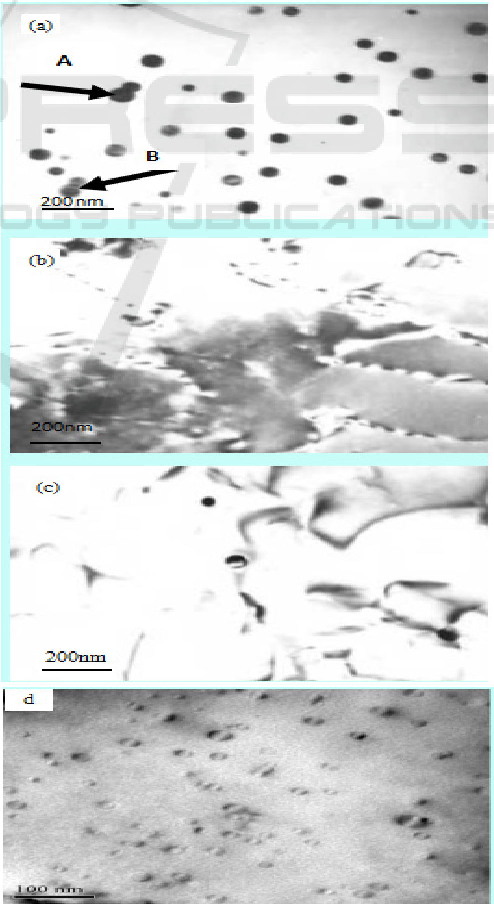


Figure 1: Optical microstructures of the two studied alloys(a)as-cast organization of alloy A; (b) as-cast organization of alloy B; (C) hot-rolled organization of alloy A; (d) hot-rolled organization of alloy B; (e) annealing organization of alloy A at 340℃/1h; (f) annealing organization of alloy B at 340℃/1h.

Alloys, thus eliminating the dendritic structure in them, whereas the grain size in alloy A is above 100μm, in alloy B only 20μm about. So the grain refinement effect of 0.25%Sc is not obvious, but trace Zr in Al-Mg-Mn-Sc alloy grain refinement has a huge role.

Microstructures of the hot rolled alloys are shown in Figure.1c-d, and Figure.1e-f is that of the stabilizing annealing processing alloy at 340℃ for 1h. Under these state the 2 alloys possess a fibrous structure along the rolling direction, never respond in recrystallization phenomenon. Due to the grain size in as-cast alloy B is much smaller than that in alloy A. Therefore, the fibrous structure in alloy B is much more delicate than that in alloy A. Dense fibrous structure tensile strength and yield strength will be higher, which is consistent with the above the tensile properties. So trace Zr can improve the organization form of alloy.

3.3 TEM Observation of the Two Studied Alloys



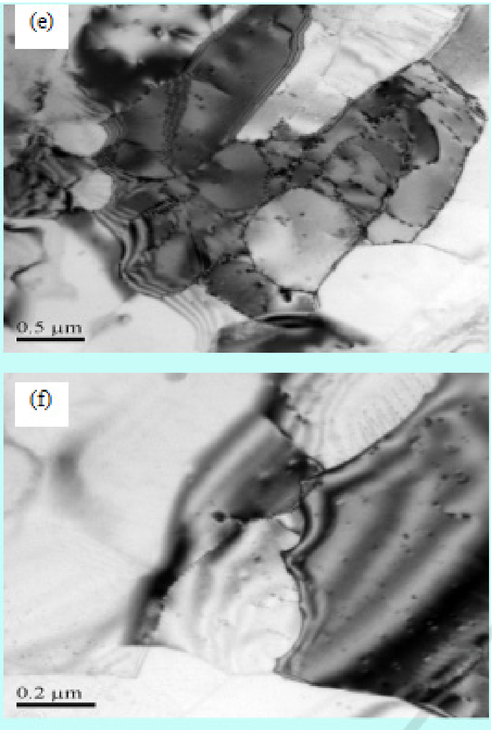


Figure 2: TEM micrographs of 340℃/1h annealed alloys(a)The fine, spherical and dispersive secondary Al_3Sc particles in alloy A; (b-c) The secondary Al_3Sc particles pinning up dislocations and subgrain boundaries in alloy A; (d) The fine, spherical and dispersive secondary $Al_3(Sc,Zr)$ particles in alloy B; (e-f) The secondary $Al_3(Sc,Zr)$ particles pinning up dislocations and subgrain boundaries in alloy A.

Figure 2 shows the TEM microstructures of two alloys, A and B, both annealed at 340°C for 1h. It is seen that a large fraction of fine and dispersive particles have precipitated within grains in these alloy. These particles are Al3Sc(Fig2.a) in Al-Mg-Mn-Sc alloy, and Al3(Sc,Zr)(Fig2.d)in Al-Mg-Mn-Sc-Zr alloy, and they tightly pin up the dislocations and subgrain boundaries(Figure2.b,c,e,f), and stabilize the substructure in deformation process. The gathering and coarsening phenomenon of Al3Sc particles is observed in fig2.a; as indicated by the arrows A and B, some particles have intersected and integrated. Based on the comparison of secondary phase particles in two kinds of alloys, it could be found that after adding Zr, the particle size of $Al_3(Sc,Zr)$ is smaller than Al_3Sc, $Al_3(Sc,Zr)$ particles are more of dispersion and uniform, and the number was larger. Thus the role of pinning dislocation and stabilizing substructure is more intense. In alloy B the intersected and integrated phenomenon of $Al_3(Sc,Zr)$ particles cannot' be found, and the substructure also haven't grown up with smaller size and a larger number of them. Therefore, Zr in Al-Mg-Mn-Sc alloy can enhance the effect of precipitation of second phase particles, retarding the growth and merging of the secondary particle and substructure more strongly.

4 DISCUSSION

4.1 Role of Zr in Refining the Grain Structure of As-cast Alloy

Aluminum alloy as-cast grain size is determined by the nature of the material itself, the cooling rate and undercooling degree in the process of solidification, heterogeneous nucleation core, and so on. Under the same circumstance, the melt provides more heterogeneous nucleation core with the grain of smaller size. According to above experimental results, compared with Al-5.8Mg-0.4Mn alloy[7], the as-cast microstructure can't reach the refinement effect significantly after adding 0.25%Sc, and the grain size is above 100μm. This illustrates that the number of heterogeneous nucleation core in the process of solidification doesn't get substantial improvement. Analyzing the phase diagram of Al-Sc[12] alloy can know that the equilibrium solubility of Sc is 0.32%. When Sc content is less than 0.25%, the primary Al_3Sc particles formed in the solidification process is not too much, so the refinement effect to grain is not significant. And most of Sc in the alloy is more inclined to form a non-equilibrium supersaturated solid solution which is unstable and is easy to precipitate in later processing.

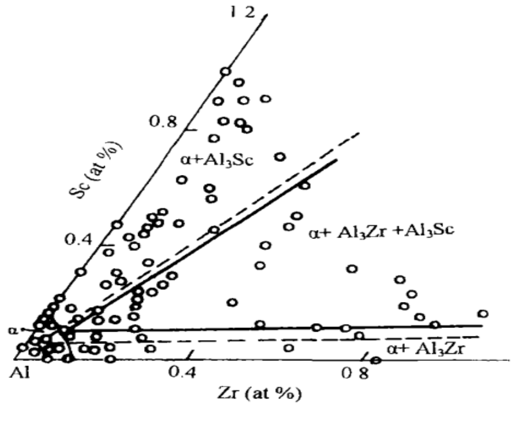


Figure 3: the phase diagram of Al-Sc-Zr at 600℃ and 550℃.

Figure 3[13] is Al-Sc-Zr isothermal phase diagram of rich aluminum angle at 600℃(solid line) and 550℃(dotted line). At 600℃ the solubility of Sc and Zr are 0.09% and 0.06% respectively; at 550℃ are 0.06% and 0.03% respectively. Therefore, Zr on the one hand, greatly reduces the Sc equilibrium solubility in Al; on the other hand, it also as a replacement atom replaces the positions of Sc atom in Al3Sc. This makes Al_3Sc particles change into $Al_3(Sc,Zr)$ particles, and let Sc atoms have more chance to form more secondary particle, which gives the melt to provides a much larger number of heterogeneous nucleation core, thus refining grain size significantly. Dependent on the experimental result, by adding 0.1%Zr in Al-5.8Mg-0.4Mn-0.25Sc alloy, the grain size reduces from 100μm to 20μm, and the effect is very good.

4.2 Role of Zr to Improve the Mechanical Properties

From the above analysis, Zr can reduce the equilibrium solubility of Sc in Al, and can also improve the degree of supersaturation of the original solid solution. The increase in degree of supersaturation makes more and more diffuse secondary phase $Al_3(Sc,Zr)$ particles precipitate in the process of deformation processing and heat treatment, making pin dislocation, boundary and sub-structure more intense, so that the strength of the alloy and recrystallization temperature have greatly improved.

Zr will also reduce the coarsening rate of secondary $Al_3(Sc,Zr)$ particles. Al_3Sc particles under the action of heat have tended to gather, grow up and dissolve back in matrix. Once the Al3Sc particles grow up, they will lose the coherence with Al matrix, and also let the distance between the particles increase, thus losing the role to pin dislocation and sub-structure, which reduces the mechanical properties of these alloys. Ye Yicong[14] had studied the precipitation and coarsening of secondary Al_3Sc phase in Al-0.4Sc alloy and found when aging temperature was greater than 400℃ Al_3Sc particles grew up quickly, and at 500℃ aging four hours, these particles had lost coherent relationship(If particle radius is larger than 20nm, it will lose coherent relationship). Christian B. Fuller[15] did the creep experiment at 300℃ for above one week, and found the $Al_3(Sc,Zr)$ particles without apparent coarsening. Figure 4 was HRTEM(high-resolution electron microscopies) image of $Al_3(Sc,Zr)$ precipitates. The preparation of TEM sample was to use cold-rolled sheet of Al-5.8Mg-0.4Mn-0.25Sc-0.1Zr alloy to anneal at 550 C for 40h. In the left top corner it was FFT transformation of white box field in the image. It illustrates that $Al_3(Sc,Zr)$ particles haven't grown up and are still less than 10 nm in good coherent relationship with matrix. When 50%Sc atoms in Al_3Sc is replaced by Zr atoms, Al_3Sc phase changes into $Al_3(Sc_{0.5}Zr_{0.5})$ phase which has the smallest aggregation bias[11]. The secondary $Al_3(Sc,Zr)$ particles have good thermal stability and always maintain good coherent relationship with matrix, so strengthening effect is significant.

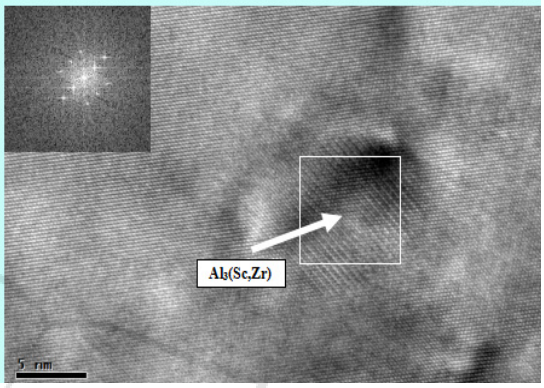


Fig.4 HRTEM image of Al3(Sc,Zr) precipitates.

5 CONCLUSIONS

(1) Adding 0.1%Zr in Al-5.8Mg-0.4Mn-0.25Sc alloy can refine the as-cast microstructure significantly, and the grain size reduces from 100μm to about 20μm. This is mainly due to the reason that after adding Zr it can precipitate more primary $Al_3(Sc,Zr)$ particles in the casting process, and can provide more heterogeneous core so as to form more grains.

(2) The comprehensive mechanical properties can be improved when 0.1%Zr is added into Al-5.8Mg-0.4Mn-0.25Sc alloy. Tensile strength(σ_b) can be improved by about 20%; the yield strength($\sigma_{0.2}$) can be increased by 30%, and maintain good elongation. The reasons are that in stabilizing annealing process more diffuse secondary $Al_3(Sc,Zr)$ particles precipitate and the quantity is larger, and that their thermal stability is better than Al_3Sc particles. So the role to pin the dislocation and sub-structure is more intense, and strengthening effect is better.

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