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Effect of Zr content on quench sensitivity of AlZnMgCu alloys

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Abstract: The effect of Zr content on quench sensitivity of AlZnMgCu alloys was investigated by mechanical properties testing and microstructure observations. The results show that with the increase of Zr the quench sensitivity relative to hardness and strength increases, while that relative to elongation decreases. From hardness and strength viewpoints, the low quench sensitivity is observed for the Zr-free and 0.05% Zr-containing alloys, which is quite quench sensitive from the ductility viewpoint. The largest quench sensitivity relative to hardness and strength is observed for 0.1% Zr-containing alloy, this is mainly due to large amount of high angle grain boundaries and incoherent Al_3Zr dispersoids caused by recrystallization, which may efficiently promote heterogeneous precipitation during air quenching. More than 0.05% Zr can significantly decrease the quench sensitivity relative to ductility, which can be primarily attributed to recrystallization inhibiting and grain refining effects of Zr.

Key words: AlZnMgCu alloys; Zr; quench sensitivity; recrystallization

1 Introduction

The age-hardenable AlZnMgCu alloys have been widely used as the structural materials in aerospace industry in the past decades. Its high strength is obtained primarily by solution heat treatment, quenching and aging. The quenching is a very critical step[1−2], because the super-saturation of the solid solution exerts dominant effect on aging hardening of the alloy. Slow quenching often results in lower strength, ductility and fracture toughness[1, 3], which often occurs in the middle of thick plates during quenching. The drop in properties due to decreased quenching rate is called quench sensitivity, which is primarily caused by heterogeneous precipitation on dispersoids and (sub) grain boundaries[4−6]. The quench sensitivity is influenced by degree of recrystallization due to heterogeneous precipitation at high angle boundaries[5]. So inhibition of recrystallization can partially lower the quench sensitivity. Some trace elements, for instance, Cr and Zr, are added to inhibit recrystallization and refine grains. Zr results in lower quench sensitivity than Cr, but there are still many coarse equilibrium η particles precipitated on Al_3Zr dispersoids during slow quenching [4, 6]. So it is supposed that the quench sensitivity of AlZnMgCuZr alloys is influenced by the amount of high angle grain boundaries and Al_3Zr dispersoids available for heterogeneous precipitation. Obviously, that is controlled to some extent by Zr content.

The aim of this study is to investigate the effect of Zr content on quench sensitivity of AlZnMgCu alloys.

2 Experimental

The nominal chemical compositions of the studied AlZnMgCu(Zr) alloys are Al-8.0Zn-2.0Mg-2.3Cu with Zr of 0, 0.05, 0.1 and 0.15 (mass fraction, %), respectively. The amount of Fe+Si is kept lower than 0.15% (mass fraction). The alloy melting was carried out in a crucible furnace. After degassed by C_2Cl_6 and held for about 10 min, the melt was cast into rectangle copper moulds, and the ingots with size of 20 mm×150 mm in cross section and 200 mm in height were obtained.

The ingots were homogenized by heating to 465 ℃ with 0.8 ℃/min and holding for 24 h, and then cooled in air. After preheating at 420 ℃ for 2 h, the homogenized ingots were rolled to a sheet of 2.5 mm in thickness with

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10 passes. The samples with size of 2.5 mm×20 mm×70 mm were cut from the sheet, solution heat treated at 470 ℃ for 1 h, and then quenched into water of 20, 60, 100 ℃ and still in air, respectively, which resulted in different cooling rates. After quenching, the samples were immediately subjected to artificial aging at 121 ℃ for 24 h.

The Vickers hardness testing (29.4 kN) of the aged sample was performed on Model HV−10B hardometer and five tests were made on each sample. The ambient temperature tensile properties tests were performed on CSS−44100 testing machine. The microstructure characterization was carried out by optical microscopy (OM) and TecnaiG^2 20 transmission electron microscopy (TEM) operated at 200 kV. The samples for optical microscopy observation were etched by Graff Seagent solution, which gives good decoration of recrystallized area[7]. The samples with 3 mm in diameter, 0.08 mm in thickness for transmission electron microscopy observation were electropolished using 30%HNO_3+70%CH_3OH solution below −20 ℃.

3 Results

3.1 Mechanical properties of alloy

Fig.1 shows the influence of Zr content and quenching rates on the hardness, strength and elongation of the aged alloys, respectively. For the 20℃ water quenched samples, higher Zr content results in higher hardness and strength, which is mainly attributed to inhibition of recrystallization, grain refinement effect of Zr and existence of Al_3Zr dispersoids[1,8]. For the 60 ℃ water quenched samples, Zr content seems to have little effect hardness, but results in higher strength. It suggests that the relationship between hardness and strength is not always linear[9]. For the 100 ℃ water quenched samples, Zr content from 0% to 0.1% lowers the hardness. While for yield and ultimate strength, the lowest value is obtained for the alloy with 0.05% Zr. For the air quenched samples, the lowest values of hardness, yield and ultimate strength are observed for the alloy with 0.1% Zr. While for ductility, the largest elongation is observed for the alloy with 0.1% Zr for all the quenching rates. It is evident that the influence of quenching rates on the mechanical properties of the alloys is dependent on Zr content.

In order to indicate the effect of Zr content on the degree of quench sensitivity of the studied alloys better, a quench sensitivity factor named Q is defined as

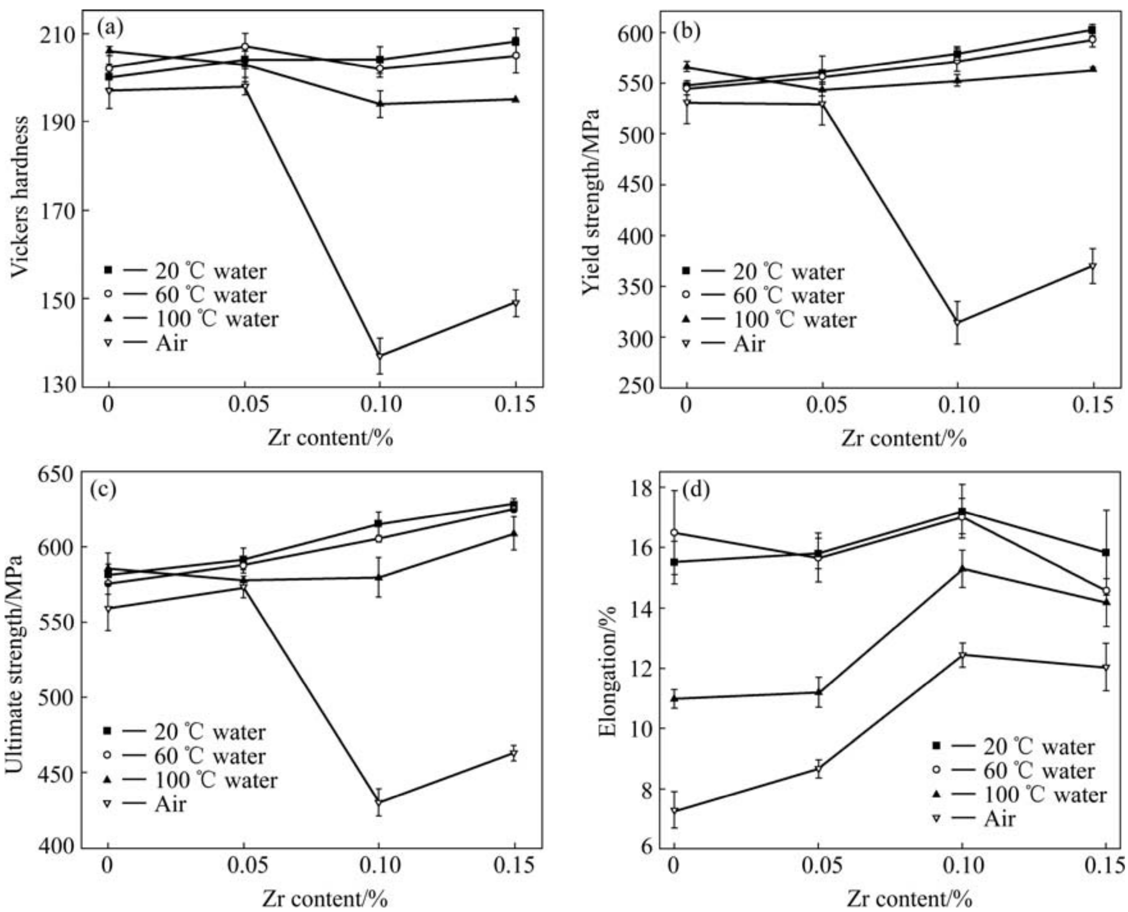

Fig.1 Effect of Zr content and quenching rates on hardness (a), yield strength (b), ultimate strength (c) and ductility (d) of aged alloys

follows:

$$Q=(P[20]-P[QM])/P[20] \quad (1)$$

where $P[20]$ is the properties obtained in the case of 20 ℃ water quenching, and $P[QM]$ is the properties obtained in the case of 100 ℃ water and air quenching. As 60 ℃ water quenching has reasonably small effect on the properties of the alloys compared with 20 ℃ water quenching, it is not taken into account. It is believed that higher value of Q means larger quench sensitivity. The results are shown in Fig.2.

From Fig.2, it can be seen that quite low quench sensitivity relative to hardness and strength, and high quench sensitivity relative to ductility are observed for the alloys without and with 0.05% Zr. Zr content higher than 0.05% results in significant increase in the quench sensitivity relative to hardness and strength, but significant decrease in that relative to ductility. According to the drop percentage in properties, it is evident that Zr content of 0.1% leads to the largest quench sensitivity relative to hardness and strength, and further increase in Zr slightly decreases the quench sensitivity.

3.2 Microstructure characteristics

Typical optical micrographs of the alloys are shown in Fig.3.

Complete recrystallization is observed after solution

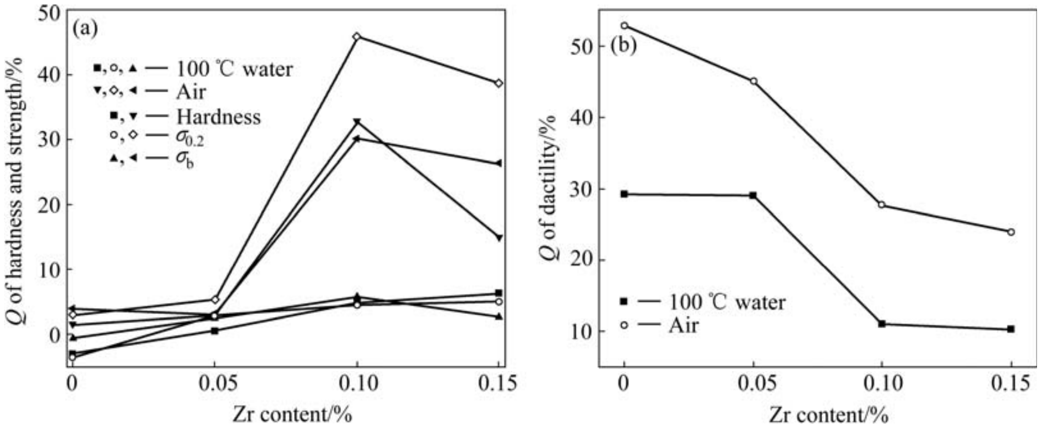

Fig.2 Results of Q of hardness and strength (a) and ductility (b)

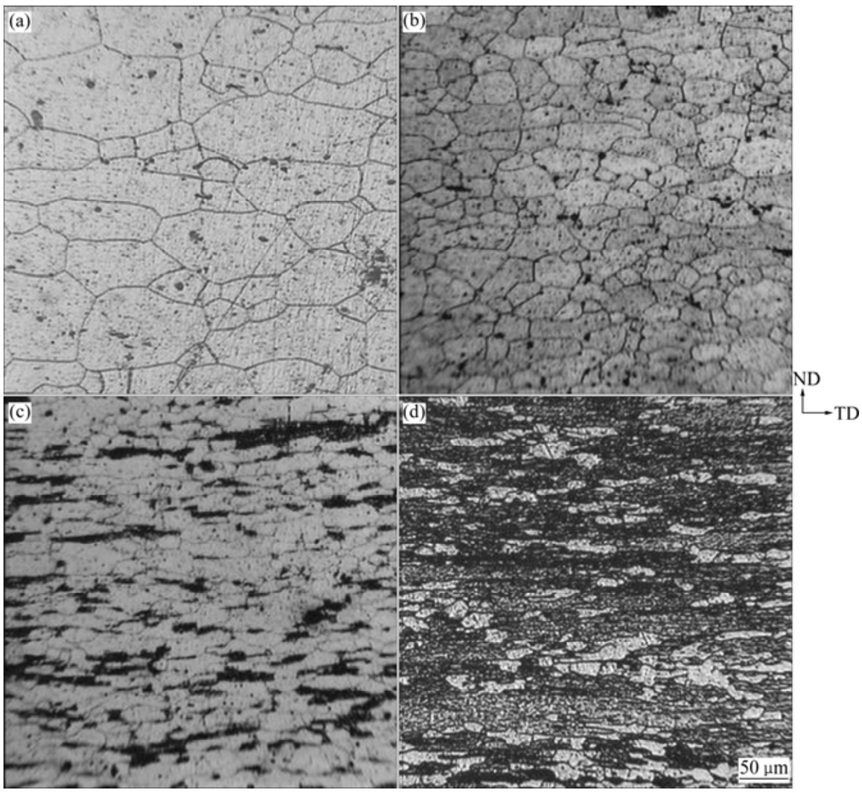

Fig.3 Optical micrographs of 20 ℃ water quenched and aged alloys: (a) Without Zr; (b) 0.05% Zr; (c) 0.1% Zr; (d) 0.15% Zr

heat treatment in the alloys without and with 0.05% Zr. The Zr content of 0.05% fails to inhibit recrystallization efficiently, but refins the recrystallized grains, as shown in Figs.3(a) and (b). After etching by Graff Seagent solution[7], which etches the subgrain boundaries first, it can be seen clearly in Figs.3(c) and (d) that the white area is recrystallized grains while the black area is unrecrystallized grains. Partial recrystallization is observed in the alloys with 0.1% and 0.15% Zr, and the recrystallization fractions are about 78% and 38% respectively. This is obviously attributed to the recrystallization inhibiting effect of Al_3Zr dispersoids [10].

After aging, the microstructures of the 20 ℃ and 60 ℃ water quenched alloys are quite similar. The hardening precipitates with high density are distributed the homogeneously in the matrix, which is responsible for high strength of the alloy, and the precipitate free zone along grain boundaries is quite narrow. Typical micrographs are shown in Figs.4(a) and (e). For the 100 ℃ water and air quenched alloys, a number of coarse particles that primarily precipitate on Al_3Zr dispersoids

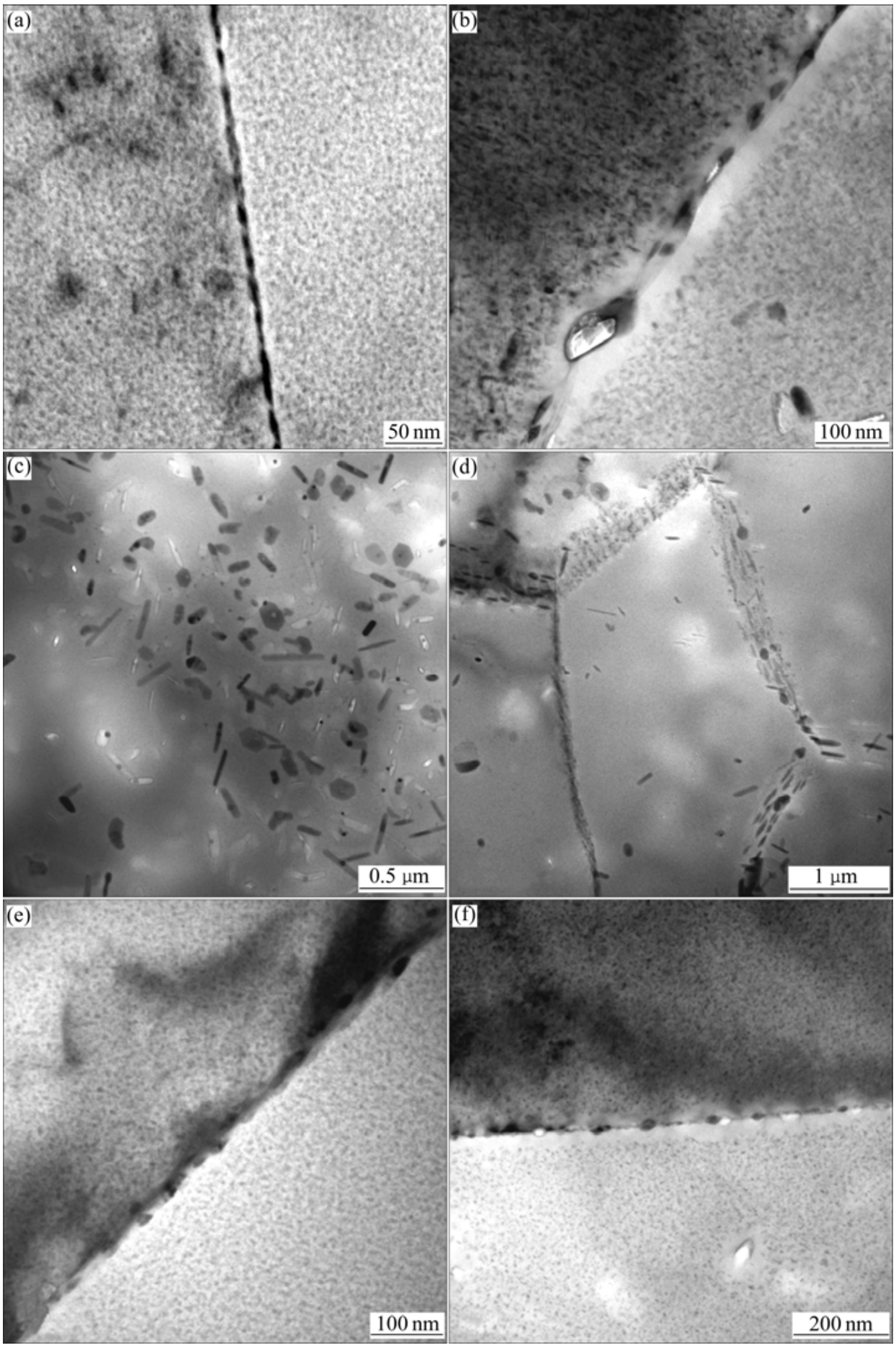

Fig.4 TEM micrographs of aged alloys: (a) 20 ℃ water quenched with 0.15%Zr; (b)−(d) Air quenched with 0.15%Zr; (c) Recrystallized grain; (d) Sub-grain; (e) 20 ℃ water quenched without Zr; (f) Air quenched without Zr

during slow quenching are observed in the matrix with an obvious precipitate free zone in the Zr-containing alloys. Though, far from these coarse precipitates there are many fine-scale precipitates, limited hardening is achieved after aging. As a result, the strength is lower as shown in Fig.1. It is noticeable that more coarse precipitates are observed in the recrystallized area than in the unrecrystallized area for the 0.1% and 0.15% Zr alloys, as shown in Figs.4(c) and (d).This may confirm the fact that incoherent Al_3Zr dispersoids due to recrystallization are more effective sites for heterogeneous precipitation[11−12]. And those coarse particles in the 100 ℃ water quenched alloys are significantly smaller than that in the air quenched ones. As for the Zr-free alloy, few coarse precipitates can be seen in the matrix after slow quenching.

After air quenching, heterogeneous precipitates are also observed at grain boundaries in the alloys. These precipitates are quite stable and grow up during subsequent aging, which inhibite nucleation and growth of new precipitates at adjacent grain boundaries. As a result, more spaced precipitates of non-uniform size at the grain boundaries are observed. The grain boundary precipitate free zone is quite wider, as shown in Figs.4(b) and (f), which can primarily be attributed to the loss of vacancies and solutes during air quenching [13].

4 Discussion

According to previous investigations[4−6], it is well known that quench sensitivity relative to strength is closely associated with the amount of sites (in this paper, these sites are supposed mainly to be high angle grain boundaries and incoherent Al_3Zr dispersoids) available for heterogeneous precipitation. During slow quenching, larger amount of such sites result in more heterogeneous precipitations, namely more loss of solutes. As a result, smaller subsequent aging hardening effect can be obtained. In the following parts, the quench sensitivity relative to hardness and strength will be discussed mainly from the viewpoint of the amount of solutes available for aging hardening.

For hardness and strength, it is obvious that quite low quench sensitivity in the case of air quenching is observed for the Zr-free alloy. In this alloy, reasonably large recrystallized grains are observed. So it is believed that high angle grain boundaries may be the only possible sites for heterogeneous precipitation during air quenching, and the super-saturation of solutes in the matrix far from the grain boundaries get little effect by air quenching. The slight drop in hardness and strength may be attributed to the lower super-saturation of vacancies, which result in less dispersed hardening precipitates, as shown in Figs.4(e) and (f). On the contrast, slightly increased quench sensitivity is observed for the alloy with 0.05% Zr. The grains are refined by addition of Zr, so the amount of high angle boundaries increases, which may be responsible for the increased quench sensitivity. In addition, as complete recrystallization occurs in this alloy, those coherent Al_3Zr dispersoids lose coherency with the matrix, thus becoming effective sites for heterogeneous precipitation of equilibrium $MgZn_2$ during slow quenching[5], which may also partially responsible for quench sensitivity. Further increase of Zr results in larger quench sensitivity in the case of air quenching. 0.1% Zr leads to the largest quench sensitivity. In this alloy, the occurrence of recrystallization is not well controlled, as shown in Fig.3(c), which results in larger quantities of high angle grain boundaries and incoherent Al_3Zr dispersoids. Therefore, the super-saturation of solutes decreases greatly due to heterogeneous precipitation on these sites, thus leading to large quench sensitivity. Recrystallization is reasonably well inhibited by addition of 0.15% Zr, as shown in Fig.3(d). As a result, the amount of high angle grain boundaries and incoherent Al_3Zr dispersoids are reduced, and the quench sensitivity decreases slightly.

Decreased quenching rates result in lower ductility of the studied alloys. This may primarily be attributed to coarse particles at the grain boundaries and wider grain boundaries precipitate free zone due to slow quenching[14−15], which may promote intergranular fracture. And the quench sensitivity relative to ductility is decreased significantly by the addition of Zr higher than 0.05%, as shown in Fig.1(d) and Fig.2(d). This may be due to recrystallization inhibiting and grain refining effects of Zr.

From above viewpoint, it is critical to control the grain structure, namely reducing recrystallization in the Zr-containing alloys can decrease the quench sensitivity.

5 Conclusions

1) Quench sensitivity relative to hardness and strength of AlZnMgCu alloys is increased by addition of Zr. The Zr-free alloy shows low quench sensitivity, and the drop in properties caused by air quenching may mainly be due to loss of vacancies. In the case of air quenching, 0.1% Zr results in the largest quench sensitivity, which may mainly be attributed to large amount of heterogeneous precipitation sites of high angle grain boundaries and incoherent Al_3Zr dispersoids due to recrystallization.

2) Quench sensitivity relative to ductility is decreased significantly with Zr content higher than 0.05%. This may be attributed to recrystallization inhibiting and grain refining effects of Zr.

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