GRAIN BOUNDARY SEGREGATION AND INTERGRANULAR BRITTLENESS IN HIGH STRENGTH ALUMINIUM ALLOY①

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ABSTRACT Effects of magnesium and hydrogen to grain boundary on the fracture energy in 7050 high strength aluminium alloy have been calculated using the quasichemical approach. The results indicated that both Mg and H segregation induce the intergranular fracture energy decrease, thus resulting in grain boundary embrittlement, and the embrittlement degree induced by hydrogen is larger than that of magnesium. This conclusion corresponds with the experimental results.

Key words high strength aluminium alloy grain boundary segregation intergranular brittleness

1 INTRODUCTION

Trace element segregation to grain boundary always has large effect on the material toughness. The investigation showed that Mg, H segregatoin on grain boundary in high strength aluminium alloy always promote intergranular fracture, it has obvious effects on stress corrosion, corresion fatigue and tension of hydrogen-charged specimen[1-3]. However, the theoretical study on Mg, H induced intergranular brittleness in high strength aluminium alloy is short of reporting as yet.

Seah[4] proposed that quasichemical approach was used to investigate the effect of grain boundary segregation on grain boundary strength. Recently, Liang *et al.* suggested some improvement based on Seah's theory, and it is more reasonable than Seah's. So we adopt the approach in reference [5] to calculate and discuss the effects of Mg, H grain boundary segregation on intergranular brittleness in high strength aluminium alloy, at last comparing with the experimental results.

2 CALCULATION APPROACH

The model of grain boundary segregation induced fracture is shown in Fig. 1.

In the case of low temperature fracture it is assumed that the grain boundary separates without redistribution of the solute atoms. The actual energy required to break the bonds across the grain boundary may be simply determined by counting up the number of dangling bounds per unit area and summing their energies. The energies may be calculated from the sublimation enthalpies.

For the convenience of calculation, assume the solute atoms segregate on one atom plane as shown in Fig. 1(a). The fracture occurs along the dotted line, and the number of bounds broken is known in Fig. 1(b).

For a binary system of solute B in solvent A the nearest neighbour energies (negative values) ε_{AA}, ε_{AB} *and* ε_{BB} are assigned to AA, AB and BB neighbours respectively. The fracture energy per unit area of the pure solvent A is given by

$$W(0) = -\alpha_{AA}\left[\frac{Z_g}{a_A^2}\right]\varepsilon_{AA} \quad (1)$$

where Z_g is the co-ordination of atoms in the layer on one side of the grain boundary to those in the adjacent layer on the other side.

a_A^2 is the area of a solvent A atom.

The fracture energy with a molar fractional monolayer, X_b, of B at the grain boundary is

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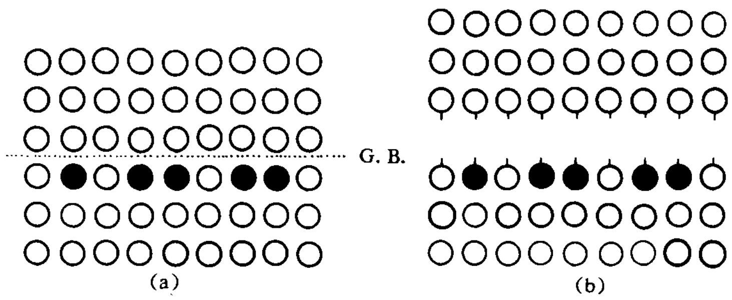

Fig. 1 schematic representation of grain boundary fracture model
(a)—before fracture; (b)—after fracture; ●—solute atom; ○—solvent atom

$$W(X_b) = -\frac{Z_g}{a_A^2}[(1 - X_b)\alpha_{AA}\varepsilon_{AA} + X_b\alpha_{AB}\varepsilon_{AB}] \quad (2)$$

From Eqs. (1) and (2), we can obtain the effect of grain boundary segregation on fracture energy as follows:

$$W(0) - W(X_b) = -\frac{Z_g}{a_A^2}[X_b\alpha_{AA}\varepsilon_{AA} - X_b\alpha_{AB}\varepsilon_{AB}] \quad (3)$$

Where $1/a_A^2$ is the number of A atom per surface area, α_{AA} and α_{AB} are the modification factors, $\alpha_{ij} \leqslant 1$, α_{ij} changes with the properties of atom.

$$\varepsilon_{AB} = \omega + \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) \quad (4)$$

Where ω is the interaction energy parameter, it can be calculated from the electronegativity difference between the components

$$N_0\omega = -96.5(\chi_A - \chi_B)^2 \quad (\text{kJ/mol}) \quad (5)$$

where N_0 is Avogadro's number.

For metal, ε_{ij} may be obtained from the molar sublimation enthalpy ΔH_j^{sub}. (6)
Where C is the chemical coordination number, $C = 4$ for the elements from Ⅰ *A* to Ⅵ *A* groups and $C = 3$ for the elements from Ⅶ *a* to Ⅴ *A* groups. Pauling's data about chemical bond are used for the calculation of ε_{ij} value of non-metals[6].

If solvent A is metal Al, $\alpha_{AA} = 1$, then Eqs. (3) can be simplified as follows:

$$W(0) - W(X_b) = \frac{Z_g}{\alpha_A^2}X_b[\alpha_{AB}\varepsilon_{AB} - \varepsilon_{AA}] \quad (7)$$

If the solute atoms segregated at grain boundary make the fracture energy $W(X_b)$ smaller than that of pure metal $W(X_0)$, it is embrittling species. In this case, the value of the equal sign right is positive. Otherwise, if the value is negative, the solute atoms is toughening species.

3 THE GRAIN BOUNDARY SEGREGATION IN 7050 ALUMINIUM ALLOY

One of the authors in this paper[3] once studied 45 mm thick 7050 aluminium alloy plate, the chemical composition (%) is: Zn 6. 09, Mg1. 91, Cu2. 14, Zr0. 08, Ti0. 045, Mn<0. 1, Cr<0. 04, Fe<0. 12, Si<0. 05 and the balance is aluminium. After being treated under various aging conditions, the composition on grain boundary was analysed using a scanning Auger microprobe. The results indicated that there existed Mg segregation on grain boundary, as shown in Table 1.

References [7,8] proved that precipitation in high strength aluminium alloy at 120~160 ℃ generally occurs in the following sequence:

α (Supersaturated solid solution) → Guinier-Prestop(G. P.) Zones→η'($MgZn_2$)→η ($MgZn_2$)

So we assume that all of Zn content on grain boundary forms $MgZn_2$, the content of solid solution Mg on grain boundary which is to subtract the content of Mg in $MgZn_2$ from the analytical composition of Mg.

4 RESULTS AND DISCUSSION

High strength aluminium alloy may be

Table 1 Contents of Mg, Zn on Grain Boundary (%)

	Aging	Mg	Zn	Solid solution Mg
A	145 ℃/5 h	8.35	3.15	6.78
B	145 ℃/8 h	6.74	3.45	5.02
C	145 ℃/16 h	6.60	2.80	5.20
D	145 ℃/24 h	6.08	4.09	5.04
E	145 ℃/36 h	6.63	4.86	4.20
	Chemical composition	2.22	2.63	

approximately treated as a binary alloy system owing to its stress corrosion, corrosion fatigue, etc, crack propagation is always along grain boundary and the fracture on grain boundary is mainly caused by Mg or H segregation.

The effects of Mg and H segregation on intergranular fracture work were calculated by means of the above theory respectively. Eqn. (7) is rewritten as follows:

$$W(0) - W(X_b) = \frac{Z_g}{N_0 \alpha_A^2} X_b \cdot [\alpha_{AB} N_0 \varepsilon_{AB} - N_0 \varepsilon_{AA}] \quad (8)$$

Now, we define the intergranular parameter Q , which is the term (7) on the right-hand side of the above equation, i. e. ,

$$Q = \alpha_{AB} N_0 \varepsilon_{AB} - N_0 \varepsilon_{AB} \quad (9)$$

while Q is positive or negative, the element is embrittling one or toughening one.

4.1 *Effect of* Mg *Segregation on Intergranular Fracture Energy*

For Mg segregation, the corresponding data as follows: $\alpha_{AB} = 1$[5]; $X_A = 1.5$, $X_B = 1.2$[9]; $a_A = 2.55$ Å , $H_A^{sub} = 328.9$ kJ/mol, $H_B^{sub} = 148.8$ kJ/mol[4]. Substituting these data into Eqn. (9), we have

$$Q_{Mg} = -155.5 - (-219.3) = 63.8 > 0$$

It can be seen from this that Mg segregation on grain boudnary will make intergranular energy decrease and grain boundary embrittlement.

The experimental results of effects of Mg segregation on the plateau velocity of stress corrosion in 7050 aluminium alloy are shown in Fig. 2[3]. It can be seen from Fig. 2 that the plateau velocity increases with the content of segregation Mg on grian boundary. As a result of the reduction degree of intergranular energy incrasing with Mg segregation content increasing, the fracture stress of grain boundary decreases, so the minimum stress strength factor to reach the plateau velocity decreases. In this way, the faster the crack propagation, the higher the plateau velocity.

4.2 Effects of Hydrogen Enrichment on Intergranular Energy

Substituting $\alpha_{AB} = 0.0833$[5]; $X_B = 2.1$, $N_0 \varepsilon_{AB} = -435.6$ kJ/mol[9] into Eqn. (9), we have

$$Q_H = 0.0833 \times (-362.2) - (219.3) = 189.1 > 0$$

So hydrogen enrichment at grain boundary in high strength aluminium alloy will make the intergranular energy decrease violently, and resulting in hydrogen embrittlement. Comparing with Mg segragation, Q_H is about two times larger than Q_{Mg}, i. e. , hydrogen, embrittles grain boundary more intense than Mg does uner the same segregation content.

Fig. 3 is the experimental results of the fractue stress changing as hydrgoen charging time for three aged states in 7050 aluminium alloy[3]. It can be easily seen from Fig. 3 that all the fracture stress of three aged states de -

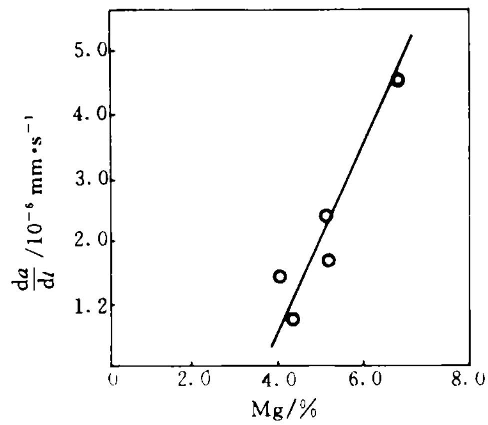

Fig. 2 Effects of Mg segregation on plateau velocity

crease obviously as hydrogen charging time increases. Ion mass microprobe analysis showed that hydrogen content increases as hydrogen charging time increase and the hydrogen content of underaged state is the most of all[3]. This indicates that the theoretical analysis is consistent with the experimental results.

4.3 *The Nature of Intergranular Brittleness*

Authors think that after Mg atoms with two valence eletrons replace Al atoms with three valence electrons at grain voundary, the common electron density will decreases, thus resulting in the reduction of electricity Coulomb's force between electron gas and atomic body, therefore grain boundary embrittles. Whereas hydrogen atoms enrich at grain boundary, it will attract the electrons of Al atom to its surroundings as a result of the electronegativity of hydrogen being larger than that of aluminium. It is due to this electricity transfer that make the electron density metal-metal bonding decrease, thus the binding force reducing and resulting in hydrogen embrittlement.

To sum up, the natrue of Mg, H segregation on grain boundary induced intergranular brittleness in high strength aluminium alloy is that it makes the electron density entering metal bond and the binding energy of grain boundary decrease.

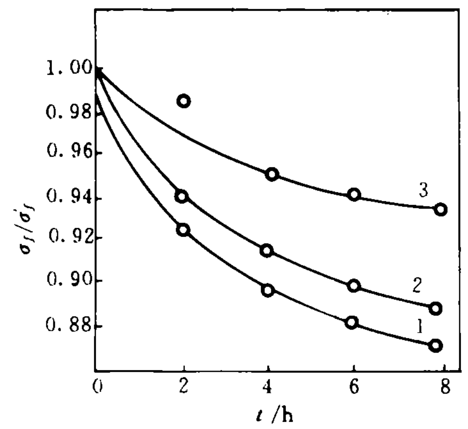

Fig. 3 Fracture stress versus hydrogen charging time

1—underaged; 2—peakaged; 3—overaged; σ'_f—Fracture stress of hydrogen uncharged specimen

σ_f—Fracture stress of hydrogen charge specimen

5 CONCLUSIONS

(1) Both Mg and H segregation make grain boundary embrittlement in high strength aluminium alloy and hydrogen embrittles grain boundary more intense than magnesium does under the same segregation content.

(2) Theoretical analysis corresponds with the experimental results.

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