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INTERNAL FRICTION ASSOCIATED WITH GRAIN BOUNDARY SEGREGATION IN Al-Mg AND Al-Na ALLOYS AFTER QUENCHING AND ANNEALING

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ABSTRACT -- The influence of solute segregation on the parameters of the grain boundary internal friction peak (GBP) and the high temperature internal friction peak (HTP) is systematically studied in two kinds of aluminium alloys (Al-Mg and Al-Na). The results show that the behavior of internal friction measured in the two kinds of Al alloys is completely different, which is attributed to different types of grain boundary (GB) segregation. The formation and resolution of second phase particles in GBs which are controlled by Mg atoms' non-equilibrium segregation at and back diffusion from GBs after quenching is the main factor to change the GBP's parameters in Al-Mg alloys. A HTP which is found in Al-Na alloy after annealing at appropriate temperature range, is supposed to be associated with Na atoms' equilibrium selective segregation at GBs which is sensitive to GB structure and temperature.

1 -- INTRODUCTION

The segregation of solute atoms to GB is believed to occur by two main mechanisms, termed equilibrium and non-equilibrium segregation according to their different driving force. It is also depended upon the structure of GBs/1,2,3/. Quenching and annealing are two basic methods for producing these two types of GB segregation. Solute segregation is undoubtedly the most influential parameter of GBs, even the GB structure itself can be altered extensively by thesegregation/2,4,5/. Large changes of internal friction curves associated with GBrelaxationare expected as a result of solute segregation. Previous results/6,7,8/ are mainly embodied in the following two aspects. a)change the parameters of GBP, b)cause a new peak other than the GBP. In this paper, it is the propose to study the relation between internal friction and solute GB segregation in Al alloys after quenching and annealing.

2 -- EXPERIMENTAL

Four kinds of Al-Mg alloy specimens (Al--0.55wt%Mg, Al--1.1wt%Mg, Al--2.4wt%Mg and Al--6.0wt%Mg) which are cold drawn from $\phi 3$ to $\phi 1\text{mm}$ (RA=89%) and one Al-Na alloy specimen (its Na concentration is within 100ppm to 300ppm) which is cold drawn from $\phi 4$ to $\phi 1\text{mm}$ (RA=94%) have been measured in the experiment. Before quenching, they were all annealed at 550°C for 0.5hr. to guarantee their same heat treatment history, their quenching temperature is respectively 350°C, 450°C, 550°C and so on. An inverted torsion pendulum apparatus is used. The situ annealing temperature can reach 640°C. The oscillation frequency is about 1hz and the effective length of specimens is about 10cm.

3 -- RESULTS

3.1. The influence of Mg concentration on the GBP's parameters after water quenching.

When Mg concentration is $< 1.1\text{wt}\%$, all GBP's parameters remained unchanged with different quenching condition and subsequently annealing condition (Fig.1,2). However, when the Mg concentration is $> 2.4\text{wt}\%$, the GBP was greatly suppressed by quenching, and it would gradually rise in the annealing process later on (Fig.3,4).

Fig.1 No effect of quenching and annealing condition on the GBP's parameters of Al-1.1wt%Mg specimen is observed. Curves 1, 2, 3 corresponding to the GBP during ascending measurement after water quenched from 590°C - subsequent descending temperature measurement with annealing time 13min. at 480°C - 3.5hr. at 460°C respectively. Curve 4 is the GBP of furnace cooling specimen during descending temperature measurement.

Fig.2 No effect of quenching & annealing condition on the GBP's Parameters of Al-0.55wt%Mg specimen is observed. Curves 1, 2 corresponding to the GBP during ascending measurement after water quenched from 550°C - subsequent descending measurement with annealing time 0.5hr. at 485°C. Curves 3, 4 corresponding to the GBP during ascending measurement after air cooled from 540°C - subsequent descending measurement with annealing time 7/4hr. at 480°C.

Fig.3 Effect of annealing time at 470°C on GBP of Al-2.4wt%Mg after water quenched from 550°C. Curves 1, 2, 3, 4, 5 are for annealing time 15min., 160min., 420min., 110min., 200min., 420min., 910min. respectively.

Fig.4 Effect of annealing temperature and time on the GBP of Al-6.0wt%Mg specimen after water quenched from 550°C. Curves 1, 2, 3 are for annealing time 15min., 160min., 420min. at 470°C respectively; curves 4, 5 are for subsequent annealing time 90min., 310min. at 520°C respectively.

3.2. The effect of quenching temperature and quenching way on the GBP's parameters in Al-2.4wt%Mg. The higher the quenching temperature and the quicker the quenching speed were, the more greatly the GBP would be suppressed. Furnace cooling or water quenching temperature $< 350^\circ\text{C}$ would not suppress the GBP any more (Fig.5).

3.3. The effect of annealing temperature and time on the GBP's parameters after water quenching from 550°C in Al-2.4wt%Mg.

When annealing temperature $\approx 400^\circ\text{C}$, the GBP's height which had been suppressed by quenching rose very slowly with annealing time, and if the annealing temperature got as high as 540°C , the rise in GBP's height was not obvious either. However, when the annealing temperature is about 470°C , we could see a clear increment in the GBP's height with annealing time (Fig.6).

Fig.5 Effect of annealing temperature on the GBP's height with annealing time after water quenched from 550°C . The annealing temperatures listed in the figure are 400°C , 450°C , 470°C , 506°C and 540°C respectively.

Fig.6 Effect of quenching temperature and quenching speed on the GBP's height with annealing time at 470°C .

Fig.7 Effect of annealing condition on the internal friction curves of Al-Na alloy. 1: $400^\circ\text{C} \times 1\text{hr.}$; 2: $478^\circ\text{C} \times 1\text{hr.}$; 3: $540^\circ\text{C} \times 1\text{hr.}$; 4: $582^\circ\text{C} \times 1\text{hr.}$; 5: $600^\circ\text{C} \times 1.5\text{hr.}$

Fig.8 Effect of annealing condition on the internal friction curves of Al-Na alloy after water quenching from 530°C . 1: $462^\circ\text{C} \times 1.5\text{hr.}$; 2: $532^\circ\text{C} \times 7/3\text{hr.}$; 3: $550^\circ\text{C} \times 1.5\text{hr.}$ then drop the temperature to 474°C and for $7/3\text{hr.}$; 4: $620^\circ\text{C} \times 1\text{hr.}$

Fig. 9 A small peak ($\sim 370^\circ\text{C}$) appears after subtraction of the background for Al-Na specimen. a: annealed at 530°C for 7/3hr after water quenching. b: annealed at 540°C for 1hr without quenching treatment.

3.4 The effect of quenching and annealing condition on GBP and HTP in Al--Na alloy (Fig.7,8)

The GBP's parameters were not influenced by water quenching. However, if the annealing temperature reached the range of $510^\circ\text{C} \sim 540^\circ\text{C}$, whatever quenching or not, a small HTP would appear (Fig.9) which was not observed in Al-Mg alloys, higher or lower temperature annealing would not favour its existence. There is a weak growth--decline relation between HTP and GBP.

4 -- DISCUSSIONS

4.1. Solute atoms' concentration in GBs and the parameters of GBP

As we discussed in (S. P. Wu and L. D. Zhang, to be published), the solute atoms in GBs can give rise to weak blocking effect on the GB's sliding. The more solute atoms in GBs are, the smaller the GBP's height will be.

4.2. Quenching temperature and non-equilibrium GB segregation

It is known that one of the most important characters of quenching process is that it can produce a lot of supersaturated quench--in vacancies, and then, there must exist a vacancy gradient--vacancy flow. The segregation generated by this vacancy flow to GBs can be considered in terms of two processes: I) reverse atom flow which is a direct of vacancy flow, and II) the dragging of solute atoms by vacancies, i.e. the vacancy--solute atom complex flow. In the first process, the solute atoms and vacancies move in the opposite while in the second they flow in the same direction. As Mg atom is a very effective vacancy trapper, the second process is dominant after quenching in Al--Mg alloy, which can give rise to the enrichment of Mg atoms at GBs.

Now let us discuss the whole Mg atoms' non-equilibrium GB segregation process by estimating some parameters after quenching.

a) The concentration of quench--in vacancies may be expressed as:

$$\Delta C_v = K_v \cdot \exp(-E_f/KT) \quad (1)$$

where K_v (10^6) contains geometric and entropy terms, and E_f , the vacancy formation energy is 0.76eV. The concentration of Mg--vacancy complexes, $[C]_c$, obeys a similar relation but also depends on ΔC_v and the Mg bulk concentration, $[C]_s$:

$$[C]_c = [C]_s \cdot \Delta C_v \cdot K_c \cdot \exp(E_b/KT) \quad (2)$$

where K_c (10^6) contains geometric and entropy terms and E_b , the Mg--vacancy binding energy, is 0.1~0.2eV.

b) The volume ratio β occupied by GBs locates in the range of $10^{-5} \sim 10^{-6}$ if the diameter of grain and the thickness of GB are 0.3mm and 10Å respectively.
 If we suppose that all the complexes may reach GBs, the increment of Mg atoms' concentration at GBs resulted from this Mg--vacancy flow may be expressed as: $\Delta[C]_{Mg} \approx [C]_c / \beta$
 The quantities of ΔC_v , $[C]_c$ and $\Delta[C]_{Mg}$ are listed in table 1 with different quenching temperature.

Table 1. The concentration of quench--in vacancies ΔC_v , Mg--vacancy complexes $[C]_c$, and the increment of Mg atoms' concentration $\Delta[C]_{Mg}$ with different quenching temperature T_q .

T_q	ΔC_v	$[C]_c$	$\Delta[C]_{Mg}$
350°C	$5 \times 10^8 \sim 10^{-7}$	$10^7 \sim 10^{-6}$	$10^1\%$
450°C	$7 \times 10^7 \sim 10^{-6}$	$10^8 \sim 10^{-7}$	$10^0\%$
550°C	$5 \times 10^6 \sim 10^{-5}$	$10^9 \sim 10^{-8}$	$10^1\%$

Clearly, when quenching temperature is as low as 350°C, there is little increment of Mg atoms in GBs, the higher the temperature prior to quenching is, the more Mg atoms will be segregated at GBs and then the more greatly the GBP will be suppressed.

As for Al--Na specimen, because of its very low bulk concentration and less effectiveness in trapping vacancies, the first process will be dominant in eliminating those quench--in vacancies. This is not favourable for the enrichment of Na atoms in GBs, and then not favourable for any suppression of the GBP and the appearance of the HTP.

4.3. Annealing temperature and Mg atoms' back diffusion from GBs after quenching--the appearance of Al--Mg phase in GBs.

The Mg atoms which has been segregated at GBs during a quench are not in thermal--equilibrium state. They will be eliminated by diffusion from GBs under certain condition. According to the relation of $\tau = P \approx v_0 \cdot \exp(-Q/KT)$ (3)

where P is the hopping frequency of Mg atom from GB, $v_0 \sim 10$ sec, Q is the activation energy of the diffusion process. The datum of P and τ are listed in table 2 for different annealing temperature.

Table 2. The hopping frequency P - time τ in different annealing temperature T_a with different activation energy Q .

$Q = Q_d + 0.5 Q_s \approx 1.4\text{ev}$			$Q = Q_d + 0.5 Q_s + Q' \approx 2.3\text{ev}$		
T_a	$P(\text{sec}^{-1})$	$\tau(\text{sec})$	T_a	$P(\text{sec}^{-1})$	τ
230°C	10^{-2}	10^2	400°C	10^{-6}	10^3hr.
400°C	10^{-2}	$10^7 \sim 10^{-2}$	470°C	10^{-4}	10^0hr.
550°C	10^{-4}	10^{-4}	540°C	10^{-3}	$10^1 \sim 10^0\text{min.}$

Now, if Mg atoms in GBs are in solid solution state, then

$$Q = Q_d + 0.5 Q_s \approx 1.4\text{ev.} \quad (4)$$

where Q_d (32Kcal/mol) is Mg atom's bulk diffusion energy and Q_s (1.4Kcal/mol) is Mg atom's GB segregation energy. From the datum in table 2, we come to the conclusion that the process of Mg atom's back diffusion would have been accomplished during the first ascending temperature process completely, even during quenching process itself! This seem to be corresponding to the case of Al--0.55wt%Mg and Al--1.1wt%Mg specimens. Certainly, there will not appear any suppression of the GBP after quenching. However, when the bulk concentration of Mg gets as high as 2.4wt%, Mg atom's enrichment will result in the appearance of Al--Mg second phase in GBs. This view point has been supported by phase analysis using X-ray diffraction techniques. In this case, resolution of the phase which acquire a activation energy Q' must be in process before Mg atom's diffusion from GBs. According to the phenomena observed in internal friction curves ($T_a=470^\circ\text{C}$, $\tau \approx 10^0\text{hr.}$), $Q'=0.9\text{ev.}$ is obtained and the parameters of P and τ for other annealing temperature are listed in table 2. For $T_a \approx 400^\circ\text{C}$, τ is too large for us to observe the obvious rise of GBP with annealing time; for $T_a \approx 540^\circ\text{C}$, however, τ is too small, the process of phase's resolution and Mg atom's diffusion have been almost accomplished during the first descending measurement. Both the two temperatures are not favorable for us to observe the obvious variation of GBP's parameters with annealing time in the subsequent descending measurement. This is in good agreement with our experiment phenomena observed.

4.4. The transformation of GB's structure and the HTP in Al--Na alloy.

The transformation of GB's structure will occur under certain condition/4,5/. In Al--Mg alloys, the process of Mg atoms' back diffusion which can eliminate the segregated Mg atoms, and the process of GB's structure transformation which permits GBs to preserve more Mg atoms are coexistence. High temperature and high concentration of Mg atoms in GBs will be favourable to this transformation. This is the main reason that the GBP's saturated height can not return to its initial position after high temperature (550°C) quenching or during high temperature (540°C) annealing.

In the Al--Na alloy, however, as Na has a larger atom radius and then a much larger GB segregation energy, its equilibrium segregation will be stronger and more sensitive to GB structure: i.e. selective segregation at GBs. Those GBs in which exist more Na atoms attribute the HTP, and those with relative fewer Na atoms attribute the original GBP. Because the annealing temperature is one of the main factors for the transformation of GB's structure which may result in increment of Na atoms' concentration in GBs, the appearance of the HTP will be greatly influenced by it.

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