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The influence of Al content on the Zener relaxation of Fe–Al alloys

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Abstract

The effect of Al content on the Zener relaxation peak of annealed Fe–Al alloys has been investigated using a computer-controlled automatic inverted torsion pendulum through the method of free decay and forced vibration. It has been shown that alloys with medium Al contents show strong relaxation while lower or higher Al contents lead to relatively weak Zener relaxation peaks. The Zener relaxation in Fe–Al alloys originates from the next-nearest-neighbour atom pairs and their interaction rather than the nearest-neighbour atom pairs. The latter may not produce Zener relaxation because of the ordered structure, which suppresses Zener relaxation.

1. Introduction

Zener relaxation is believed to occur due to a stress-induced reorientation of solute atom pairs present in the solid solution in a nearest-neighbour configuration [1], which has been observed in many alloys. Fischbach and Zener were the first to find Zener relaxation, in bcc Fe₈₅Al₁₅ and in Fe₈₃Al₁₇ at 520 °C, 1.3 Hz with an activation energy of 2.47 eV [1]. Subsequently, Golovin also found this relaxation phenomenon in Fe–Al–C alloys with Al content over 11 at.% [2]. From the reported results, it appears that Zener relaxation is a general property of Fe-based alloys and correlated with Al atoms. However, there is very little work that systematically studies the effect of Al content on Zener relaxation for Fe–Al alloys.

Fe–Al alloys have recently attracted much attention because of their low density, better oxidation resistance and mechanical properties when considered as high temperature structural materials. Their structures and properties are greatly dependent on the Al content and heat treatment regime. Slowly cooled Fe–Al alloys possess a disordered single α phase at 0–22 at.% Al, or with a DO₃ structure at 23–36% Al or a B₂ structure at 36–50% Al [3]. But in fact, several different phases can coexist near stoichiometric compositions. It is extremely important

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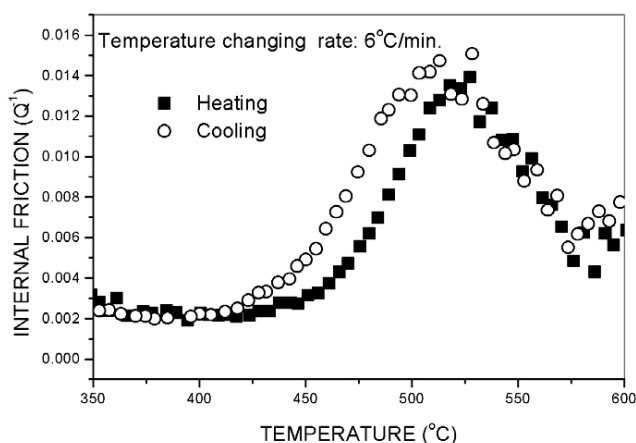


Figure 1. Internal friction versus temperature during heating and cooling cycles for furnace-cooled Fe₇₁Al₂₉ alloy (free decay, strain amplitude 4.5×10^{-5} , vibration frequency $f \approx 1.7$ Hz).

to study the laws of transformation among the structures from the atomic scale and to recognize the dependence of these changes on Al atoms. Almost all of the studies performed so far were based on diffusion and defect measurements [3–7], which have to be carried out under higher temperature.

In the present study, the internal friction technique was utilized to study the atom movement and the phase transformation in Fe–Al alloys, particularly the effect of Al on the microstructure of the alloys, in the expectation of obtaining clear information on the microstructure development of Fe–Al alloys.

2. Experimental details

Fe–Al alloy specimens with Al contents of 10.5, 17, 23, 29 and 38 at.% were prepared in a vacuum induction furnace. The commercially pure Fe and Al were melted at about 1600 °C and poured into a mould with a diameter of 40 mm. The specimens used in the internal friction measurement were cut from ingots and had dimensions 68 mm × 1.7 mm × 0.9 mm. In order to guarantee the same specimen state, they were annealed at 900 °C for 1 h in an argon atmosphere. Internal friction (Q^{-1}) measurements were performed using a computer-controlled automatic inverted torsion pendulum by the method of free decay and forced vibration. This apparatus basically consists of an inverted torsion pendulum, a temperature programmer and a photoelectron transformer. The whole measurement is controlled using an IBM* PC586 computer and an 8087 processor and the data can be processed in real time. The range of the maximum excitation torsion strain amplitude is 10^{-6} – 10^{-4} . The resolution in the internal friction measurement is 1×10^{-4} . The details of the experimental apparatus were described in [8]. The specimen state was determined using x-ray diffraction (XRD) at room temperature ($\lambda_{Cu} = 1.54056$ Å).

3. Results and discussion

Figure 1 shows the internal friction curves in a heating and a cooling cycle for annealed Fe₇₁Al₂₉ alloy. It can be seen that a peak appears in both curves at around 510 °C. The peak temperature during cooling is relatively low compared to that during heating.

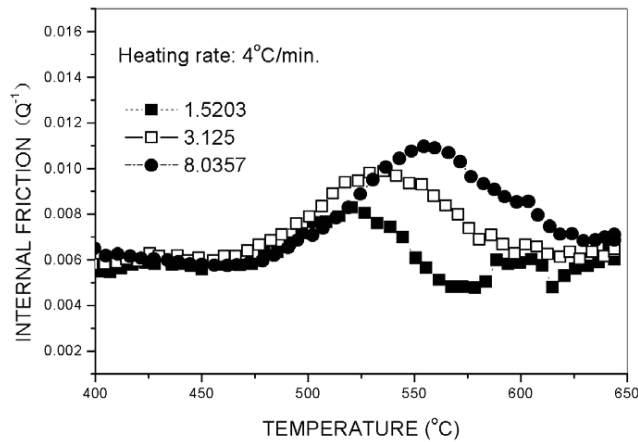


Figure 2. The dependence of the Zener peak on the measuring frequencies (forced vibration).

Figure 2 shows the dependence of the peak on the measuring frequency for the $\text{Fe}_{71}\text{Al}_{29}$ alloy. It is obvious that the peak shifts to higher temperature with increasing frequency. In order to get the exact peak temperature corresponding to each measuring frequency, the internal friction background was subtracted from the curves by the following procedure. It is known that an internal friction background, Q_b^{-1} , as a function of temperature, T , can be expressed as [9]

$$Q_b^{-1} = A + B \exp(-C/kT) \quad (1)$$

where A , B and C are constants and k is the Boltzmann constant. It is shown from equation (1) that the internal friction background monotonically increases with temperature. However, the present results show a different tendency, as shown in figure 2. There is no discernible dependence of the internal friction background on the temperature and the two sides of the peaks have almost the same background. Therefore, the peak temperatures can be directly read from the curves. On the basis of the peak temperature, a Napierian logarithm plot of the circular frequency ω ($=2\pi f$, where f is measuring frequency) versus the reciprocal of the peak temperature $1/T_m$ (T_m is the peak temperature) can be drawn in terms of the Arrhenius relation [1], as shown in figure 3. As is known, the relaxation peak arises when $\omega\tau = 1$ [1] (τ is the mean relaxation time). From the slope and the intercept of the straight line in figure 3, the mean activation energy H for this peak was obtained as 2.46 (± 0.11) eV and the mean pre-exponential factor as $\tau_0 = 2.4 \times 10^{-17(\pm 1)}$ s. It is suggested that the peak could originate from the diffusion of Al atoms because this activation energy is comparable to the self-diffusion activation energy of Al atoms in Fe–Al alloys. As is known, the self-diffusion activation energy values of Al and Fe atoms in Fe–Al alloys are of the same order of magnitude. For Fe atoms in $\text{Fe}_{74.5}\text{Al}_{25.5}$ alloy, the activation energy values are 2.26 eV ($8.1_{-4.7}^{+9.1} \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$) for A2 structure and 2.88 eV ($3.3_{-1.9}^{+0.4} \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$) for DO_3 structure, respectively [3]. Obviously, the activation energy of the peak is between those for A2 structure and DO_3 structure, indicating that the alloy does not have a perfect DO_3 structure.

According to [1], the pre-exponential factor for the diffusion process is given by

$$D_0 = \alpha a^2 \omega_0 \quad (2)$$

where D_0 is the pre-exponential factor for a diffusion process, α is a constant, a is the lattice parameter and ω_0 is the pre-factor of the diffusional jump rate for jumps between nearest-neighbour sites.

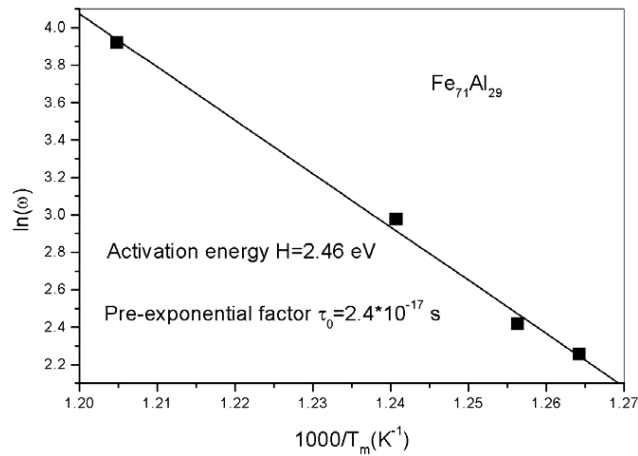


Figure 3. The Napierian logarithm of the circular frequency ω versus the reciprocal of the peak temperature ($1/T_m$) (forced vibration).

For a point defect relaxation process [1], we have

$$\tau_0^{-1} = b\omega_0 \quad (3)$$

where τ_0^{-1} is the reciprocal of the pre-exponential factor for a relaxation process and b is a numerical factor. By introducing equation (2) into (3), we have

$$D_0 = \frac{\alpha a^2}{b\tau_0}. \quad (4)$$

For substitutional diffusion in the bcc lattice, α equals 1 and b is estimated to be of the order of 10 for point defect relaxation [1]. For α -Fe, $a = 2.8664 \times 10^{-10}$ m [10]; thus D_0 is $3.4 \times 10^{-4(\pm 1)}$ m² s⁻¹. As mentioned above, D_0 for the peak is larger than that for A2 structure and smaller than that for DO₃ structure. The observed relaxation peak is therefore related to the process of diffusion of point defects in Fe–Al alloys.

Golovin found an internal friction peak in Fe–Al–C alloys with Al content over 11 at.% at about 515 °C and proved it to be a Zener relaxation [2]. Fischbach also observed Zener relaxation in Fe₈₅Al₁₅ alloy at 520 °C with an activation energy of 2.47 eV [1]. These reported activation energies and peak temperatures are in good agreement with the present data, suggesting that the observed internal friction peak is a Zener relaxation arising from the diffusion of Al atoms in α -Fe.

Since the peak originates from Al atoms, the variation in Al concentration should have some influence on it. Figures 4 and 5 show the relationship of the relaxation strength of the peak with the Al content. It is seen that the Al content has a nonmonotonic influence on the relaxation strength; i.e. the peak height first increases with Al content until it reaches a maximum and then declines with further increasing Al content. The alloy with a medium Al content shows the highest relaxation strength.

It is well known that substitutional atom pairs and their interaction are the essential origin of the Zener relaxation in Fe-based alloys. For Fe–Al alloys (0–22% Al) in the disordered α -structure state, Fe atoms and Al atoms randomly distribute over the bcc lattices with almost all the Al atoms in the form of atom pairs. While most Al atom pairs are located at next-nearest-neighbour sites at the ‘corners’, such as the a , c positions shown in figure 6 [2], there are fewer atom pairs at the next-nearest-neighbour locations. Accordingly, the interaction

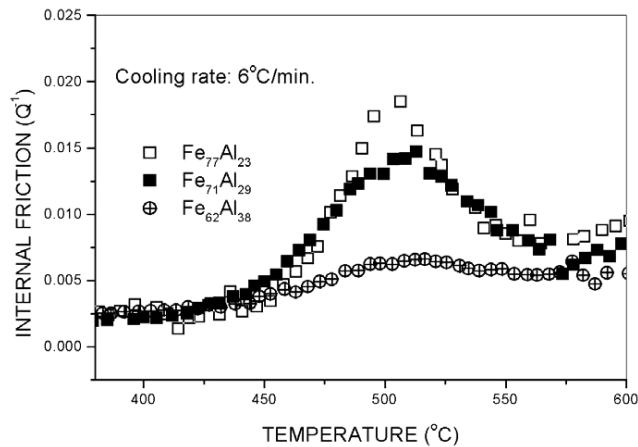


Figure 4. Internal friction versus temperature for furnace-cooled Fe–Al alloys with varied Al content (free decay).

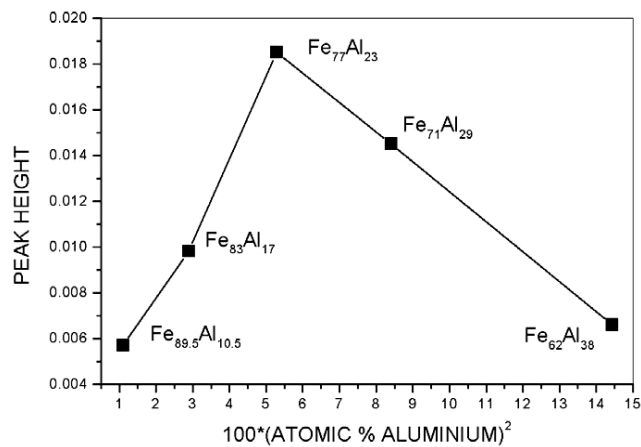


Figure 5. The variation of the peak height with the Al content.

among the Al atom pairs in the latter case is relatively weak and thus the internal friction peak is not very high even if a relaxation process is induced. However, the Al atom pairs in the next-nearest-neighbour locations will increase in number as the Al content increases, leading the interaction among the atom pairs to intensify and thus the Zener relaxation strength to increase. This phenomenon has in fact been summarized by Nowick *et al* [1] using the expression $\Delta \propto X^2$, where Δ is the relaxation strength and X is the solute concentration; i.e. the Zener relaxation strength will rapidly rise with increasing solute concentration.

When the Al content is over 22%, however, there will be surplus Al atoms entering the ‘centre’ positions, such as the *b*, *d* sites shown in figure 6, forming some nearest-neighbour Al atom pairs in ‘corner’ positions and producing short-range ordering or even long-range ordering. This is well demonstrated by the XRD results on the furnace-cooled Fe₇₁Al₂₉ and Fe₇₇Al₂₃ alloys shown in figure 7. There is a (100) reflection in Fe₇₁Al₂₉ alloy that is direct evidence of short-range ordering corresponding to the DO₃ structure. In contrast, no (100) reflection appears in the Fe₇₇Al₂₃ alloy, indicating that no ordering phase exists in it.

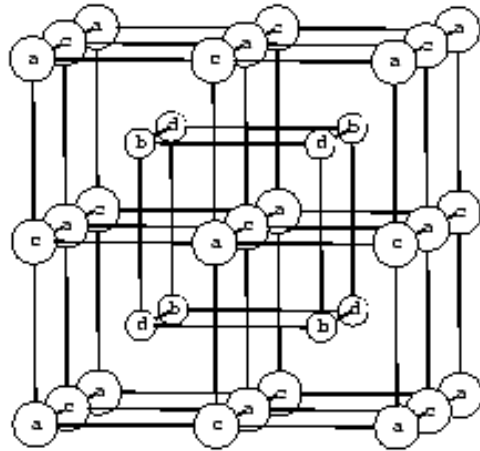


Figure 6. The schematic arrangement of atoms in Fe–Al alloys: *a* and *c* indicate ‘corner’ positions; *b* and *d* indicate ‘centre’ positions. The DO₃ structure is such a structure with sites *a*, *c* and *d* occupied by Fe atoms while sites *b* are occupied by Al atoms. The B₂ structure is such a structure with the *a* and *c* positions occupied by Fe atoms while sites *b* and *d* are occupied by Al atoms.

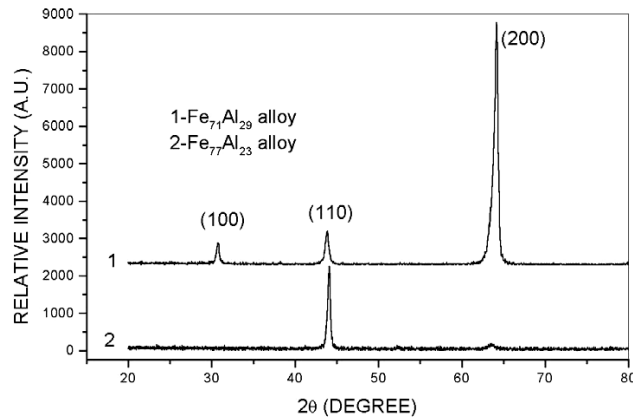


Figure 7. XRD curves for the furnace-cooled Fe₇₁Al₂₉ and Fe₇₁Al₂₉ alloys.

Generally speaking, the relaxation strength produced by the nearest-neighbour atom pairs is much stronger than that produced by the next-nearest-neighbour atom pairs. As mentioned above, Al atoms in ‘centre’ positions may promote short-range ordering that will suppress the Zener relaxation. It is therefore quite difficult for the nearest-neighbour Al atom pairs to produce Zener relaxation. Theoretically, there are no Al atoms in the ‘corners’ for Al content between 25 and 50 at.% because they have been preferentially occupied by Fe atoms. This is why the relaxation strength is relatively low when Al contents fall inside this range.

The effect of the Al content on the relaxation strength can also be understood from the following expression [1]:

$$\delta J = [v_0 f(\chi_0, X) X^2 (1 - X)^2 / kT] \sum_p (\lambda^{(p)})^2 \quad (5)$$

where δJ is relaxation magnitude, v_0 is atom volume, $f(\chi_0, X)$ is a function of χ_0 and X , $f(\chi_0, X) = 1$ for complete randomness and $f(\chi_0, X) = 0$ for perfect long-range ordering

and

$$\sum_p (\lambda^{(p)})^2 = \beta \eta^2 a^2 / v_0 \quad (6)$$

where β is a dimensionless geometrical parameter and $\eta = du_p/da_p$, where u_p is the ordering energy and a_p is the interatomic spacing in the direction of p .

Combining the equations (5) and (6), we get

$$\delta J = [f(\chi_0, X)X^2(1 - X)^2/kT]\beta\eta^2a^2. \quad (7)$$

For a disordered alloy with Al content in the range 0–22%, $f(\chi_0, X) \approx 1$; thus the relaxation strength roughly follows a square law with the Al content, X , according to equation (7). For higher Al content, e.g. 23–38% Al, $f(\chi_0, X)$ is between 0 and 1 and increases with Al content. Also, a higher Al content can cause a smaller u_p and a greater a_p , producing smaller η . Both situations lead to decaying relaxation strength.

4. Conclusions

An internal friction peak was found at around 510 °C for Fe–Al alloys and the peak was proved to be a Zener relaxation peak with an activation energy of 2.46 (± 0.11) eV. The present results show that the Al content has a significant influence on the relaxation strength. With lower Al content, Al atoms only occupy the ‘corner’ positions, forming a limited number of next-nearest-neighbour atom pairs. The alloy shows a relatively weak Zener relaxation peak due to the weak interaction among these atom pairs. The next-nearest-neighbour atom pairs will increase in number with Al content, making the interaction and thus the relaxation strength increase. However, excessively high Al content can force some Al atoms to move to the ‘centre’ positions and increase the degree of order, resulting in DO₃ or B₂ structure. Zener relaxation is therefore significantly suppressed. It is therefore concluded that the Zener relaxation in Fe–Al alloys is attributable to Al atom pairs in next-nearest-neighbour positions.

Acknowledgments

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