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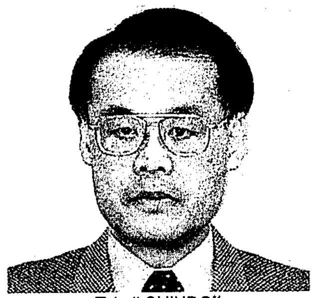
Effect of Alloying Elements on Grain-Boundary Relaxation in α-Titanium



Takuji SHINDO*1

Abstract

Internal friction measurements at high temperatures ranging from 300K to 993K have been conducted on various titanium alloys :Ti-O, Ti-N, Ti-C, Ti-X (X=Ni, Cu, Fe, V, Mo, Al). Effects of interstitials and substitutionals on grain-boundary relaxation peaks in α-titanium were discussed especially in respect to grain boundary segregation of solutes or formation of second phase such as β-phase or intermetallic compounds.

1. Introduction

When metals are exposed to high temperatures above 0.4 Tm (Tm: melting point), softening at grain boundaries in the primary stage of creep can be identified, for example, by grain-boundary relaxation[1-2] which is related to the viscous sliding at the grain boundary. Although the creep resistant properties in the primary stage of titanium and titanium alloys critically depend on the softening characteristics at the grain boundaries, few basic studies so far have been conducted on grain-boundary relaxation phenomena[3-7] and further clarification is required. In this study, to investigate the effect of alloying elements on grain-boundary relaxation peaks, measurements were made of the variation of internal friction with temperature ranging from 300 K to 993 K for various titanium alloys, such as Ti-O alloy, Ti-N alloy, Ti-C alloy, Ti-X (X = Ni, Cu, Fe, Cr, V, Mo, and Al) system binary alloys, Ti-6Al-4V alloy, and Ti-O-N-Fe system alloy[8]. Experimental results have been intensively discussed in terms of grain boundary segregation of solutes and the formation of second phases such as β-phase and intermetallic compounds .

2. Experimental procedures

2.1 Materials used and preparation of test specimens

The materials used for the measurements were nine types of binary system titanium alloys, (1) through (9) listed below, and also two types of multi-components commercial titanium alloys, (10) and (11) listed below.

(1) Ti-O (0.42 mass%O) alloy
(2) Ti-N (0.05-0.8 mass%N) alloy
(3) Ti-C (0.05-0.4 mass%C) alloy
(4) Ti-Ni (0.05-0.8 mass%Ni) alloy
(5) Ti-Cu (0.5-2.5 mass%Cu) alloy
(6) Ti-Fe (0.01-0.5 mass%Fe) alloy
(7) Ti-Cr (0.05-0.8 mass%Cr) alloy
(8) Ti-Mo (0.05-2.0 mass%Mo) alloy

*1 Inoue Superliquid Project, Exploratory Research for Advanced Technology, Japan Science and Technology Corporation

(9) Ti-Al (6 mass%Al) alloy
(10) Ti-6 mass%Al-4 mass%V alloy
(11) Ti-0.2 mass%O-0.1 mass%N-0.5 mass%Fe alloy

These alloys were melted, using 100-g button vacuum arc melting, and subsequently underwent hot forging (heating at 1,173 K, forged to dimensions of 15 mm in diameter and 100 mm in length), hot rolling (heating at 1,123 K, rolled from the dimensions of 15 mm in diameter to 4 mm in thickness), then followed by annealing (at 973 K for 3.6 ks). The annealed sheet thus made was mechanically ground to sheet specimens (dimensions: 0.8 mm in thickness, 1.0 mm in width, and 60 mm in length) for internal friction measurements. The prepared sheet specimens were further processed by short time annealing (at 973 K for 300 s) to eliminate the microscopic strains induced by the mechanical grinding, and then quenched by the blowing of inert gas.

2.2 Internal friction measurement at high temperatures

Internal friction (Q^{-1}) is known to be a structure-sensitive physical property that is highly dependent on the metallurgical states of solute atoms which exist as precipitates or in solution in the matrix, the interactive behaviors between solutes and dislocations, and the degree of grain boundary segregation[9]. Therefore, it is possible to observe in-situ such microstructural evolutions by internal friction measurements from room temperature up to high temperatures at which grain-boundary relaxation peaks appear. In this study, the temperature was controlled from room temperature to about 800 K at a heating rate of 0.05 K/s (3°C/min) and internal friction values (Q^{-1}) were measured by the inverted torsion pendulum method in which torsional oscillation was applied at a frequency of about 1 Hz. The atmosphere in the vacuum chamber was maintained at the pressure of about 1.0×10^{-2} Torr., with a feeding of trace amounts of He gas to keep the temperature of the specimen at the same level as the thermocouples which are closely arranged to the specimen. The effective dimensions of the specimen were 0.8 mm (thickness) × 1.0 mm (width) × 50 mm (length).

2.3 Grain-boundary relaxation and mathematical models

Internal friction due to grain-boundary relaxation phenomena is usually observed at temperatures higher than about 723 K at which micro creep starts to appear at the grain boundary. The grain-boundary relaxation phenomenon is explained by using the following mathematical models[10]. If the grain-boundary section is assumed to be an anelastic solid with viscous sliding at the grain-boundary, the following relationship is established between the modulus of elasticity M of the anelastic solid, elastic compliance J, flow stress σ, and strain by viscous sliding at the grain boundary ε.

$$\sigma = M\varepsilon \quad (1)$$

$$\varepsilon = J\sigma \quad \text{(where, } M = 1/J\text{)} \quad (2)$$

An anelastic solid system containing a viscous solid system (viscosity: $\eta = \tau_\sigma / \delta J$, τ_σ: stress dependent relaxation time constant), which corresponds to the grain-boundary and is called as Newton's dashpot, can be regarded as a Voigh's type standard linear solid. In such a system, the following relationship is established between the stress σ, time-variable rate of stress $\dot{\sigma}$, strain ε, and strain rate $\dot{\varepsilon}$, which serves well as a model of the grain-boundary relaxation mech-anism:

$$J_R \sigma + \tau_\sigma J_u \dot{\sigma} = \varepsilon + \tau_\sigma \dot{\varepsilon} \quad (3)$$

where, J_R is relaxed elastic compliance and J_U is unrelaxed elastic compliance.

The solution to equation (3) at time t is expressed by equations (4)-(8) below.

$$J(t) = \varepsilon(t)/\sigma_0 = J_U + \delta J(1 - e^{-t/\tau}) \quad (4)$$

$$J_R/J_U = 1 + \Delta \quad (5)$$

The relaxation strength Δ above is defined by the following equation:

$$\Delta \equiv (J_R - J_U)/J_U \quad (6)$$

The vibrational stress σ at an angular frequency of ω is obtained by:

$$\sigma = \sigma_0 e^{i\omega t} \quad (7)$$

The internal friction Q^{-1} under this vibrational stress is expressed by:

$$Q^{-1} = \Delta \cdot \omega\tau/(1+\omega^2\tau^2) \quad (8)$$

Equation (8) produces the maximum value (relaxation peak) when the condition of

$$\omega\tau = 1 \quad (9)$$

is satisfied. If ω remains invariant, in other words if kept under 1-Hz torsional oscillation stress, the grain-boundary relaxation peak is observed at the temperature T which satisfies the equation $\omega\tau = \omega\tau_0\exp(Q/RT) = 1$. In this case, Q is the activation energy in relaxational kinetics and R is a gas constant. Thus, the model predicts fairly well the appearance of relaxation peak observed in the experiment. The actual measured value Q^{-1} of polycrystalline materials consists of two component parts, a background steadily increasing with temperature (as like a single crystal without any grain boundary) and a peak confined to a limited temperature range.

3. Results and discussion

3.1 Grain-boundary relaxation peaks of Ti-O, Ti-N, and Ti-C alloys

This section discusses the influence of interstitial type atoms O, N, and C on the grain-boundary relaxation peaks in α-Ti phase. **Fig. 1** shows the results of measurement of internal friction Q^{-1} of Ti-0.42 mass %O and Ti-0.05 mass %N alloy at high temperatures. Both alloys showed an increase in the value of Q^{-1} due to the grain-boundary relaxation phenomenon at temperatures higher than 773 K (500°C) approximately. In the case of Ti-0.05 mass% N alloy, a relaxation peak was apparently observed at about 927 K (640°C).

Fig. 2 shows the internal friction Q^{-1} measurements of four types of Ti-N alloys each having a different N content. Single relaxation peak for each alloy is identified as is well known that only the characteristic grain-boundary relaxation peak of α-Ti phase is observed in the α-solid-solutions containing interstitial O or N. The grain boundary peak in this case is equivalent to be a solvent peak, which is discussed later, and subject to the influence of the solutes. In this study, the amount of N content was varied between 0.05 mass % to 0.8 mass % and each alloy showed a single grain-boundary relaxation peak in a temperature range between 927 K and 953 K (640°C and 680°C). TP is defined as the critical temperature of relaxation peak at which the value Q^{-1} reaches the maximum. Tp in the Ti-N

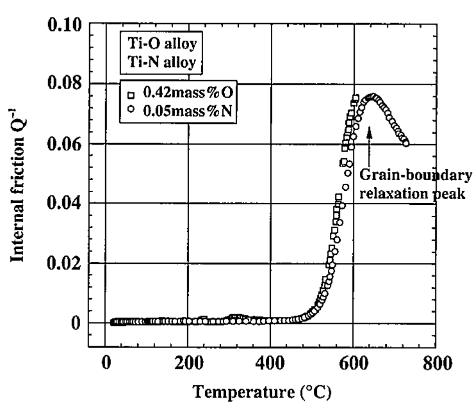


Fig. 1 Results of internal friction measurement of Ti-0.42 mass %O alloy and Ti-0.05 mass %N alloy at high temperatures

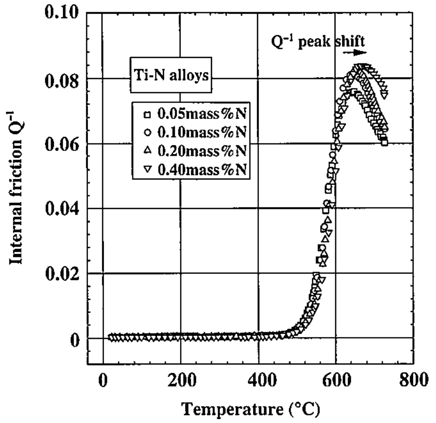


Fig. 2 Results of internal friction measurement of Ti-N alloys at high temperatures

alloy moves toward higher temperatures with the increase of N content. The Q^{-1} value at Tp (Q^{-1} value(Tp), hereafter) also increased slightly with the increase of N content.

Fig. 3 shows the influence of N on the temperature dependence of the ratio of shear modulus, G_T/G_{298K}, which is obtained by calculating the ratio from the oscillation frequency at a temperature T on the basis of the relationship (Oscillation frequency)^2 = Const.(G_T/G_{298K}). As Fig. 3 clearly demonstrates, the apparent shear modulus decreases remarkably due to softening at grain boundaries in the temperature range above 833 K (560°C) at which the grain-boundary relaxation peaks begin to increase. The decrease in the apparent shear modulus with increase in temperature is suppressed by the large amount of N content. **Fig. 4** shows the Q^{-1} values for Ti-C alloys.

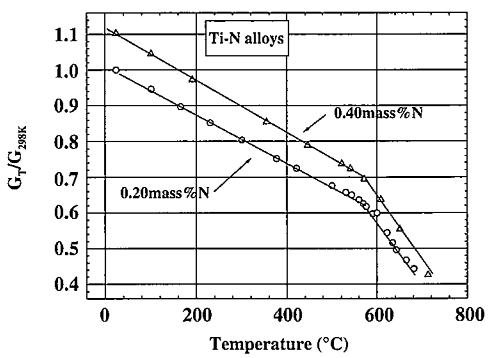


Fig. 3 Influence of the amount of N content on the temperature dependence of ratio of shear modulus G_T/G_{298K} in Ti-N alloys

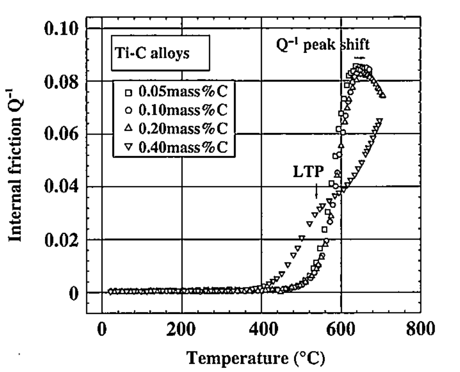


Fig. 4 Results of internal friction measurement of Ti-C alloys at high temperatures

The 0.05-0.2 mass %C various materials whose C contents are lower than the maximum solubility limit of α-Ti phase (0.3 mass%) showed a single grain-boundary relaxation peak, while the peak temperature Tp slightly increased with the increase of C content. On the other hand, the 0.4 mass %C material showed a low temperature peak (LTP) at about 813 K (540°C). The appearance of LTP can be attributed to the precipitation of TiC at grain-boundaries due to the addition of large amount of C which exceeds the maximum solubility limit of α-Ti phase, thus changing the characteristics of viscous sliding at the grain-boundary.

3.2 Grain-boundary relaxation peaks of β-eutectoid Ti-X (X = Fe, Cu, and Ni) system alloy

Of the substitutional atoms which influence the grain-boundary relaxation peaks in α-Ti phase, the influence of β-eutectoid atoms such as Fe, Cu, and Ni was studied. **Fig. 5** shows the Q^{-1} values of Ti-Fe alloys. The grain-boundary relaxation peak profile of the 0.012 mass% Fe and 0.044 mass% Fe materials which contain a trace amount of Fe of less than the maximum solubility limit of α-Ti phase (about 0.056 mass% Fe, beyond which supersaturation of solute is maintained) resembles the solvent peak profile of the Ti-N alloy which contains only interstitial type atoms as shown in Fig. 1. In the case of the 0.094 mass %Fe material, the entire Q^{-1} value profile moves to lower temperatures by about 50 K. This is considered to be caused by the grain-refinement induced by the precipitation of Fe-enriched β-phase at grain-boundary of α-Ti phase.

Fig. 6 shows the Q^{-1} values of Ti-Cu alloys. All the Cu-containing materials ranging from 0.5 to 2.5 mass %Cu showed grain bound-

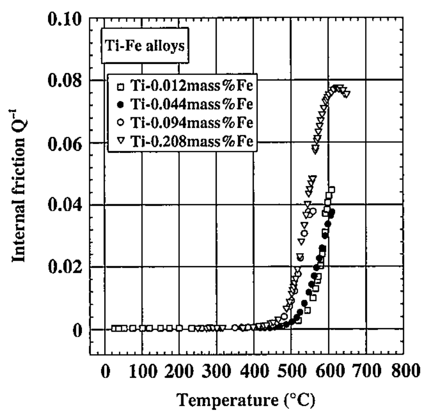


Fig. 5 Results of internal friction measurement at high temperatures of Ti-Fe alloys

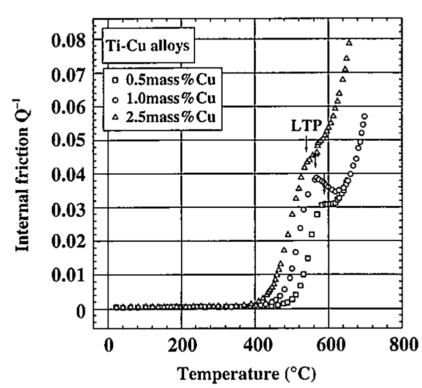


Fig. 6 Results of internal friction measurement at high temperatures of Ti-Cu alloys

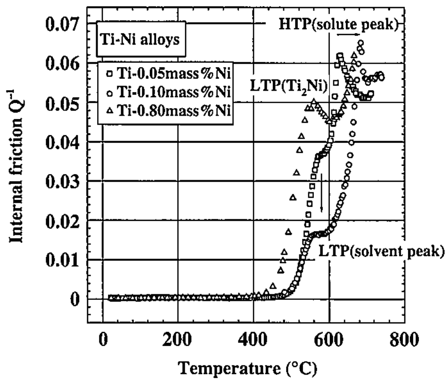


Fig. 7 Results of internal friction measurement at high temperatures of Ti-Ni alloys

ary relaxation low temperature peaks LTPs (the peak temperature is referred to as T_{PL} hereafter). Although the T_{PL} reduced with the increase of Cu content from 853 K (580°C) to 803 K (535°C), the Q^{-1} value (T_{PL}) increased with the increase of Cu content. The maximum solubility limit of Cu in the α-Ti phase at the eutectoid temperature (1,063 K) of a Ti-Cu alloy is about 2.1 mass %, however, the solubility limit of Cu at around 853 K reduced to 0.4 mass % or lower. Accordingly it is highly probable that all the alloys with Cu content varying from 0.5 to 2.5 mass % produce Ti_2Cu precipitates at the grain boundaries[11]. Therefore, it is considered that the low temperature peaks LTPs for Ti-Cu alloys are attributed to Ti_2Cu precipitates.

Fig. 7 shows the Q^{-1} values of Ti-Ni alloys. The variation of relaxation peaks with temperature of these alloys is different from that of Ti-Cu alloys. In the case of 0.05 mass %Ni material, a low temperature peak LTP at 833 K (560°C) and a high temperature peak HTP at 893 K (620°C) were observed. Regarding the 0.10 mass %Ni material, the Q^{-1} value (T_{PL}) at the low temperature peak reduced, while T_{PH} at the high temperature peak moved toward higher temperatures by about 60 K. The low temperature peaks and high temperature peaks of these materials correspond to solvent peaks and solute peaks[12], respectively. The relaxation process of the solvent peak is principally controlled by the grain boundary sliding which is influenced by segregation of solute atoms. Under those circumstances, it is believed that the Q^{-1} value of solvent peak and solvent peak temperature Tp decrease as the segregation of solute atoms at grain boundaries increase with increasing the concentration of the total solute element.

On the other hand, the relaxation rate of the solute peak is believed to be controlled by the Ledge Migration Process[13] caused by the solute segregation in equilibrium at grain-boundaries. The solute segregation in equilibrium at grain-boundaries is likely to be caused by elastic distortion associated with the gap between solvent and solute atomic radiuses. As the drag effect by the solute atoms near the grain boundary increases with increased solute concentration, Ledge Migration becomes less likely to work effectively. In the case of a material with Ni increased to 0.8 mass%, the low temperature peak Q^{-1} value increases again. As the concentration greatly exceeds the saturation point (0.2 mass %Ni) as in this case, Ti_2Ni intermetallic compound precipitates[11] and so causes a sharp evolution of low temperature peaks as in the cases of TiC (Fig. 4) and Ti_2Cu (Fig. 6).

3.3 Influence of alloying elements on critical starting temperatures of grain-boundary relaxation TcGB

Based on the experimental results and discussion described in sections 3.1 and 3.2, the critical temperature equivalent to the initial stage of grain-boundary relaxation where the Q^{-1} value under grain-boundary relaxation phenomenon stands at 1.0×10^{-2} was defined as TcGB. In this section the influence of alloying elements on TcGB was examined.

Fig. 8 shows the influence of O, N, and C on TcGB of Ti-O, Ti-N, and Ti-C alloys, respectively. It clearly indicates that N content raises the value of TcGB.

Fig. 9 shows the influence of β-eutectoid elements such as Fe, Cu, Ni, and Cr. With Cr, Cu, or Ni of more than 0.5 mass%, TcGB decreased. On the other hand, Fe reduced TcGB by about 50 K even at a content between 0.04 and 0.09 mass%. This suggests that a trace amount of Fe segregates at the grain-boundary of α-Ti and accelerates the precipitation of β-phase, thus enhancing softening at grain-boundaries. The TcGB value of Ti-0.2 mass%O-0.1 mass%N-0.5 mass%Fe alloy is very close to that of Ti-0.42 mass%Fe alloy, suggesting that the grain-boundary relaxation phenomenon of both alloys is developed mainly by Fe element even at their relatively low content.

Fig. 10 shows the influence of β-isomorphous type elements such as V and Mo. TcGB of Ti-V alloy does not fluctuate much in this range of V content. TcGB of Ti-Mo alloy slightly increases at 0.1 mass %Mo, presumably due to the grain boundary segregation of Mo. In the range from 0.1 to 0.8 mass %Mo, TcGB dropped by about 100 K, probably due to a trace amount of precipitation of β-phase at the grain boundary. TcGB rose again at 2 mass % Mo, which seems to be caused by both the solid solution strengthening of the matrix and the strengthening of grain-boundaries by segregation of excessive Mo solute atoms.

Fig. 11 shows the influence of Al. TcGB of Ti-6 mass %Al alloy which is composed of an α-phase is higher than that of commercial Ti-6 mass%Al-4 mass %V alloy which is composed of α+β-phase by about 100 K, implying that the former is less likely to develop

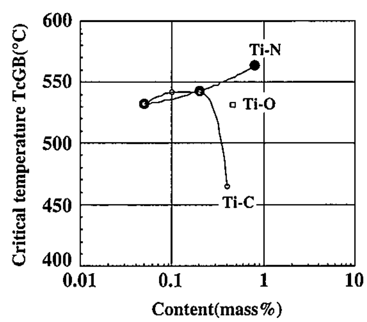


Fig. 8 Influence of the concentrations of solute atoms on the critical starting temperatures of grain-boundary relaxation TcGB of Ti-O, Ti-N, and Ti-C alloys

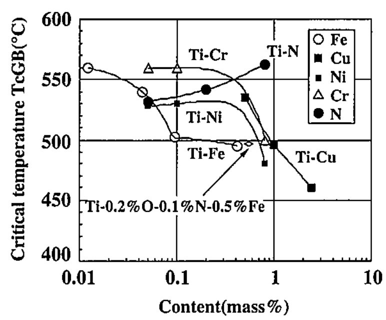


Fig. 9 Influence of the concentrations of solute atoms on the critical starting temperatures of grain-boundary relaxation TcGB of Ti-Fe, Ti-Cu, Ti-Ni, and Ti-Cr alloys

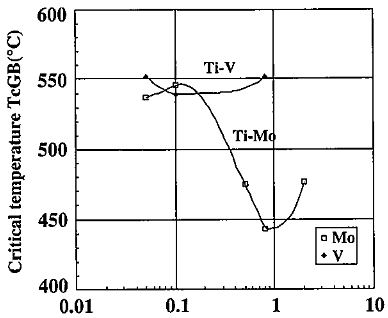


Fig. 10 Influence of the concentrations of solute atoms on the critical starting temperatures of grain-boundary relaxation TcGB of Ti-V and Ti-Mo alloys

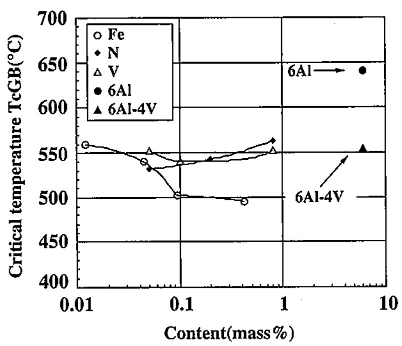


Fig. 11 Critical starting temperatures of grain-boundary relaxation of Ti-6 mass %Al and Ti-6 mass %Al-4 mass %V alloy

grain-boundary relaxation.

From the results of the present study, the effects of the interstitial elements, β-eutectoid elements, and α-type elements on the structural formation and the mechanical strengthening of the grain-boundary are briefly discussed as follows. It seems that N as an interstitial element is soluble in the α-Ti matrix in a range of 0.05-0.8 mass % and improves the mechanical strength of both the matrix and grain-boundary. The effect of improving the mechanical strength of the grain-boundary of O seems to be smaller than that of N. The β-eutectoid elements segregate at α-Ti phase grain-boundaries or precipitate as a β-phase or as intermetallic compound and tend to accelerate softening at grain-boundaries. Fe in particular, compared with Cu and Ni, accelerates softening at grain-boundaries at its lower content. Regarding Al, only if a sufficient amount on the order of 6 mass % is supplied in alloys, it can improve both the mechanical strength of the matrix and mechanical strength of the grain-boundary. It is rational that α-type alloy Ti-5Al-2.5Sn is utilized as an alloy having excellent creep resistant behavior at high temperatures, judging from the influence of Al on the mechanical strength of the matrix and of the grain-boundary as confirmed in this study. These findings provide useful guidelines for designing alloys in consideration of softening at grain boundaries at high temperatures.

4. Conclusions

The internal friction of Ti-interstitial elements (N, O, and C) binary alloys, Ti-X (X = Ni, Cu, Fe, Cr, V, Mo, and Al) system binary alloys, Ti-6Al-4V alloy, and Ti-O-N-Fe system alloy, was measured at high temperatures ranging from 300 K to 993 K, and the following conclusions were obtained.

(1) Ti-N alloys have a single α-Ti phase grain-boundary relaxation peak in the at about 893 K. N raises the critical temperature (TcGB) at which the grain-boundary relaxation peak critically starts to develop.

(2) The temperatures at the grain-boundary relaxation peaks and the internal friction peak-strength of Ti-X system alloys containing β-eutectoid elements Fe, Cu, or Ni, vary remarkably depending on the types and the content of the substitutional solute elements, X. Especially in the case of Ti-Ni alloys, a low temperature peak LTP (solvent peak) at around 833 K and an high temperature peak HTP (solute peak) at 893 K were observed, presumably due to grain-boundary segregation of Ni. If the alloying elements exceed the maximum solubility limit of α-phase, the formation of intermetallic-compound precipitates such as Ti_2Cu and Ti_2Ni cause the LTP. Even a trace amount of Fe reduces TcGB but does not produce a low temperature peak LTP.

(3) The influence of a β-isomorphous type element V on the grain-boundary relaxation peak is small. Another β-isomorphous type element Mo has similar effects to Fe.

(4) An α-type alloying element Al raises the temperature of the grain-boundary relaxation peak of α-Ti. At the content of 6 mass%Al, TcGB increases by about 110 K in comparison with Ti-O alloy.

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