A Study on the Low Temperature Internal Friction Relaxation Peak in a Ti$_{49.8}$Ni$_{50.2}$ Alloy

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The low temperature relaxation peak appearing around 200 K in Ti$_{49.8}$Ni$_{50.2}$ shape memory alloy is a multiple relaxation process with activation energy $Q = 0.39$ eV and frequency factor $f_0 = 6.2 	imes 10^7$ s$^{-1}$ and is associated with the interaction of dislocations with pinning vacancies. Due to the increase of dislocation density and the annihilation of quenched-in vacancies after thermal cycling, the height of relaxation peak $P_R$ decreases with increasing the number of thermal cycling. Higher amounts of dislocation-vacancy reaction cause a higher relaxation damping under the condition of higher quenching temperature. The quenched-in vacancies can have a significant effect on the transformation rate, and thus the heights of transformation peaks $P_{HI}$ and $P_{CI}$ decrease with increasing quenching temperature. Dislocations introduced by both thermal cycling and quenching from high temperature will depress the martensitic transformation, and hence decrease the peak temperatures of $P_{HI}$ and $P_{CI}$.

1. Introduction

The internal friction and shear modulus of TiNi alloys have been investigated by many authors.\cite{1-4} It has been confirmed that the internal friction peaks corresponding to shear modulus minima are associated with the premartensitic and martensitic transformations. In addition to these transformation peaks, a relaxation peak appearing at the temperature around 200 K, and not corresponding to the shear modulus minimum has also been observed.\cite{1-3} Iwasaki and Hasiguti\cite{1} have proposed that the 200 K peak in TiNi alloys is a thermally activated relaxation peak and is related to dislocations. Zhu et al.\cite{5} reported that the quenched-in vacancies may also be involved in the occurrence of 200 K peak. However, there has been no systematic investigation of experimental parameters, such as the solution treatment, quenching temperature, thermal cycling etc., on the variation of the 200 K peak in TiNi alloys. Its characteristics have still not been clarified.

The K–G–L model proposed by Kochler\cite{6} and developed by Granato and Lücke\cite{7} has been made to explain the relaxation of dislocations with point defects. There are two mechanisms of energy loss based on the string model of dislocations. The first mechanism is amplitude independent and results from forced vibrations of the dislocation segment between two pinning points (dislocation resonance damping). The second one is amplitude dependent and increases strongly with strain amplitude which is caused by pulling the dislocations away from their pinning points (dislocations break-away damping). According to this relaxation model, the $Q^{-1}_{\text{max}}$ value should increase with increasing dislocation density from a simplified point of view. In addition, there is a critical range of the loop length $\ell$ for the generation of the relaxation peak, which should not be ignored. When $\ell$ is very large, i.e. the pinning points are small, the number of dislocation loops pinned by point defects which are responsible for the relaxation peak is too small to give rise to an experimentally detectable peak. On the other hand, when $\ell$ is very small, dislocations with very high amounts of point defects are pinned so densely that they cannot be unpinned with the help of measured stress. Thus the peak cannot be observed in this case. It should be expected therefore that there exists an optimum range of point defects for the appearance of the peak. The above mentioned dislocation-pinning point relaxation model is thus used to explain the characteristics of the 200 K peak in Ti$_{49.8}$Ni$_{50.2}$ alloy in this study. Meanwhile, some important factors affect this relaxation peak will also be discussed.

2. Experimental Procedure

The Ti$_{49.8}$Ni$_{50.2}$ binary alloy was employed in this study and was prepared by the conventional vacuum arc remelting technique. The as-melted ingot was homogenized at 1050°C for 72 h and quenched in water, then hot-rolled at 800°C to a plate with thickness reduction of 90%. Specimens with size 110 mm $\times$ 4 mm $\times$ 1 mm for internal friction tests were carefully cut from the plate. The long axis of the specimens is parallel to the rolling direction. Then specimens were sealed in evacuated quartz tubes, annealed at 800 to 1000°C for 2 hrs and quenched in water. These specimens may have some rolling textures during the hot rolling process. However, it is believed these hot-rolling textures hardly changed in the subsequent annealing at 800 to 1000°C.\cite{8,9} Meanwhile, all specimens are prepared from the same hot-rolled plate with their rolling direction parallel to the long axis of the specimens. Therefore, the effect of hot-rolling texture during the internal friction tests can be prevented.

The internal friction measurements were made using an SINKU-RIKO 1500-M/L series inverted torsion pendulum in temperatures ranging from −150 to 100°C. The measuring frequency range was set from about 0.6 to 1.6 Hz and the changing temperature rate was 2 K/min. The test strain

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amplitude was set to $1.66 \times 10^{-3}$ radian ($2.5 \times 10^{-3}$ of maximum true strain). The recording of the data was completely automatic; calculation and plots of internal friction and frequency versus temperature were performed on a digital computer. Thus results with a rather good resolution could be obtained.

3. Results and Discussion

3.1 Frequency and internal friction measurements

Figures 1(a) and (b) show the frequency and internal friction vs. temperature, respectively, of the 800°C-quenched Ti$_{49}$:Ni$_{50}$:2 specimen. In Fig. 1(b), peak $P_{HI}$ appears at 60°C in heating and peak $P_{CI}$ appears at 27°C in cooling. Based on the reported studies, 2–4) we confirmed that $P_{HI}$ and $P_{CI}$ are associated with the martensitic transformation. In addition to peaks $P_{HI}$ and $P_{CI}$, there are peaks $P_{HR}$ and $P_{CR}$ appearing at around −73°C (200 K) in heating and cooling, respectively. As shown in Fig. 1(a), peak $P_{HR}$ and $P_{CR}$ do not correspond to the frequency $f$ minima, but to the monotonous frequency change. According to the anelastic relaxation theory, 10) they are relaxation-type internal friction peaks.

A series of the relaxation peaks $P_R$ (including $P_{HR}$ and $P_{CR}$) in internal friction spectra for the Ti$_{49}$:Ni$_{50}$:2 alloy are plotted as a function of $1/T$ for five different frequencies of 1.63, 1.10, 1.01, 0.69 and 0.64 Hz. The plotted results are shown in Fig. 2(a). From the data of Fig. 2(a), the Arrhenius graph relating the reciprocals of peak temperatures to the logarithms of vibration frequencies is plotted and shown in Fig. 2(b). From Fig. 2(b), activation energy $Q$ and frequency factor $f_0$ for the $P_R$ of Ti$_{49}$:Ni$_{50}$:2 alloy are calculated to be $Q = 0.39$ eV and $f_0 = 6.2 \times 10^9$ s$^{-1}$. These values are in good agreement with the reported ones. 1) In Fig. 2(a), a single relaxation peak (Debye peak) is plotted theoretically with the activation energy $Q = 0.39$ eV. On comparing this peak with other relaxation peaks in Fig. 2(a) that also have $Q = 0.39$ eV, we find that the ratio of the half-peak-width-height of these other peaks to that of Debye peak is 2.6. This means that the low temperature relaxation peak appearing in Ti$_{49}$:Ni$_{50}$:2 alloy is due to a multiple relaxation process, but not a single relaxation process. This phenomenon is reasonable because there is a distribution in the loop length $\ell$ in which the unpinning activation energies are different.

3.2 The effect of quenching temperature on the relaxation peak $P_R$

Figure 3 shows the internal friction vs. temperature of the different temperature-quenched Ti$_{49}$:Ni$_{50}$:2 specimens in the cooling test run. In Fig. 3, the $P_{CR}$ temperature seems hardly
to be affected by the quenching temperature. However, there is a significant change in the peak height. The peak height increases with increasing quenching temperature. Meanwhile, it is very interesting to find that the quenching temperature also has a significant effect on both the peak temperature and peak height of PC1, which is associated to the martensitic transformation. The peak temperature of PC1 decreases with increasing quenching temperature, say about 12°C drop if the quenching temperature increases from 800 to 1000°C. The peak height of PC1 also decreases significantly with increasing quenching temperature, e.g. the 1000°C quenched specimen has a Q_{max} = 18 x 10^{-3} and the 800°C quenched specimen has a Q_{max} = 43 x 10^{-3}. The variation of the peak height for PC1 with different quenching temperatures is opposite to that for the relaxation peak PR. These phenomena will be further discussed in Section 3.4.

3.3 The effect of thermal cycling on the relaxation peak PR

Figures 4(a) and (b) show the same plots as Figs. 1(a) and (b), but now the specimen has subjected to 100 thermal cycles (N = 100). In Fig. 4, peaks PH1 and PC1 are also associated with the martensitic transformation and appear at 45 and 8°C, respectively. However, the relaxation peak is not conspicuous in both heating and cooling. The experimental results of other Ti_{49.8}Ni_{50.2} specimens with 2, 10 and 20 thermal cycles are very similar to those specimens with 1 and 100 thermal cycles, except the shifts in peak temperature and peak height Q_{max}.

Figure 5 shows the effect of the thermal cycling number N on the Q_{max} of the relaxation peak PH in the Ti_{49.8}Ni_{50.2} alloy. Figure 5(a) is the plot of Q^{-1} vs. temperature and Fig. 5(b) is Q_{max} vs. N. From Fig. 5(a), we find that the peak temperature of PH decreases not significantly affected by N, but the Q_{max} of peak PH decreases sharply in the beginning 20 cycles, and approaches a stable background value when N = 100. In Fig. 5, the internal friction measurements for the thermal cycling test were carried out in the temperature range from -150 to 100°C in which the martensitic transformation occurs completely on both heating and cooling. Therefore, the martensitic transformation peaks, PH1 and PC1, are all observed for different thermal cycling numbers. Figure 5(b) also plots the peak temperature of PH1, PC1 vs. N. From Fig. 5(b), the same tendency of PH1, PC1 and Q^{-1} curves can be easily recognized. Besides, the peak heights of PH1 and PC1 in Figs. 1 and 4 are nearly the same. This indicates that
the transformation peaks $P_{H1}$, $P_{C1}$ of Ti$_{48.8}$Ni$_{50.2}$ specimen exhibit no conspicuous variation with different number of thermal cycling.

3.4 The characteristics of the relaxation peak $P_R$

As mentioned in Section 1, Iwasaki et al. and Zhu et al. have proposed that the 200 K peak in TiNi alloys is a thermally activated relaxation peak and is related to dislocations and vacancies. In previous reported articles, the 200 K relaxation peaks in the aged Ti$_{49}$Ni$_{51}$ alloys are found to originate from the interaction of twin-related dislocations with the pinning agents by quenched-in vacancies or Ti$_3$Ni$_4$ precipitate-vacated lattice sites. The 200 K relaxation peak can occur at the R-phase or martensite phase but not at the B2 phase, since there are no twin-related dislocations available in the latter. Therefore, it is reasonably believed that the 200 K relaxation peak $P_R$ in this study is also closely related to the twin-related dislocations with pinning vacancies for the Ti$_{49.4}$Ni$_{50.2}$ alloy.

Figure 5 shows that the relaxation peak height $Q_{\text{max}}^{-1}$ decreases rapidly with increasing thermal cycling. It has been reported that the dislocation density increases with the thermal cycling. Meanwhile, the quenched-in vacancies are reasonably believed to be partially annihilated during the thermal cycling, because there is a driving force to reduce the vacancy concentration to approach an equilibrium value. The thermal-cycling induced dislocations and the annihilation of quenched-in vacancies will significantly increase the loop length $\ell$ for the generation of the relaxation peak. It is assumed that $\ell$ is larger than a critical value, the pinning-unpinning reaction will be too weak to give rise to an experimentally detectable peak. This indicates that the thermal cycling tends to enlarge the unpinned dislocation segments above the critical value, and hence the peak height of $P_R$ decreases with the increase of thermal cycling, as shown in Fig. 5. In Fig. 5(b), one can easily find that the thermal cycling will depress the martensitic transformation. In addition, the shear strain can be enhanced during the martensitic transformation. In other words, the more quantity of thermal-stress induced dislocations can exist in the specimen quenched from higher temperature. In other words, the quenched-in dislocation density might be more for the higher temperature solution-treated and quenched specimen. Because the vacancies and dislocations are both increased, the average loop length $\ell$ may not change considerably. However, the increase of the effective amounts of dislocation-vacancy interaction causes the relaxation to significantly increase with increasing quenching temperature, and thus results in a higher damping relaxation, as shown in Fig. 3.

In Fig. 3, one can also find that the quenching temperature has significant effect on the peak temperature and peak height of $P_{C1}$, which is associated with the martensitic transformation. The peak temperature of $P_{C1}$ decreases with increasing quenching temperature from 800 to 1000°C. This phenomenon can be ascribed to the more quantity of quenched-in dislocations existing in the specimen after quenching from higher temperature. These quenched-in dislocations will depress the martensitic transformation temperatures, i.e. the peak temperatures of $P_{H1}$ and $P_{C1}$ are shifted to lower ones. This effect is similar to that of thermal-cycling induced dislocations. In Fig. 3, the peak height of $P_{C1}$ also decreases significantly with increasing quenching temperature. This phenomenon is different from the effect of thermal cycling, in which the peak heights of $P_{H1}$ and $P_{C1}$ are nearly the same for specimens 1–100 thermal cycles. This indicates that the large quantity of quenched-in vacancies, which exist in the quenched specimen but not in the thermal-cycled specimen, will play more important role on the peak heights of $P_{H1}$ and $P_{C1}$. In other words, from Fig. 3, the quenched-in vacancies will significantly reduce the martensitic transformation rate, and hence dramatically decrease the peak heights of $P_{H1}$ and $P_{C1}$.

4. Conclusions

The 200 K relaxation peak in Ti$_{49.4}$Ni$_{50.2}$ alloy is a multiple relaxation process and is associated with the interaction of dislocations with pinning vacancies. The activation energy and frequency factor are found to be $Q = 0.39$ eV and $f_0 = 6.2 \times 10^9$ s$^{-1}$, respectively. Due to the increased dislocation density and the annihilation of quenched-in vacancies after thermal cycling, the height of relaxation peak $P_R$ decreases with increasing the number of thermal cycling. There is no conspicuous variation of the martensitic transformation rates after thermal cycling, and hence the peak heights of $P_{H1}$ and $P_{C1}$ are nearly the same for specimens 1 and 100 thermal cycles. The increase of the effective amounts of dislocation-vacancy reaction causes a higher relaxation damping under the condition of higher quenching temperature. Besides, the peak temperatures of transformation peaks $P_{H1}$ and $P_{C1}$ decreases with increasing quenching temperature due to the more quantity of thermal-stress induced dislocations existing in the specimen. The large quantity of quenched-in vacancies with increasing quenching temperature will also significantly reduce the martensitic transformation rate, and hence dramatically decrease the peak heights of $P_{H1}$ and $P_{C1}$.
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