Effect of Hydrogen on Damping Capacity of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Alloy^{*1}

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Ternary Ti–Ni–Cu alloy is known to exhibit higher damping capacity than binary Ti–Ni alloy. Hydrogen doping was used to further improve the damping capacity of this ternary alloy. Considering ease of manufacture, the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy was produced by a lamination process. As a result of hydrogen doping, a new damping peak appeared at around 260 K. The peak temperature shifted with changes in oscillation frequency. The activation energy (H) and the relaxation time constant (τ_0) of the damping peak were calculated according to the Arrhenius plot as $H = 57.5$ kJ/mol, and $\tau_0 = 2.2 \times 10^{-13}$ s, respectively. The damping capacity due to hydrogen doping increased with increasing hydrogen concentration up to 0.45 at%, showing the maximum peak value of $\tan \phi = 0.05$, but thereafter decreased. On the other hand, the peak temperature increased monotonically with increasing hydrogen concentration, and the peak shape was broader than the single Debye relaxation peak. From these results, we concluded that this damping peak was not the Snoek peak but the Snoek-Koester peak caused by hydrogen-dislocation interaction. The decrease of the Snoek-Koester peak with increasing hydrogen concentration is explained by formation of hydrogen clusters or hydrides. Schoeck's theory for the Snoek-Koester peak may be applicable. On further hydrogen doping, both the Snoek-Koester peak and the transformation peak were hardly visible above 5 at% hydrogen. This was found to be due to destruction of the martensitic phase by excess hydrogen doping.

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1. Introduction

In recent years, there have been growing concerns about environmental issues. To reduce the amount of exhausted carbon dioxide, we need to improve fuel efficiency. Reducing the weight of vehicles is one promising way to improve fuel efficiency. On the other hand, we also need to reduce the vehicle's noise and vibration, but reducing the weight of vehicles makes these characteristics worse. Our challenge is to accomplish these two requirements simultaneously.

One approach we have considered is to apply damping alloys to vibrating sources in the vehicle. Ti–Ni alloy is one of the more promising alloys due to its high damping capacity and high strength. Ti–Ni is a well-known shape memory alloy and many researchers have studied its damping capacity.^{1–5)} Moreover Ti–Ni–X alloys (specifically $X = \text{Cu}$) are well studied too.^{6–10)} It is reported that Ti–Ni–Cu alloys ($\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$) undergo different phase changes according to the concentration x ,¹¹⁾ i.e. $\text{B2} \Leftrightarrow \text{B19}'$ ($x \leq 7.5$), $\text{B2} \Leftrightarrow \text{B19} \Leftrightarrow \text{B19}'$ ($7.5 \leq x \leq 15$), $\text{B2} \Leftrightarrow \text{B19}$ ($15 \leq x$) (where B2 = austenite phase and B19 and B19' = martensitic phase). Both the Ti–Ni and Ti–Ni–Cu alloys exhibit a transient damping peak near the transformation and a rather high damping capacity in the martensitic phase.

Generally speaking, the transient damping peak is not useful due to many limitations. Therefore, we can utilize only the damping capacity in the martensitic phase. However, this damping capacity is not high enough for vehicle applications.

In the present work, we have tried to improve the damping capacity further by doping hydrogen into Ti–Ni–Cu alloy^{12,13)} (we selected $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ because of its particularly high damping capacity¹⁴⁾), and discussed the role of hydrogen as it affects the damping capacity of the Ti–Ni–Cu alloy.

Fig. 1 Schematic drawings of the processing of Ti/Ni–Cu laminated material.

2. Experimental Procedures

2.1 Materials

Ti–Ni–Cu has a poor workability owing to its crystal structure. Taking account of this, Ti–Ni–Cu sheet was produced by lamination and diffusion processes.^{15–17)} Figure 1 shows a schematic diagram of this procedure. Rectangular titanium sheets (purity 99.9%, 100 mm $\times$ 70 mm) with a thickness 0.2 mm and nickel–copper (copper 50 at%) sheets (purity 99.9%, 100 mm $\times$ 70 mm) with a thickness 0.13 mm were stacked to 181 layers. The laminated plate was packed in steel frames with 5 mm thick top and bottom (cover) plates. This package was evacuated to less than 1 kPa and the steel frames were welded. Next, the package was annealed at 1023 K for 3.6 ks and hot rolled to 4 mm. After air-cooling, the top and bottom steel plates were peeled off and the laminated plate was cold rolled to 0.5 mm as shown in Fig. 1. To homogenize the alloy, the cold rolled plate was cut into small pieces of plate and again sealed in a stainless steel case, adding BN powder to prevent counter diffusion from the case. After evacuating to less than 1 kPa, the case was annealed at 1163 K for 260 ks and quenched in

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Fig. 2 Schematic drawings of sample sealing and heat treatment.

Fig. 3 A schematic diagram for the measurement of the damping capacity ($\tan \phi$) by the forced flexural oscillation method.

air as shown in Fig. 2. The resulting plate was cut into specimens ($30 \text{ mm} \times 10 \text{ mm} \times 0.3 \text{ mm}$) for measuring damping capacity and Young's modulus.

Then we doped hydrogen into the specimen by electrolysis in KOH (6N) solution under a surface current density of 0.032 mA/mm^2 . We prepared samples containing a wide range of hydrogen concentrations by changing the charging time from 0.03 to 6 h. The amount of the doped hydrogen was measured by gas chromatography (JISZ2641).

2.2 Measurements

The damping capacity and Young's modulus were measured using a Dynamic Mechanical Analyzer (DMA) illustrated in Fig. 3. The measurements were carried out between 173 and 423 K at a heating rate of 3 K/min and at a strain amplitude of about 3.0×10^{-5} . The oscillation frequencies were 0.1, 1 and 5 Hz.

3. Results and Discussion

3.1 Properties of Ti-Ni-Cu Before Intentional H Doping

Figure 4 shows the temperature dependent variations of Young's modulus and $\tan \phi$ for the Ti-Ni-Cu alloy before intentional H doping. A damping peak appears at around 340 K and the Young's modulus undergoes a drastic change simultaneously. Judging from the ternary phase study of Ti-Ni-Cu,¹⁸⁾ this damping peak is caused by the phase transformation ($\text{B19} \rightarrow \text{B2}$). The observed damping peak decreases with increasing oscillation frequency because the amount of transformation during one oscillation decreases with increasing oscillation frequency.

The background damping capacity in the martensitic phase is higher than in the austenitic phase at high temperature. The damping capacity in the martensitic phase must be caused by the hysteretic motion of twin boundary dislocations. We recognize that the damping capacity near R.T in the martensitic phase increases with decreasing oscillation

Fig. 4 Young's modulus and $\tan \phi$ as a function of temperature during heating before intentional H doping.

frequency. The frequency dependent damping together with the temperature dependent damping indicates that the damping mechanism is not due solely to a pure mechanical unpinning of twin boundary dislocations but also involves a thermal process in the dislocation motion. A possible explanation is that motion of the dislocation after unpinning may not be a free motion but a thermally activated motion due to the solute copper atoms in Ti-Ni.

3.2 Properties of Ti-Ni-Cu After H Doping

Figure 5 shows a typical example of the temperature dependent variations of the Young's modulus and $\tan \phi$ for the Ti-Ni-Cu after H doping. A new damping peak appears at around 260 K and the Young's modulus decreases simultaneously. To reveal the character of the new damping peak, we subtracted background damping from the new damping peak. Figure 6 shows the result. The temperature of the damping peak shifts with change in oscillation frequency.

Figure 7 is an Arrhenius plot showing the oscillation frequency dependence of the peak temperature. From the figure, we calculated the activation energy and the relaxation

Fig. 5 Young's modulus and $\tan \phi$ as a function of temperature during heating after intentional H doping by 1.33 at%.

Fig. 6 Damping capacity due to hydrogen as a function of temperature obtained by subtracting the background for the specimen of Fig. 5.

Fig. 8 Comparison of experimental hydrogen peak and the calculated single Debye's peak.

Fig. 7 Arrhenius plot of frequency dependence of the peak temperature in Fig. 6.

time constant as $H = 57.5 \text{ kJ/mol}$ (0.60 eV) and $\tau_0 = 2.2 \times 10^{-13} \text{ s}$. The new damping peak may be the Snoek peak resulting from hydrogen dispersion in the lattice according to the activation energy and the relaxation time constant.¹⁹⁾

Figure 8 shows a comparison of the experimental damping peak and the calculated single Debye peak for the above values. The experimental damping peak is twice as broad as the single Debye relaxation peak.

3.3 Influence of Hydrogen Concentration on Damping Capacity

Figure 9 shows the temperature dependent variations of the Young's modulus and $\tan \phi$ for the Ti–Ni–Cu alloys as a function of hydrogen concentration. The damping capacity increases with increasing hydrogen concentration up to 0.45 at%, then decreases and almost disappears above 7 at%.

Figure 10 shows the hydrogen damping peak at around 260 K after subtracting the background damping. The peak temperature increases monotonically with increasing hydrogen concentration. Those results are inconsistent with the

behavior of the Snoek peak. If the damping peak is the Snoek peak, the reason why the damping capacity decreases above 0.45 at% hydrogen must be a site-blocking effect. The site-blocking effect is a phenomenon in which a hydrogen atom cannot jump into sites close to other hydrogen atoms. The allowed minimum distance between hydrogen atoms in many kinds of hydride is reported to be about 0.2 nm.²⁰⁾ In our case, the average distance is about 0.9 nm even when hydrogen concentration is 2.11 at%. So we can hardly believe that the site-blocking effect occurred in the specimens. The activation energy of hydrogen diffusion in Ti, Ni and Cu are 30–40 kJ/mol and hence the activation energy of the present case is 1.5–2 times greater than those values. Moreover, the experimental peak is much broader than single Debye relaxation peak as shown in Fig. 9. Taking the above facts into account, it is reasonable to think that the damping peak at around 260 K is not the Snoek peak but the Snoek-Koester peak.

The Snoek-Koester peak is a relaxation peak resulting from dislocation movement controlled by the diffusion of segregated interstitial atoms.^{21,22)} If the new damping peak is the Snoek-Koester peak, the reason for decreasing damping capacity above 0.45 at% hydrogen is interpreted as follows: When the hydrogen concentration is low in the specimen, hydrogen atoms segregate individually around dislocations and the dislocation can move, dragging hydrogen atoms. When the hydrogen concentration becomes high (above 0.45 at%), the hydrogen atoms begin to coagulate to form clusters or even hydrides.²³⁾ The hydrogen clusters or the hydrides restrict the movement of the dislocation. As a result, the damping capacity decreases. The reason why the peak temperature increases monotonically with increasing hydrogen concentration can be interpreted in terms of Schoeck's theory on the Snoek-Koester peak.²⁴⁾

As shown in Fig. 9, both the Snoek-Koester peak and the transformation damping peak decrease drastically above 5 at% hydrogen. Figure 11 shows the XRD patterns of specimens with various amounts of hydrogen. It is found that orthorhombic peaks in the specimens above 5 at% hydrogen disappear and the diffraction pattern becomes amorphous-

Fig. 9 Temperature dependence of Young's modulus and Damping capacity of specimen with various amounts of hydrogen.

Fig. 10 Hydrogen damping peak for various amounts of hydrogen.

Fig. 11 XRD patterns of specimens with various amounts of hydrogen.

4. Conclusion

- (1) A new damping peak different from the transformation damping peak appeared at around 260 K in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy by doping hydrogen. The damping peak shifted with the oscillation frequency. The activation energy ($H = 57.5 \text{ kJ/mol}$ (0.60 eV)) and the relaxation

like. This means that the doping of hydrogen beyond the solubility limit destroys the B19 martensite phase and suppresses the transformation itself.

time constant ($\tau_0 = 2.2 \times 10^{-13}$ s) were obtained by the Arrhenius plot. This new damping peak enhances the damping capacity near the room temperature in the martensitic phase of the Ti–Ni–Cu alloy.

- (2) The damping peak increased up to 0.45 at% hydrogen concentration (the maximum $\tan \phi \approx 0.05$) and then decreased. The peak temperature increased monotonically with increasing hydrogen concentration. The experimental peak was broader than the single Debye relaxation peak. From these results, we conclude that the new damping peak at around 260 K is not the Snoek peak but the Snoek-Koester peak caused by hydrogen-dislocation interaction; Schoeck's theory for the Snoek-Koester peak may be applicable.
- (3) In case of excessive hydrogen doping beyond the solubility limit (above 5 at%), both the Snoek-Koester peak and transformation damping peak hardly appeared. X-ray diffraction spectra revealed that the structure of the Ti–Ni–Cu martensite phase was destroyed by the excess hydrogen doping.

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