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Effects of Hydrogen on $Ni_{47}Ti_{44}Nb_9$ Shape Memory Alloy

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The effects of hydrogen on the transformation characteristics of $Ni_{47}Ti_{44}Nb_9$ shape memory alloy were investigated. Cathodic hydrogen charging was performed at a current density of 20 mA/cm^2 in 0.5 mol/L H_2SO_4 solution at room temperature. The transformations of the hydrogenated specimens were characterized by differential scanning calorimetry, x-ray diffraction, and electrical resistivity measurement in details. For the hydrogen-charged NiTiNb alloy, the original reversible transformation between B2 and B19′ phase disappeared. Meanwhile, new transformation around 120 °C was present. This high temperature reversible transformation was confirmed to be the transformation between β-NbH phase and α-Nb(H) solid solution phase.

Keywords β-NbH, hydrogen charging, NiTiNb, phase transformation

1. Introduction

Hydrogen can be inadvertently added to NiTi-based devices through electropolishing, caustic cleaning, or exposure to other acidic environment. The main hydrogen effects observed in NiTi include reduced ductility, loss of shape memory properties, and shorter fatigue life (Ref 1-5). Pelton et al. (Ref 6) found that even relatively small amounts of hydrogen can affect the crystal structure of NiTi alloy. Moreover, they observed the formation of hydride based on the additional diffraction peaks when NiTi wires were immersed in H_3PO_4 solution. Yokoyama et al. (Ref 7, 8) have recently reported the confirmation of hydride NiTiH by XRD analysis and the degradation of the mechanical properties of NiTi alloy after cathodic hydrogen charging. However, for ternary NiTiNb alloys, these effects have not been clarified so far.

Due to large hydrogen solubility and high hydrogen diffusivity of pure niobium (Ref 9), the effects of hydrogen on ternary NiTiNb alloy may be different from NiTi alloy. As the most typical and commercially used among the ternary NiTiNb alloys (Ref 10, 11), $Ni_{47}Ti_{44}Nb_9$ alloy is used in this study. In this alloy, the microstructure consists of NiTi phase and Nb-rich phase which contains some of titanium (Ref 12). When this type of alloy is used in a long period of service, the effects of hydrogen should be considered. As there have been very few studies on this viewpoint, this paper intends to summarize a series of experiments to monitor the effects of hydrogen on NiTiNb alloy by cathodic hydrogen charging.

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2. Experimental

$Ni_{47}Ti_{44}Nb_9$ alloy (wire of 0.6 mm diameter) was obtained from the Generous Research Institute for Nonferrous Metals, China. Specimens were annealed at 850 °C in vacuum for 1.2 ks and then mechanically polished with 800-grid SiC paper. Transformation temperatures measured by DSC were as follows: Ms = −27.9 °C, Mf = −60 °C, As = 3.9 °C, and Af = 35 °C. Hydrogen was charged cathodically in 0.5 mol/L H_2SO_4 solution at room temperature for 30 h. The current density of cathodic hydrogen charging was 20 mA/cm^2.

After hydrogenation, the charged samples were characterized by differential scanning calorimetry (DSC), x-ray diffraction (XRD), and electrical resistivity (ER) measurement. Samples of 3 mm long were cut from the charged specimens using a low-speed diamond saw for DSC measurements. DSC measurements were carried out using a NETZSCH DSC 204 F1 in argon atmosphere at a heating/cooling rate of 10 °C/min. The phase composition of the resulting sample was analyzed by using an x-ray diffractometer with Cu Kα radiation operated at 40 kV and 40 mA at 25, 150, and 300 °C. The precise four-probe DC current technique was used to measure the ER of ternary NiTiNb alloys. The ER is measured at temperatures ranging from 30 to 156 °C under a controlled cooling/heating rate of 5 °C/min. Paperless recorder is used to measure the voltage variation between the two inner probes, while a constant current is passed through the two outer probes using a DH1715A-3 DC power supply.

3. Results and Discussion

DSC data obtained as a function of temperature for noncharged and 30 h-charged NiTiNb wires are shown in Fig. 1. The endothermic and exothermic peak temperatures of the noncharged specimen are 30 and −28 °C, respectively. The transformation hysteresis is 58 °C which is consistent with the previous results (Ref 10-12). Compared with the noncharged NiTiNb wire, an anomaly appears in the DSC curves of the

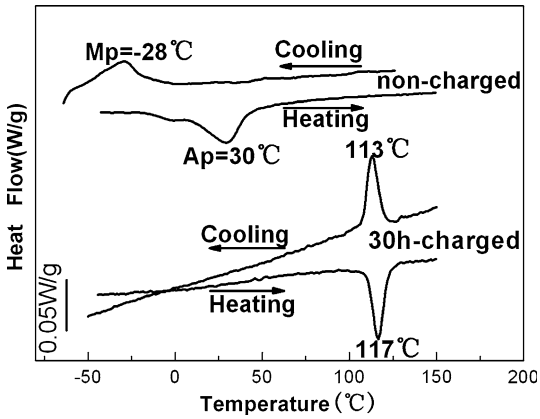

Fig. 1 DSC results of noncharged and 30 h-charged NiTiNb wires

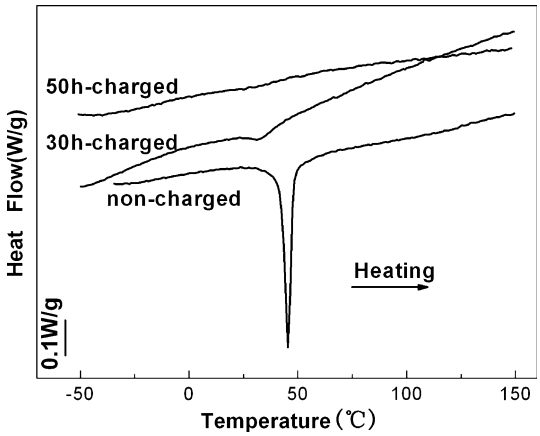

Fig. 2 DSC results of NiTi wires hydrogenated for different times

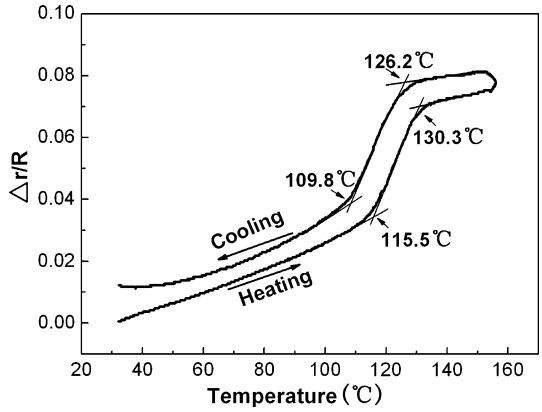

Fig. 3 The curve of $\Delta r/R$ vs. temperature of the hydrogenated NiTiNb alloy for charging 30 h

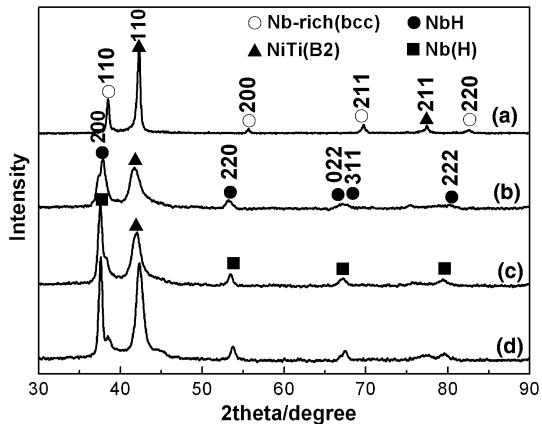

Fig. 4 XRD patterns of (a) noncharged NiTiNb alloy, (b) 30 h-charged NiTiNb alloy measured at 25 °C, (c) 150 °C, and (d) 300 °C

30 h-charged sample shown in Fig. 1. First, for the hydrogen-charged NiTiNb specimen, the original reversible transformation peaks between B2 and B19′ disappear, implying that the NiTi phase in ternary NiTiNb alloy loses its reversible transformation due to hydrogenation. Second, new reversible transformation peaks of the charged sample are present at higher temperature around 120 °C, while the endothermic and exothermic peak temperatures are 117 and 113 °C, respectively. Correspondingly, the thermal hysteresis is only 4 °C.

To analyze the nature of the peaks at high temperature side, the effects of hydrogen on the transformation behaviors of the near equiatomic $Ni_{49.8}Ti_{50.2}$ wires (0.6 mm diameter) which have the identical hydrogen charging conditions as NiTiNb wires are investigated. In the DSC curves, two important characteristics of the hydrogenated NiTi wires which are different from the hydrogenated NiTiNb wires can be seen from Fig. 2. The first one is that there is no new transformation peak around 120 °C for the charged NiTi wires. The other important one is that the reverse martensitic transformation peak still exists in the 30 h-charged NiTi sample, except that there is a pronounced shift in the transformation temperatures and decrease in the relative enthalpy of the reactions shown in the DSC heating curve. When charged for 50 h, the transformation of NiTi wire is completely suppressed, similar to the work of Pelton et al. (Ref 1). Consequently, from the above experimental results we can conclude that it takes shorter charging time for NiTi phase in NiTiNb alloy to lose reversible transformation compared with NiTi alloy. The reason for this may be explained to the existence of Nb-rich phase in NiTiNb alloy which is beneficial to the hydrogen absorption as reported in the literature (Ref 13).

To further characterize the transformation behaviors of high temperature phases around 120 °C, the change of the ER of 30 h-hydrogen-charged NiTiNb wire versus temperature is measured. Figure 3 shows the curves of relative ER ($\Delta r/R$) versus temperature of the hydrogenated NiTiNb alloy. In Fig. 3, we can find there is a significant increment of $\Delta r/R$ value from 115.5 to 130.3 °C in the heating curve. Meanwhile, in the cooling process, the relative resistivity decreases sharply from 126.2 to 109.8 °C. Correspondingly, an approximate 5 °C thermal hysteresis occurs during heating and cooling, as illustrated in Fig. 3, similar to the DSC measurement. The curves exhibit a typical reversible transformation depending on the variation of relative ER.

For the purpose of identifying the structural change of hydrogen-charged NiTiNb alloys in the heating process, the XRD tests are carried out at different temperatures. Before hydrogenation, this alloy consists of Nb-rich phase (bcc) and NiTi phase (B2) as shown in Fig. 4(a). Comparing Fig. 4(a) with (b), we can find that a series of Bragg peaks appear in the

lower angle side than those of bcc-Nb phase, which confirms the formation of hydride β-NbH in the hydrogenated NiTiNb alloy at room temperature. The lattice parameters of β-NbH calculated from XRD pattern are: a = 4.83 Å, b = 4.192 Å, and c = 3.472 Å. The NbH structure was identified to be face-centered orthorhombic (fco) (Ref 14).

When XRD tests are measured at 150 and 300 °C which are above the transformation finishing temperature, no hydride peaks were detected owing to hydride decomposition shown in Fig. 4(c) and (d). On the other hand, the lattice expanded bcc-Nb(H) solid solution phase is present with the two diffraction peaks {022} and {311} disappearing. Though the differences between α-Nb(H) solid solution and β-NbH are difficult to identify due to the almost same diffraction peak positions in XRD patterns, as reported in Luo et al.'s research (Ref 15), the transformation between the two phases is clearly confirmed by DSC and ER measurements in this study. That is, the transformation from β-NbH phase to α-Nb(H) solid solution phase occurs during heating. These results indicate that the β-NbH forms at room temperature during hydrogenation and transforms to α-Nb(H) solid solution during heating.

Semboshi et al. (Ref 16) investigated the thermal stability of relevant phases in the pure niobium hydrogenated by DSC measurement. They pointed out that β-NbH could decompose to α-Nb(H) solid solution during the heating process. However, there are no cooling curves in his DSC results. From Fig. 1, we can see that an exothermic peak appears in the cooling curve of the charged NiTiNb wire. Consequentially, this peak is in agreement with the transformation of the α-Nb(H) solid solution to β-NbH. Additionally, the variation of relative ER also reflects the transformation between β-NbH phase and α-Nb(H) solid solution. All of the above results indicate that the transformation of β-NbH phase to α-Nb(H) solid solution is reversible in the hydrogenated NiTiNb alloy.

4. Conclusion

This study investigated the effects of hydrogen on transformation behaviors of $Ni_{47}Ti_{44}Nb_9$ shape memory alloy by cathodic electrolysis. After charging for 30 h, the NiTiNb wires lost its original reversible transformation and the hydride β-NbH formed at room temperature. β-NbH could decompose to α-Nb(H) solid solution during the heating process. Moreover, the transformation from α-Nb(H) to β-NbH was confirmed by DSC and ER tests during the cooling process. Therefore, it is confirmed that the transformation between β-NbH phase and α-Nb(H) solid solution is reversible in the hydrogenated NiTiNb alloy.

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