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Effects of Thermal Cycling on the Temperature Memory Effect of TiNiNb Alloy

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The temperature memory effect (TME) of a $Ti_{48}Ni_{17}Nb_{35}$ alloy consisting of B2-TiNi(Nb) and bcc-NbTi with Ti_2Ni precipitation was investigated by using differential scanning calorimetry (DSC). Results showed that the TME of the alloy persisted on the second global DSC heating curve. This repeatable TME persisted even after 30 complete thermal cycles from below M_f to above A_f. With a further 30 incomplete thermal cycles upon heating up to a specific arrested temperature, the TME was enhanced and persisted in the next 32 complete testing cycles. This is different from the previous understanding that TME was a one-time phenomenon.

Keywords shape memory alloy, temperature memory effect (TME), TiNiNb

1. Introduction

When shape memory alloys (SMAs) are deformed at a low temperature, some residual strain remains after unloading. However, the residual strain vanishes and SMAs return to its original shape by a reversible transformation upon heating. This phenomenon is known as the shape memory effect (SME). The property is related to the reversible martensitic phase transformations, which are solid-solid diffusionless processes between a crystallographically ordered phase (austenite) and a less-ordered phase (martensite). Besides the SME, some researches have also shown that SMAs have the ability of memorizing their thermal history (Ref 1-4). If the reverse transformation of a SMA is arrested, a kinetic stop will appear in the next complete reverse transformation, as seen in the splitting of the endothermic differential scanning calorimetry (DSC) peak. The kinetic stop temperature always falls in a position a little higher than the previous arrested temperature and is regarded as a "memory" of the previous arrested temperature. Previously this phenomenon was named thermal arrest memory effect (Ref 3) or step-wise martensite to austenite reversible transformation (Ref 4, 5), and recently it was named temperature memory effect (TME) (Ref 6). This new memory effect was extensively investigated in TiNi-based alloy (Ref 7-12) and copper-based SMAs (Ref 13, 14).

However, many studies have reported that the TME in thermally induced martensite is a one-time phenomenon (Ref 1-4), that is, the TME can be wiped out by a complete transformation cycle and disappear in the second cycle. He et al. (Ref 11) investigated the TME in $Ti_{44}Ni_{47}Nb_9$ alloy after 10 incomplete transformation cycles in a decreasing temperature order. They found that in the following cycle a multipeak DSC curve appeared, but in the next cycle the endothermic peak reverted to its original shape. Yu et al. (Ref 8) found that the capability of TME was enhanced by performing repetitive incomplete cycles with the same temperature in TiNiCu and TiNi springs. With increasing number of incomplete cycles, the plateau on the contraction rate-temperature curve was widened toward higher temperature. However, they did not give the second contraction rate-temperature curve on the second complete transformation cycle. Liu et al. (Ref 15) have shown that even incomplete thermal cycling up to 80 times cannot retain the memory of the arrest temperature.

In this paper, a $Ti_{48}Ni_{17}Nb_{35}$ alloy was developed and it was shown the TME of this alloy is actually a multitime phenomenon, that is, the kinetic stop persists for many cycles.

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2. Experimental

Ternary TiNiNb alloy was prepared by arc melting Ti (99.8 mass%), Ni (99.96 mass%), and Nb (99.9 mass%) in a water-cooled copper crucible. The alloy button was melted for six times repeatedly and afterward annealed at 950 °C for 10 h in vacuum furnace at 1×10^{-3} Pa for homogenization. The composition of the alloy was $Ti_{48}Ni_{17}Nb_{35}$. Samples for TME investigation were spark cut from the button. They were divided into three groups. Some of the samples (Group 1) were directly tested by DSC. The rest of samples were subjected to 30 complete transformations cycling from below M_f (martensite transformation finishing temperature) to above A_f (reverse martensite transformation finishing temperature) in order to stabilize the transformation temperature, then some of them (Group 2) was tested for TME investigation. The rest (Group 3) were further subjected to 30 incomplete thermal cycling up to a specific arrested temperature and then tested for TME investigation. All the samples for DSC testing were conducted by using a Netzsch DSC 204 F1 Phoenix with a heating/cooling rate of 10 °C/min. X-ray diffraction was carried out on a XD-2 diffractometer.

3. Results and Discussion

The $Ti_{48}Ni_{17}Nb_{35}$ alloy consists of B2-TiNi(Nb), bcc-NbTi, and some Ti_2Ni precipitation by XRD test, as can be seen in Fig. 1.

Figure 2 shows the TME results of one Group 1 sample, i.e., from those without prior thermal cycling. The gray line corresponds to a full transformation. The arrested temperature was set to be 76 °C, as marked by a dashed line in Fig. 2. After an incomplete cycle, the sample was tested by DSC and the results of the first two global cycles were shown in Fig. 2. The numbers beside the curves indicate their sequence. The kinetic stop is clearly observed on the first global heating (curve 1). During the second global transformation (curve 2), a less evident but still clear kinetic stop can be observed. This kinetic stop temperature is more close to the previous arrested temperature than that in the first global heating. This repeatable TME is different from the previous understanding that TME could be wiped out totally by the second complete thermal cycle (Ref 6, 8, 11, 15).

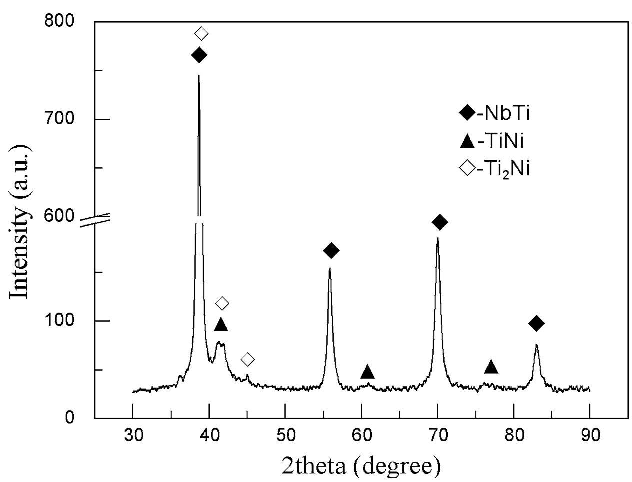

Fig. 1 XRD pattern of the $Ti_{48}Ni_{17}Nb_{35}$ alloy

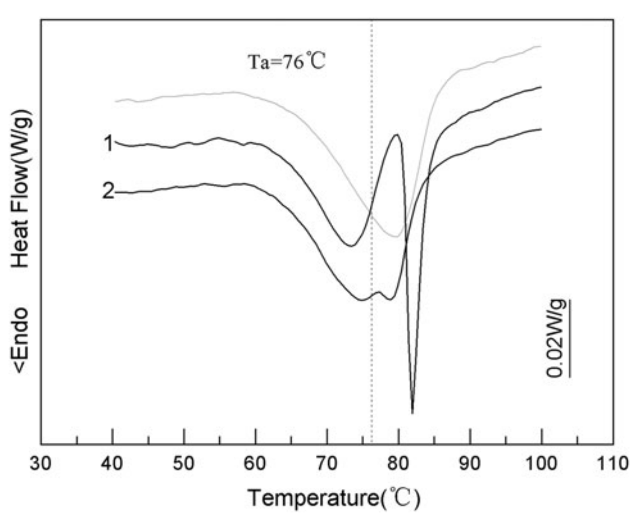

Fig. 2 The repeatable TME in $Ti_{48}Ni_{17}Nb_{35}$ alloy without complete thermal cycling

Figure 3 shows the TME phenomenon of the $Ti_{48}Ni_{17}Nb_{35}$ alloy after 30 complete thermal cycling (Group 2). The gray line is a full transformation after these 30 cycles. The sample was then incompletely cycled up to 62 °C, and afterward tested by DSC. The first seven DSC testing curves shown in Fig. 3 all indicates successfully the arrest temperature, although the last four curves are less distinct than the first three.

The TME phenomenon of the sample after 30 incomplete thermal cycling from below M_f up to 65 °C, the arrested temperature, is shown in Fig. 4. It can be seen that the memory of the arrested temperature T_a persists for at least 32 cycles, and the kinetic stops from the second to the fifth complete transformation cycles (curve 2 to curve 5) are much more obvious than the counterpart in Fig. 3. This suggests that incomplete thermal cyclings are more effective in enhancing this repeatable TME.

It also can be seen that the kinetic stop temperature marked by arrow during the first global transformation cycling (curve 1) is about 3 °C higher than the arrested temperature T_a. Then this

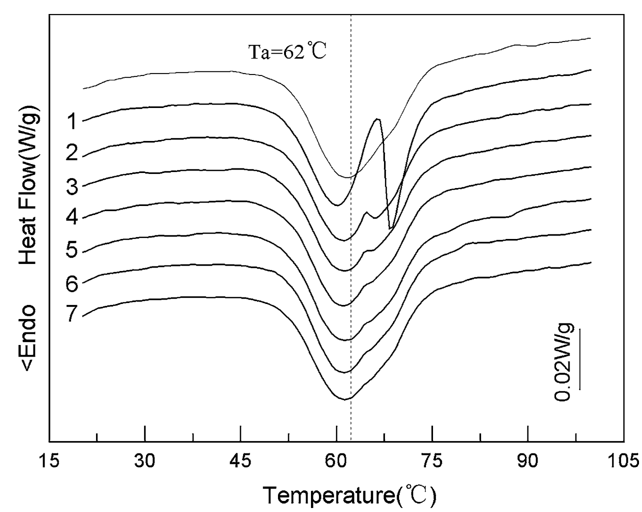

Fig. 3 The repeatable TME in $Ti_{48}Ni_{17}Nb_{35}$ alloy after 30 complete thermal cycling

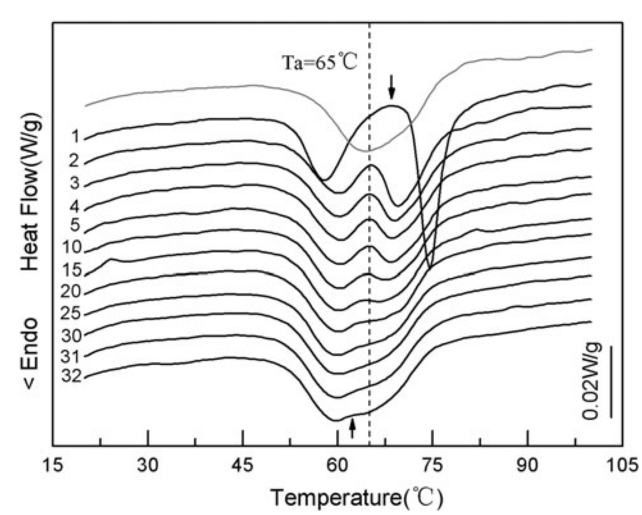

Fig. 4 The repeatable TME in $Ti_{48}Ni_{17}Nb_{35}$ alloy after further 30 incomplete thermal cycling

memory shifts toward lower temperature with increasing number of the testing cycles, and eventually is about 3 °C lower than the arrested temperature T_a during the last global transformation cycling (curve 32). It is well known that dislocations induced by thermal cyclings could contribute to the variation of transformation temperatures, but the variation of the memory shown in Fig. 4 might not be caused by the generation of dislocations. As one can see from the figure, the A_s and A_f temperatures are almost unchanged after 32 testing runs. If dislocations are more enough to change the memory temperature, the A_s and A_f temperatures will by no means be left unchanged.

The mechanism of TME is still not well understood, which makes it even more difficult to explain this repeatable TME. Many researchers (Ref 6, 10, 11) attributed the TME to the different orientation structures and different elastic energies of two kinds of martensite (remained M1 and newly formed M2). From Fig. 3 and 4, it can be concluded that thermal cycling plays an important role in introducing this repeatable TME, especially incomplete thermal training. As confirmed by SEM observations, there exists a large amount of interfaces between the TiNi(Nb), NbTi, and Ti_2Ni phases. This unique microstructure may give arise to large internal stress which may contribute to this repeatable TME. However it is still difficult at the moment to verify this and further experimental proof is necessary to clarify the issue.

4. Conclusion

In this work, the TME in $Ti_{48}Ni_{17}Nb_{35}$ alloy was studied. Without prior thermal cycling, the TME can still persist in the second global DSC testing curve. The alloy can memorize the arrest temperature several times even after 30 complete thermal cycling. A further 30 incomplete thermal cycling up to the arrest temperature can make the TME persist in the next 32 testing cycles.

Acknowledgments

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