Phase transformation behavior of Ti-rich NiTi alloy by a calorimetric method

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Nowadays a lot of shape memory alloys are known, and of these the NiTi alloy has excellent properties not only in shape memory but also in corrosion and wear resistance, so that it is more commonly used in various engineering fields in comparison with any other shape memory alloys [1–3]. A near equiatomic NiTi alloy shows a thermoelastic martensitic transformation, and it is known that the shape memory and transformation pseudoelasticity are caused by the reverse transformation from the phase with B19' structure to the parent phase with B2 structure [4–6]. These phenomena are sensitive to the crystal structure, inner stress and defects. Therefore, factors such as Ni concentration, thermal treatment, mechanical working and addition of a third element play important roles in controlling the behavior of the shape memory in NiTi [7–10].

It is known that the transformation behavior of near equiatomic NiTi is sensitive to the composition and thermal cycles [11–15]. However, the investigation on the effect of thermal cycles has been scarcely carried out for Ti-rich NiTi alloys. The purpose of this study is to reveal the phase transformation behavior of a Ti-rich NiTi alloy. Details of the experiment are as follows.

Ti-rich NiTi alloys were prepared using an arc melting furnace. The prepared samples were $Ni_{48}Ti_{52}$, $Ni_{49}Ti_{51}$, and $Ni_{50}Ti_{50}$ in at%. Several remelts were carried out for homogenization and then the samples were annealed at 1000 °C for an hour for homogenization. After cutting, the obtained samples were reannealed at 1000 °C. The transformation behavior was measured by using a differential scanning calorimeter with a liquid nitrogen cooling accessory.

Fig. 1 shows exothermic behavior as a function of temperature during cooling. The onset point of a sharp peak in the high-temperature side corresponds to the start temperature of the transformation to the low temperature phase (Ms). The Ms of $Ni_{48}Ti_{50}$ alloy, $Ni_{49}Ti_{51}$, $Ni_{50}Ti_{50}$ is 65.95, 75.09, and 45.81 °C, respectively. Because the Ms of a Ni-rich NiTi alloys is lower in comparison with that of $Ni_{50}Ti_{50}$, the Ms reaches a maximum temperature in the vicinity of 51 at.%Ti [16]. Moreover, small variations in the Ms are observed for Ti-rich NiTi alloys in contrast to Ni-rich NiTi.

Fig. 2 shows the shift of the Ms against the number of thermal cycles. It can be seen that the Ms is gradually decreased with increasing number of thermal cycles. The shift of the Ms between the 2nd and the 10th thermal cycle for $Ni_{49}Ti_{51}$, $Ni_{48}Ti_{52}$, and $Ni_{50}Ti_{50}$ is about

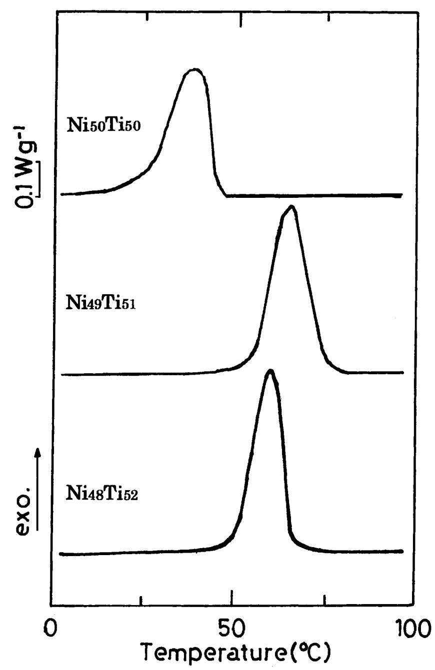


Figure 1 The exothermic behavior during cooling for 2nd cycle.

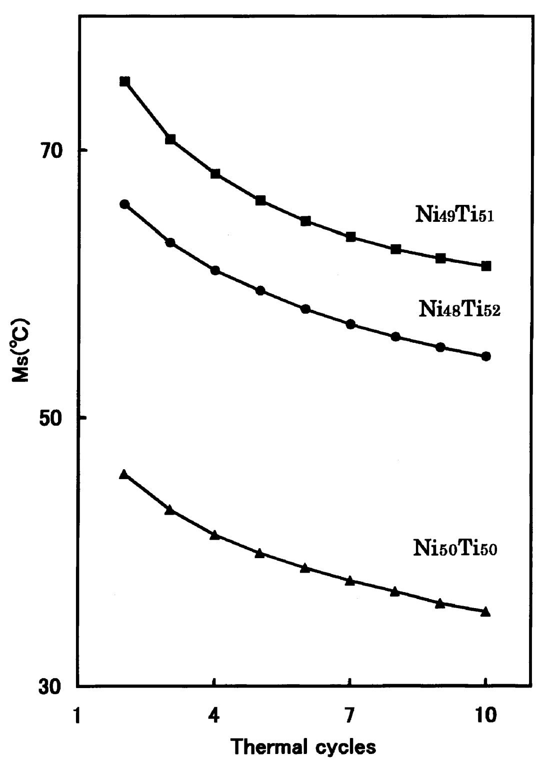
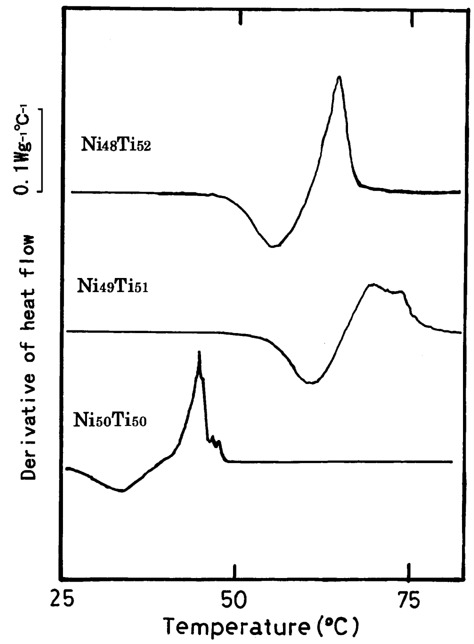
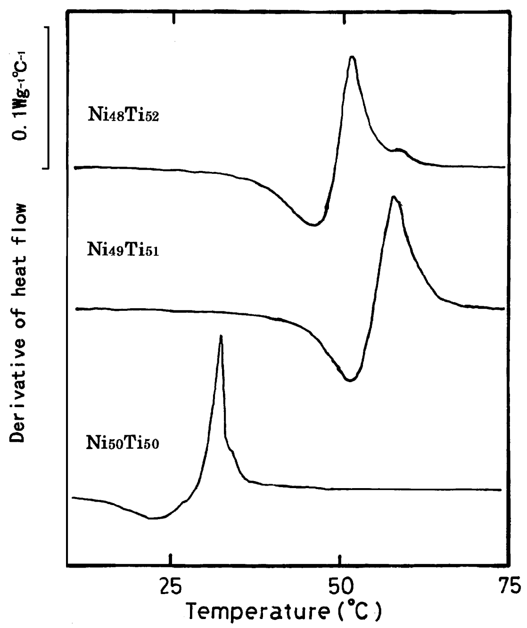


Figure 2 Temperature of the Ms against the number of thermal cycles.



(a)



(b)

Figure 3 (a) Differential curve with respect to temperature for the DSC themogram during 2nd cycle. (b) Differential curve with respect to temperature for the DSC themogram during 10th cycle.

14, 11, and 10 °C, respectively. Therefore, NiTi with a lower Ms shows a smaller shift of the Ms, although the Ms decreases with increasing number of thermal cycles.

Fig. 3a and b show differential curves with respect to temperature for the DSC thermogram during the 2nd and the 10th cooling ,respectively, in order to characterize the transformation. The complicated shape of the differential curve is shown for $Ni_{50}Ti_{50}$ in comparison with that of $Ni_{48}Ti_{52}$ and $Ni_{49}Ti_{51}$, although the differential curves during the 2nd cooling differ from those during the 10th cooling. The features in the shape of the DSC peak shown in Fig. 1 are enhanced by differentiating the thermogram, and the progress of the transformation can be characterized as shown in Fig.3. The phase transformation for $Ni_{50}Ti_{50}$ proceeds rapidly at the initial stage of transformation and then proceeds gradually. So a differential curve of the DSC thermogram is useful for characterizing the progress of the phase transformation.

We propose the following as conclusions:

1. The Ms reaches the maximum temperature near a titanium concentration of 51 at.%.
2. The Ms decreases with increasing number of thermal cycles.
3. Variation in the Ms is small for Ti-rich NiTi alloys.
4. The shape of the exothermic peak of $Ni_{50}Ti_{50}$ is more complicated and is dependent on number of thermal cycles in comparison with that of Ti-rich NiTi.

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