TRANSFORMATION BEHAVIOUR OF TiNi ALLOYS WITH ONE-WAY OR TWO-WAY SHAPE MEMORY EFFECT①

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ABSTRACT

The transformation behaviour of the near-equiatomic TiNi alloys with one-way or two-way shape memory effect has been examined using DSC and TEM. The transformation sequence with cooling is $B_2 \rightarrow M$ for the one-way memory specimens and the $B_2 \rightarrow R \rightarrow R+M$ for the two-way memory specimens. The transformation from B_2 to R is a first-order transformation and the R phase is not premartensitic, which is associated with a two-way memory effect.

Key words: transformation one-way memory two-way memory TiNi alloy

1 INTRODUCTION

The parent phase of TiNi alloys at high temperature is of B_2 structure and the phase of TiNi at low temperature is the martensite[1-2]. That the transformation from B_2 to martensite and the reverse process occur during cooling and heating shows the characterization of memory behaviour. The experimental results[3-7] of X-ray diffraction and electron diffraction have revealed the existence of extra reflections located at one third the spacing of the normal B_2 reflections during the B_2 to martensite transformation, which shows a rhombohedral structure, called R phase. Therefore, the transformation sequence may be described as $B_2 \rightarrow R \rightarrow$M.

The shape memory behaviours are classified as one-way and two-way memory. In order to understand the relationship between the memory effect and the phase transformation, it is necessary to examine the transformation behaviour of the memory alloys. This paper reports the experimental results of DSC and TEM examination about the transformation behaviour of the near-equiatomic TiNi alloys with one-way or two-way memory effects.

2 EXPERIMENTAL

The material used in the study was a bar composed of Ti–49.1 Ni–50.9 (at.–%). The strips 70mm × 50mm × 0.6 mm were obtained from the bar using a spark-cutting machine and then stretched to different degrees of deformation. The deformation was 7.25% for the one-way and 3.26% for the two-way memory specimens. Both kinds of specimens were annealed for 1h at 735 K in a vacuum of 1.5×10^{-4} Pa and then cooled down to room temperature in the furnace. To know the transformation temperature DSC experiments from 373 K to 240 K were carried out with a Perking-Elmer DSC–2c at a scanning rate of 10 K / min.

The TEM foils were prepared as follows. The strips were chemically thinned in a solution of $1HF{:}1HNO_3{:}1H_2SO_4{:}1H_2O$ and mechanically polished by grinding on abrasive papers. Discs of 3 mm in diameter were cut from

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the strips and then electro-polished in a methanol solution of 7 vol.−% perchloric acid at 260 K under an applied potential of about 40 V. The TEM experiments were carried out with a JEM−200CX electron microscope operating at 200 kV, and in-situ observation was performed under the microscope using both heating and cooling stages.

3 RESULTS AND DISCUSSION

3. 1 *Transformation behaviour of one-way memory specimens*

Fig.1 is the thermograph of the one-way specimens. On cooling from 373 K, the curve does not change until about 330 K where the curve starts to descend and an exothermal peak appears, which indicates that a phase transformation occurs at 330 K. On further cooling, no other peaks appear in the thermograph. The DSC result indicates that only one transformation occurs during cooling for this kind of one-way memory specimens.

The TEM in-situ observation experiments from 350 K to room temperature prove that the transformation shown in Fig. 1 is a martensitic transformation. At 320 K, the martensites begin to form and their morphology is needle-like. On further cooling, the martensites grow gradually, and the twin structures can be

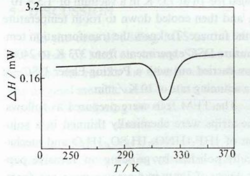


Fig. 1 The DSC curve of the one-way memory specimen with a cooling rate of 10 K / min

seen clearly. Fig. 2, taken at room temperature, is the bright field image of the needle-like martensites.

Fig. 3 shows a bright field image of the plate-like martensite and its corresponding Selected Area Electron Diffraction pattern. It has been reported[1−2] that the martensite has a monoclinical structure. In these experiments, the lattice parameters of monoclinical martensite calculated from SAED patterns are: a = 0.286 nm, b = 0.410 nm, c = 0.456 nm and β = 97(°).

The appearance of an exothermal peak in the DSC measurement is coincident with the formation of martensites in the TEM observation when cooling to about 330 K, which confirms that a martensitic transformation takes place and $M_s \sim 330$ K.

The *R* transformation has not been observed

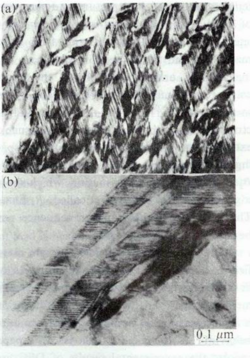
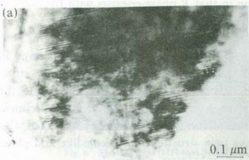


Fig. 2 Micrograph of the needle-like martensites at room temperature



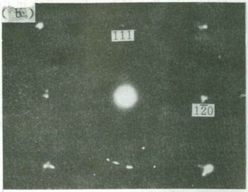


Fig. 3 Plate-like martensite and corresponding SAED pattern

(a)—BFM; (b)—[213]patterns

in the one-way memory specimens, which implies that it is not necessary the R transformation to take place before the marensite appears. So the R is not premartensitic in the sense that it is not a necessary precursor for the martensitic transformation.

3.2 *Transformation Behaviour of Two-way Memory Specimens*

For comparision, the transformation behaviour of the two-way memory specimens was also examined with DSC and TEM. Fig. 4 is the DSC curve of the two-way memory specimen from 373 K to 240 K, in which there are two exothermal peaks and their transformation points are 333 K and 283 K respectively. The DSC result shows that two transformations take place in the two-way memory specimen, a behaviour which is different from that of the one-way memory specimen. In association with the TEM experiment, the two phase transformations can be determined to be R (T_R~ 333 K) and martensite(M_s~ 283 K) transformation respectively.

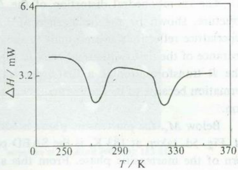


Fig. 4 The DSC curve of the two-way memory specimen with a cooling rate of 10 K / min

Fig. 5 shows the change of [111] zone SAED pattern of the B_2 structure of the two-way memory specimen with cooling. Fig. 5a taken at 360 K is a SAED pattern of the parent phase with the B_2 structure having a lattice parameter a = 0.301 nm. At 328 K, the super- lattice reflections located at the one third interplannar spacing of B_2 strucuture start to appear and their intensities are weaker, and they exhibit the 1 / 3(110) type reflections, see Fig. 5b. Further decreasing the temperature, the superlattice reflections are increased and intensified, see Fig. 5c. These changes are the typical feature of the R transformation[1,5-7]. The electron diffraction analysis confirms that the B_2 structure transforms into a rhombohedral structure with the R transformation. The R phase in these experiments has dimensions of a = 0.736 nm and c = 0.521 nm. The relative orientation relationship between the B_2 and R phases can be obtained from Fig. 5c and described as

$$(1\bar{1}0)_{B_2} \mathbin{//} (10\bar{1}0)_R,\ [111]_{B_2} \mathbin{//} [0001]_R$$

The rhombohedral distortion of the B_2 structure, shown by the occurrence of 1 / 3 superlattice reflections, corresponds to the appearance of the first exothermal peak in Fig.4. The R transformation is a first-order transformation because of its exothermal phenomenon.

Below M_s, the martensitic phase is formed. Fig. 5d, taken at 183 K, is the SAED pattern of the martensitic phase. From this and other diffraction patterns, the momoclinical structure can be determined, and the lattice parameters are the same as those of the martensite in the one-way memory specimens. Compared with Fig. 5c, some 1 / 3 superlattice reflections in Fig. 5d disappear, so it is supposed that the R phase has transformed into the martensitic phase.

On other hand, it is clear from the arrowed spots in Fig. 5d that some other 1 / 3 superlattice reflections are still visible in spite of the weaker intensities, which implies that the R phase does not fully transform into martensite. Strictly speaking, therefore, the R transformation is not a premartensitic transformation in that R phase coexists with the martensitic phase.

Not only the 1 / 3(110) reflections, but also the 1 / 3(111) reflections are observed in the [110] zone SAED pattern of the B_2 structure upon cooling, see Fig. 6. Similar to the marten- sites in the one-way memory specimen, those in the two-way memory specimen also have twin structure and needle-like and plate-like morphologies, see Fig. 7.

Unlike the $B_2 \rightarrow M$ transformation in the one-way memory specimens, the transformation behaviour of the two-way memory specimens may be described as follows: $B_2 \rightarrow R \rightarrow R+M$. It is apparent that the R transformation is related to the two-way memory effect since the 1 / 3 superlattice reflections arising from the R transformation are always present.

4 CONCLUSIONS

(1) The one-way and two-way memory effects of TiNi alloys are connected with $B_2 \rightarrow$M and $B_2 \rightarrow R \rightarrow R+M$ transformation, respectively.

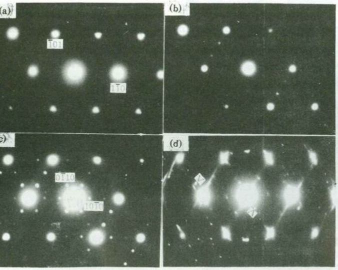


Fig. 5 The change of [111] zone SAED pattern of the B_2 structure at 360 K(a); 328 K(b); 300 K(c); 183 K(d)