PHASE TRANSFORMATIONS IN RAPIDLY SOLIDIFIED TiNi SHAPE MEMORY ALLOYS[①]

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ABSTRACT   The transformation behaviors associated with R -phase and martensitic transformations in rapidly solidified TiNi shape memory alloys have been studied systematically using differential scanning calorimetry, X-ray diffraction, etc. It was found that rapid solidification more significantly depresses the temperature ranges of R -phase and martensitic transformations than solution treatment and makes it possible that the martensitc transformation is separated from R -phase transformation. After aging the rapidly solidified Ni-rich TiNi binary shape memory alloy the martensite can be separated from the R -phase in not only the forward but also reverse transformations. With increasing aging time both the forward and reverse transformation temperature ranges of martensite and R -phase shift to high temperature.

Key words: solution treatment   shape memory alloy R -phase transformation   martensitic transformation   rapid solidification

1 INTRODUCTION

The rapid solidification (RS), by which TiNi shape memory alloys (SMAs) are prepared simplifies fabrication steps and minimizes costs. Moreover, the TiNi SMAs obtained by RS possess high strength and excellent shape memory effect (SME)[1,2]. Unfortunately, few papers have been reported on the transformation characteristics of rapidly solidified and RS plus aged TiNi SMAs. It has been confirmed in many reports that only martensitic transformation takes place in both Ti-rich and Ni-rich solution-treated TiNi binary SMAs, however the R -phase transformation can only be observed in Ni-rich TiNi binary SMAs, solution treated and then aged.

In this paper the transformation behaviors of rapidly solidified and RS plus aged TiNi binary SMAs will be systematically studied.

2 EXPERIMENTAL

The rapidly solidified ribbon was prepared by single roller melt-spinning in an argon atmosphere. The mother alloys were Ti-50. 0 at.-% Ni and Ti-50. 8 at.-% Ni and remelted by induction heating in quartz-BN composite crucible.

The surface linear velocity of pure copper chill roller (dia = 230 mm) was 21 m/s. The ribbon obtained is 0. 05~0. 07 mm thick and 5 ~6 mm wide.

The DSC were made with Perkin-Elmer DSC-7. X-ray diffraction experiment has been conducted by Regaku D/Max rotating target X-ray diffractometer.

3 RESULTS AND DISCUSSION

3.1 *R- phase and Martensitic Transformations in Rapidly Solidified* TiNi SMAs

The DSC curves of rapidly solidified Ti-50. 8 at.-% Ni is shown in Fig. 1, in which the exothermal and endothermal peaks are flat. In order to identify the transformation types cor-

responding to these peaks, X-ray diffraction experiments were carried out in turn at 293, 203, 133, 77 and 213 K, and the X-ray diffraction spectra at different temperatures are shown in Fig. 2. The rapidly solidified alloy is completely composed of $B2$ at 293 K and composed of R and $B2$ at 203 K. It is demonstrated that $B2 \rightarrow R$ takes place on the higher temperature side of the exothermal peak during cooling. At 133 K R-phase disappeared and martensite (M) came out. Besides this, the integrating intensity of $[110]$ $B2$ at 203 K was not considerably varied as compared with that at 133 K. Thus, it is supposed that $R \rightarrow M$ transformation occurs on the lower temperature side of the exothermal peak. In other words, the exothermal peak is thought to be an overlap of the $B2 \rightarrow R$ and $R \rightarrow M$ transformations, as shown by dotted line in Fig. 1. At 77 K the integrating intensity and distribution of diffraction peaks are the same as those at 133 K, which indicates that no transformation occurs in this temperature range. Heating from 77 K to 213 K, we find that the integrating intensity of M diffraction peaks decreases and that of R-phase increases. Obviously, the $M \rightarrow B2$ transformation takes place on the endothermal peak, whether or not the $M \rightarrow B2$ transformation proceeds through R-phase. Goubaa et al[7] pointed out that the R-phase is supposed to be an unavoidable transformation stage in TiNi binary or TiNiX ternary alloys.

Consequently, $M \rightarrow R \rightarrow B2$ transformation is thought to take place on endothermal peak.

The DSC curves of rapidly solidified Ti-50. 0 at. -% Ni TiNi SMA are shown in Fig. 3. As compared with Fig. 1, two exothermal peaks C_1 and C_2, associated with martensitic and R-phase transformations, respectively, were obviously separated from each other on cooling curve. There was an endothermal peak on the heating curve, which corresponds to $M \rightarrow R \rightarrow B2$ transition.

RS more significantly depresses the transformation temperature ranges (TTRs) of R-phase and M and makes it possible that martensitic transformation is separated from
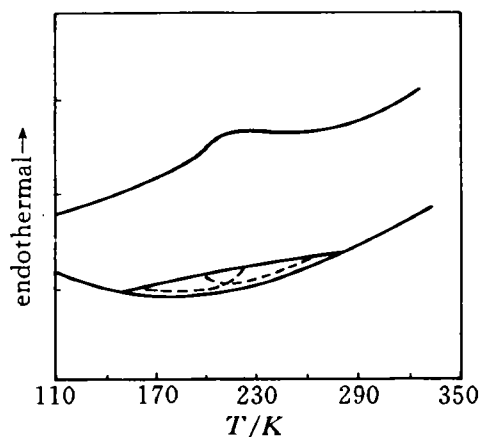

Fig. 1   DSC curves of rapidly solidified Ti-50. 8 at. -% Ni samples
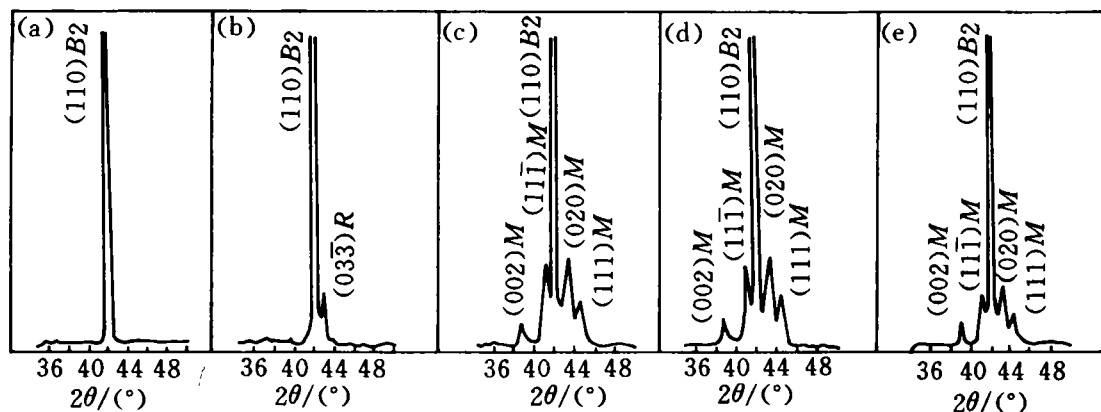

Fig. 2   X-ray diffraction spectra of rapidly solidified Ti-50. 8 at. -% Ni samples at 293(a), 203(b), 133(c), 77(d) and 213 K(e)

R-phase transition. By comparison between Fig. 1 and Fig. 3, it follows that M_s and T_R (starting point of R-phase transition) are sensitive to Ni content. However, the reasons why RS depresses transformation temperatures can be expressed as follows: Firstly, a great many non-thermal balance point defects — vacancies have been introduced into alloys during RS. The interaction between the strain field around defects and that associated with transformation will affect the transformation behavior. Because the transformation strain associated with martenstitic transformation is about ten times larger than that associated with R-phase transition[3]. Therefore, the M_s is depressed more considerably than T_R and martensitic transformation is separated from R-phase transition. Secondly, the grain size of rapidly solidified TiNi SMAs is smaller than that of ST[8]. The grain boundries act as potential barriers to phase transformation as a result of extra volume free-energy difference required as a driving force for transformation shear[1]. Thus, RS remarkably decreases TTRs of R-phase and martensite and makes them separated.

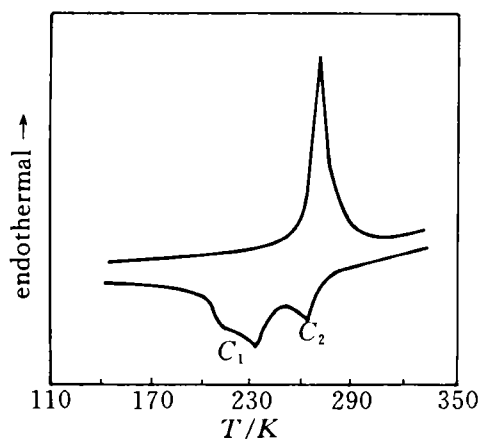### 3.2 Effect of Aging on R-Phase and Martensitic Transformation after RS

The DSC curves of RS plus 723 K, 30 min aged Ti-508 at.-% Ni SMA are shown in Fig. 4. There are two peaks C_1 and C_2 on cooling, and two peaks H_1 and H_2 on heating. The incomplete cycle result is shown by dotted line in Fig. 4, which indicates that H_2 and C_2 correspond to each other.

X-ray diffraction experiments were made in turn at 298, 253, 213, 133 and 297 K, and the results are shown in Fig. 5.

According to phases existing at different temperatures it follows that C_2 and C_1 are associated with $B2 \to R$ and $B2 \to R \to M$ on cooling, respectively, small amount of parent $B2$ was remained cooling to below the temperature range of C_1; H_2 is due to $R \to B2$ and H_1 due to $M \to R \to B2$ on heating. The DSC curves for spun Ti-50. 8 at.-% Ni specimens aged at 723 K with various aging time are all similar to those of Fig. 4. With increasing aging time, the peaks C_1 and H_1 shifted to high tmperature and the height of these peaks raised; but peaks C_2 and H_2 are not varied very much. When aging time comes up to 24 h peaks H_1 and H_2 completely coincided with each other.

The coherent particles $Ti_{11}Ni_{14}$ are known to precipitate in Ni-rich TiNi SMA aged at 723 in early stage. The strain field around precipitates interacts with that associated with phase
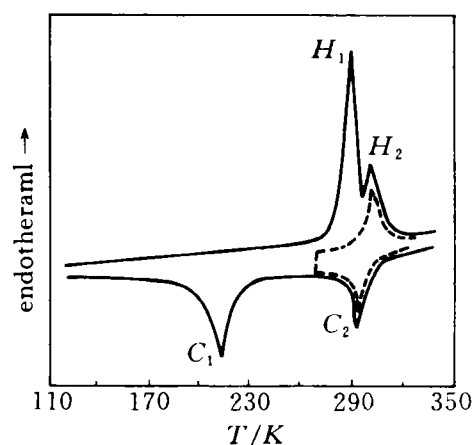

Fig. 3 DSC curves of rapidly solidified Ti-50. 0 at.-% sample

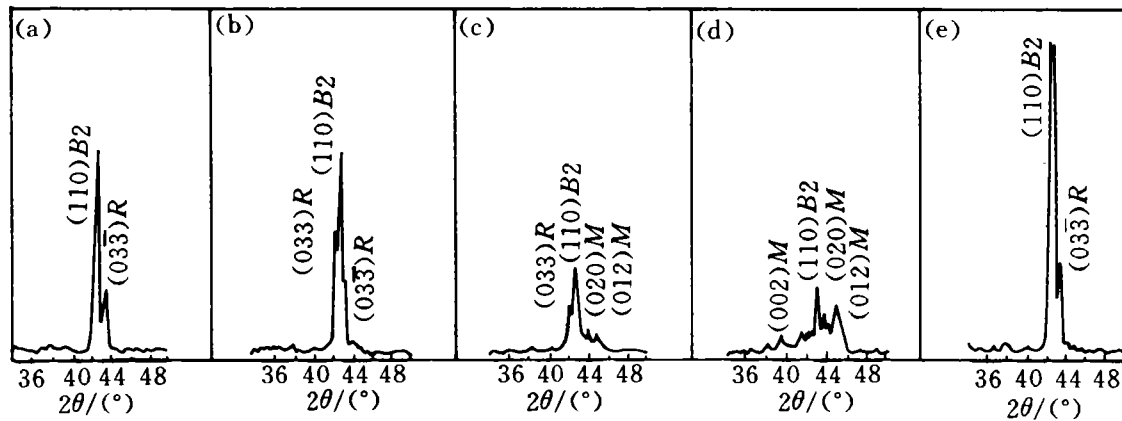Fig. 4 DSC curves of RS plus 723 K, 30 min aged Ti-50. 8 at.-% Ni sample

Fig. 5 **X-ray diffraction spectra of RS plus** 723 K, 30 min **aged Ti-50. 8 at. -% Ni samples at** 298(a), 253(b), 213(c), 133(d) **and** 297 K(e)

transformation, which prevents forward transformation and promotes the reverse one. The strain field with martensitic transformation is much larger than that with R -phase transition. Consequently, this interaction affects martensitic transformation more strongly than R -phase transition; Both forward and reverse martensitic transformation temperatures are lower and martensitic transformation is separated from R -phase transition. But, with increasing aging time, the Ni content in parent phase $B2$ decreases and the strain field around precipitates relaxes, all these raise the transformation temperatures but forward and reverse martensitic transformation temperatures raise faster than R -phase. After aging at 723 K for 24 h, the reverse TTRs of M and R -phase completely coincide, i. e, H_2 and H_1 merge into one.

4 CONCLUSIONS

(1) RS depresses the TTRs of M and R phases more strongly than ST. The influence of RS on the martensitic transformation is larger than that on the R -phase transformation and makes it possible for martensitic transformation to be separated from R -phase transition.

(2) On both cooling and heating the ob-

servation of separating martensitic transformation from R -phase transition is made in RS plus 732 K aged Ti-50. 8 at. -% Ni SMA. With increasing aging time the TTRs of M and R -phase shift to high temperature, but the influence of aging time on M is stronger than that on R -phase. Finally, the reverse TTRs of M and R -phase completely coincide with each other after aging at 723 K for 24 h.

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