

Influence of cooling rate on phase transformation and microstructure of Ti–50.9%Ni shape memory alloy

ZHANG Yan-qiu, JIANG Shu-yong, ZHAO Ya-nan, TANG Ming

Industrial Training Centre, Harbin Engineering University, Harbin 150001, China

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Abstract: Heat treatment of Ti–50.9%Ni (mole fraction) alloy was studied by differential scanning calorimetry, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis to investigate the influence of cooling rate on transformation behavior and microstructures of NiTi shape memory alloy. The experimental results show that three-stage phase transformation can be induced at a very low cooling rate such as cooling in furnace. The cooling rate also has a great influence on the phase transformation temperatures. Both martensitic start transformation temperature (M_s) and martensitic finish transformation temperature (M_f) decrease with the decrease of the cooling rate, and decreasing the cooling rate contributes to enhancing the $M \rightarrow A$ austenite transformation temperature. The phase transformation hysteresis ($A_f - M_f$) increases with the decrease of the cooling rate. Heat treatment is unable to eliminate the textures formed in hot working of NiTi sample, but can weaken the intensity of them. The cooling rate has little influence on the grain size.

Key words: NiTi alloy; shape memory alloy; phase transformation; cooling rate; martensitic transformation temperature; austenite transformation temperature

1 Introduction

Near-equiatomic nickel-titanium shape memory alloy (NiTi SMA) is the most widely used shape memory material due to its good mechanical properties, excellent shape memory effect and superelasticity as well as a perfect biological compatibility. The shape memory effect of NiTi SMA is closely related to its phase transformation. The austenite phase $B2$ (ordered CsCl-type structure) of NiTi SMA will be transformed into martensite phase $B19'$ (distorted monoclinic structure), or will be transformed into intermediate phase R (rhombohedral structure) and then into martensite phase $B19'$ in the course of cooling, while reversible transformation of martensite phase to austenite phase will occur in the course of heating. If NiTi SMA is deformed in the martensite phase, it will recover its shape of austenite phase, which results in shape memory effect along with the reversible transformation. Phase transformation temperature is one of the key parameters influencing the practical application of NiTi SMA, which is influenced by nickel content, ageing after solution treatment, thermo-mechanical treatment, thermal cycling,

processing techniques and so on [1–4].

Over the last decades, many scholars have studied the phase transformation behavior of NiTi SMA [5–13]. However, many studies ignored the influence of cooling rate on the phase transformation behavior of NiTi SMA. In fact, cooling rate is really another concern in testing SMAs, which is particularly important in bulk SMAs due to a prolonged period of heat transfer. So far, the study of the influence of cooling rate on the phase transformation behavior of NiTi SMA is still limited. WANG et al [14] studied the effects of heating-cooling rates on the transformation temperatures in a ternary NiTiCu SMA by differential scanning calorimetry (DSC), which showed that the martensitic finish transformation temperature (M_f) and austenite finish transformation temperature (A_f) depended strongly on the scanning rate of the heating-cooling process. NURVEREN et al [15] investigated the influence of heating-cooling rate on the transformation characteristics of a near-equiatomic NiTi SMA by means of differential scanning calorimeter (DSC) measurements for four NiTi SMAs, which showed that the heating-cooling rate had a strong influence on the transformation temperatures, the absorbed-released heat, and the elastic and irreversible

energies during transformation. MOTEMANI et al [16] studied the effects of the cooling rate on the phase transformation behavior and the mechanical properties of Ni-rich NiTi SMA.

In the present work, the influence of the cooling rate on the phase transformation behavior and microstructure of Ti–50.9%Ni (mole fraction) SMA was studied by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX).

2 Experimental

The investigated material was a polycrystalline NiTi bar with a diameter of 12 mm and a nominal composition of Ti–50.9%Ni (mole fraction), which was prepared by initial vacuum induction melting, subsequent rolling at 800 °C and final drawing at 400 °C. Four specimens were cut from the NiTi bar by wire cutting apparatus with water-cooling. One of the specimens is used for analysis as the as-received sample, the other three specimens were vacuum-sealed in three quartz tubes separately and annealed at 850 °C for 2 h. After annealing, one of the samples was quenched into ice-water, the second one was cooled to room temperature in air, and the third one was cooled to room temperature in furnace.

Differential scanning calorimeter (DSC) with a liquid nitrogen-cooling accessory was used to characterize the transformation behavior. The DSC samples were cut into cube with side length of 2 mm from the four specimens prepared above by wire cutting, and then were polished by mechanical method. Afterward, the specimens were degreased in acetone and cleaned with ultrasonic cleaner. In the experiment, the samples were heated up to 100 °C from room temperature with heat preservation of 3 min to establish thermal balance, and then were tested at a heating-cooling rate of 10 °C/min between –100 and 100 °C.

The phase formations of the samples were analyzed by X-ray diffraction (XRD) at the ambient temperature using a Philips X'Pert Pro diffractometer with Cu K_α radiation. The XRD samples were cut into disks with the height of 3.5 mm and the diameter of 6 mm. The samples were scanned over 2θ ranging from 20° to 100° by continuous scan with tube voltage of 40 kV and tube current of 40 mA.

The microstructure observation and EDX were used for microscopy analysis on a FEI Quanta200 SEM. The samples were cut from the four specimens prepared above by wire cutting, which were proceeded by grinding, polishing and etching using a solution of HF:HNO₃:H₂O with volume ratio of 1:2:10.

3 Results and discussion

3.1 DSC analysis

Figure 1 shows the influence of cooling rate on the DSC curves of NiTi alloy. It can be seen that all the samples except the sample cooled in furnace undergo one-stage $M \rightarrow A$ austenite transformation on heating and one-stage $A \rightarrow M$ martensitic transformation on cooling. The sample cooled in furnace undergoes one-stage $M \rightarrow A$ austenite transformation on heating and three-stage phase transformation ($A \rightarrow R$, $R \rightarrow M_1$ and $A \rightarrow M_2$) on cooling, which is also observed in the aged NiTi alloy by ZHENG et al [2]. This implies that multi-stage phase transformation can be induced at a very low cooling rate. Such behavior resembles the phase transformation induced in some ageing treatments because the cooling condition in furnace is actually a course of ageing at a gradually decreasing temperature, in which some intermetallic phases such as Ni₄Ti₃, Ni₃Ti₂ or Ni₃Ti may be precipitated.

The evaluation of the influence of the cooling rate on the phase transformation temperatures is shown in Fig. 2. It can be seen from Fig. 2 that all the phase transformation temperatures of the sample cooled in air are nearly equal to those of the as-received NiTi sample. Both M_s and M_f decrease with the decrease of the cooling rate, while the influence laws of the cooling rate on A_s and A_f are not very clear. But it is evident that both A_s and A_f of the sample cooled in furnace are much higher than those of the other three conditions, which shows that decreasing the cooling rate can enhance the $M \rightarrow A$ austenite transformation temperature. The phase transformation hysteresis ($A_f - M_f$) increases with the decrease of cooling rate, and the sample cooled in furnace has a much higher phase transformation hysteresis than the other two samples which are cooled at the high cooling rates and the as-received sample, respectively.

3.2 XRD analysis

Figure 3 shows the XRD patterns of the as-received sample and the heat-treated samples cooled at different cooling rates. Only four austenite peaks were observed in the first three patterns, which contain (110), (200), (211) and (220) peaks. There is a small (21 $\bar{2}$) peak of Ni₄Ti₃ spreading in a wide range of 2θ in addition to the four austenite peaks in the sample cooled in furnace, which reveals that the precipitated Ni₄Ti₃ particles are very fine and few Ni₄Ti₃ particles are formed at the room temperature because the $A \rightarrow R$ transformation temperature is near the room temperature. It is well

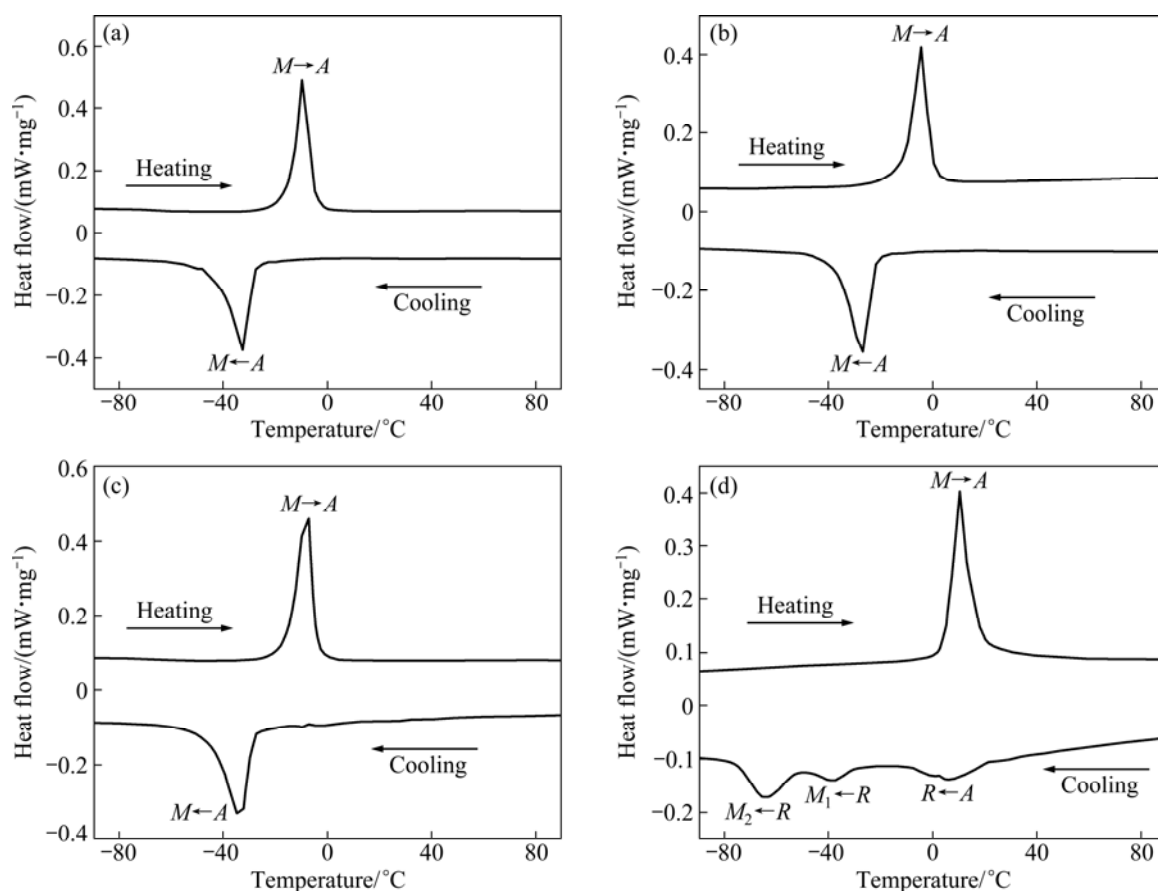


Fig. 1 DSC curves of NiTi samples cooled under different conditions: (a) As-received; (b) Quenched in ice water; (c) Cooled in air; (d) Cooled in furnace

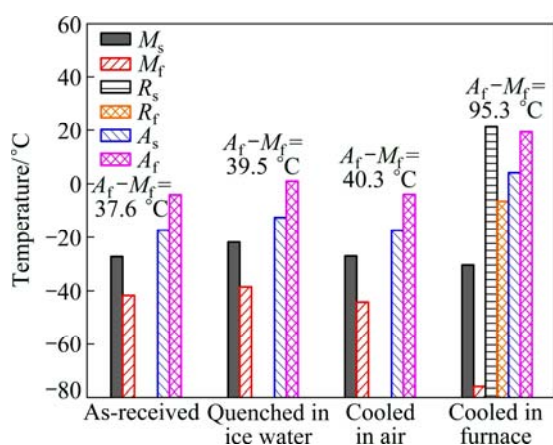


Fig. 2 Evaluation of phase transformation temperatures under different cooling conditions

known that Ni_4Ti_3 particles have an influence on the features of the martensitic transformation by supporting the formation of the R-phase and affecting the Ni-content of the matrix [15–17]. Therefore, the three-stage transformation observed in Fig. 1(d) can be attributed to the presence of Ni_4Ti_3 particles formed in the specimen cooled in furnace. The precipitation of Ni-rich

intermetallic phases can lead to reduction of Ni content in the matrix, which subsequently results in the increase of martensitic phase transformation temperatures and reverse phase transformation temperatures, such as M_s , M_f , A_s and A_f . However, only austenitic phase transformation temperatures such as A_s and A_f are increased in the present study, while the martensitic phase transformation temperatures such as M_s and M_f are decreased. Therefore, the future work will be done to understand the above behavior.

In the XRD patterns of the as-received sample (Fig. 3(a)), the (110) peak shows the highest relative intensity in the four peaks, which means that there are many initial (110) textures in the as-received NiTi bar, i.e., the grains preferentially grow up along the (110) lattice plane in the process of material manufacturing. The relative intensities observed in the heat-treated samples are different from those observed in the as-received sample, because the (110) peak shows much lower relative intensity than that of the as-received sample. The reason may be that the initial (110) texture intensities in the as-received NiTi bar are weakened due to the heat treatment. In other words, the preferred growth of the

grains occurs during the heat treatment. It can also be observed that the (110) peak of the sample quenched in ice water shows a higher relative intensity than that of the samples cooled in air and in furnace, which reveals that the larger cooling rate can prevent the grains from growing up preferentially and is in favor of preserving

the initial textures.

3.3 SEM–EDX analysis

Figure 4 shows the microstructures of specimens of the NiTi alloy cooled under different conditions. The microstructure in the as-received sample in Fig. 4(a) is

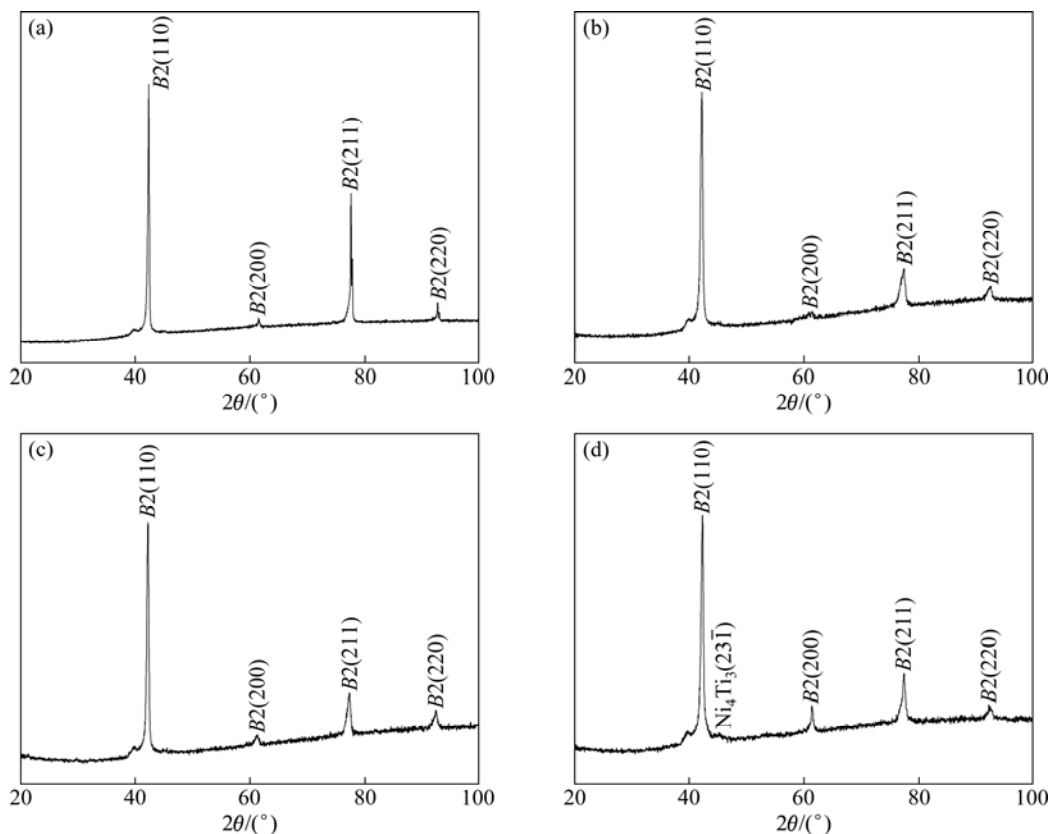


Fig. 3 XRD patterns of NiTi samples cooled under different conditions: (a) As-received; (b) Quenched in ice water; (c) Cooled in air; (d) Cooled in furnace

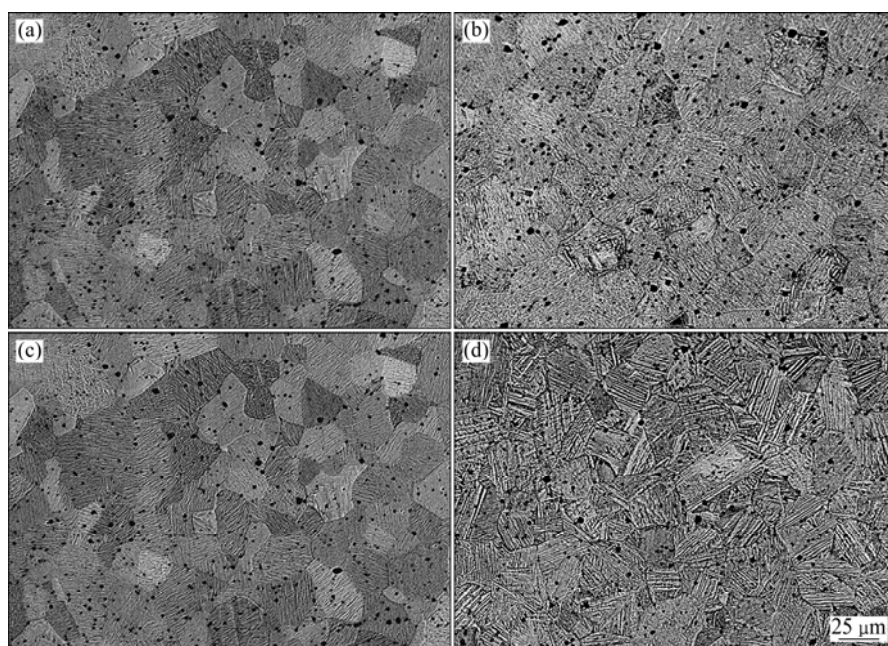


Fig. 4 Microstructures of NiTi specimens cooled under different conditions: (a) As-received; (b) Quenched in ice water; (c) Cooled in air; (d) Cooled in furnace

characterized by regular and uniform grains with the size of 20–30 μm . There are strong initial (110) textures at the grain scale, which evidently results from hot deformation in the process of material manufacturing. There are also many black impurities with different sizes distributing in the NiTi matrix, which are determined as TiC particles by EDX (see Fig. 5). From Figs. 4(b)–(d), it can be observed that there are not evident differences among the three specimens in terms of the grain sizes, and there is a slight difference in grain sizes between the as-received sample and the heat treated samples. Therefore, it can be concluded that the heat treatment has little influence on the grain size of Ni-rich NiTi SMAs. It can also be seen that there are still relatively strong (110) textures in the heat-treated samples, which reveals that heat treatment is unable to eliminate the textures formed in the deformation, but can weaken the intensity of them. This phenomenon is consistent with the previous XRD results.

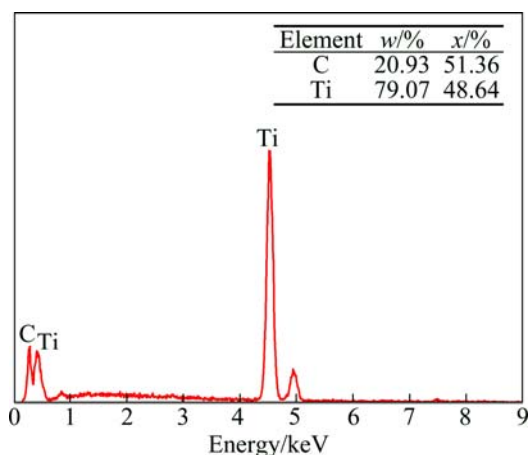


Fig. 5 EDX spectra of NiTi samples cooled in furnace

4 Conclusions

1) The cooling rate is an important factor that influences the phase transformation behavior of NiTi SMA in the heat treatment. Three-stage phase transformation can be induced at a very low cooling rate such as cooling in furnace, which is attributed to the presence of Ni_4Ti_3 particles formed in the specimen cooled in furnace. The cooling rate also has a great influence on the phase transformation temperatures.

2) The heat treatment has no significant influence on the texture orientation of the NiTi alloy, but it is able to weaken the texture intensity. The cooling rate has little influence on either the texture intensity or the texture orientation, and the textures of all samples parallel to (100) crystal plane.

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冷却速度对 Ti-50.9%Ni 形状记忆合金相变行为和 组织的影响

张艳秋, 江树勇, 赵亚楠, 唐 明

哈尔滨工程大学 工程训练中心, 哈尔滨 150001

摘 要: 为了探索冷却速度对镍钛形状记忆合金相变行为和组织的影响, 通过差热扫描、X 射线衍射、扫描电镜、X 射线荧光分析等方法研究 Ti-50.9%Ni(摩尔分数)合金的热处理。结果表明: 当冷却速度非常低时(如炉冷)可诱发三级相变的产生; 冷却速度对相变温度也有很大的影响, M_s 和 M_f 都随冷却速度的降低而下降, 降低冷却速度有利于提高 $M \rightarrow A$ 奥氏体相变温度, 相变滞后宽度($A_f - M_f$)随着冷却速度的降低而增大; 热处理不能消除镍钛合金热加工时所形成的组织, 但能减弱其强度; 冷却速度对晶粒大小影响不大。

关键词: 镍钛合金; 形状记忆合金; 相变; 冷却速度; 马氏体转变温度; 奥氏体转变温度

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