



Effect of annealing temperature on martensitic transformation of $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy processed by equal channel angular pressing

Dian-tao ZHANG^{1,2}, Bao GUO^{1,2}, Yun-xiang TONG^{1,2}, Bing TIAN^{1,2}, Li LI^{1,2},
Yu-feng ZHENG^{2,3}, Dmitry-V GUNDEROV⁴, Ruslan-Z VALIEV⁴

1. Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, China;
2. Center for Biomedical Materials and Engineering, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China;
3. Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China;
4. Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa 450000, Russia

Received 3 March 2015; accepted 12 October 2015

Abstract: The effect of annealing temperature on the martensitic transformation of a $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy processed by equal channel angular pressing (ECAP) was investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The as-ECAP processed and subsequently annealed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloys consist of B2 parent phase, $\text{Ti}_4\text{Ni}_2\text{O}$ phase and B19' martensite at room temperature. Upon cooling, all samples show B2→R→B19' two-stage transformation. Upon heating, when the annealing temperature is less than 400 °C, the samples show B19'→R→B2 two-stage transformation; when the annealing temperature is higher than 500 °C, the samples show B19'→B2 single-stage transformation. The B2→R transformation is characterized by wide interval due to the dislocations introduced during ECAP.

Key words: TiNi alloy; equal channel angular pressing; martensitic transformation; annealing temperature

1 Introduction

TiNi shape memory alloys (SMAs) have attracted much attention in many engineering and biomedical applications due to their excellent shape memory effect (SME), superelasticity and biocompatibility [1]. In nature, both SME and superelasticity are based on the diffusionless martensitic transformation. The former is related to thermally-induced martensitic transformation, and the latter is governed by stress-induced martensitic transformation. In order to suppress the irreversible dislocation movement that deteriorates the shape recovery properties, several approaches have been developed, such as aging strengthening, thermo-mechanical treatment [2] and grain refinement [3,4].

Recently, equal channel angular pressing (ECAP) has been recognized as one of the effective methods to

refine the microstructure of TiNi-based SMAs. The first report was published by PUSHIN et al [5] in which an ultrafine-grained state with a grain size of 0.2–0.3 μm was obtained in bulk $\text{Ti}_{49.4}\text{Ni}_{50.6}$ and $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloys as a result of ECAP. To date, several important aspects of as-ECAP processed TiNi SMAs have been reported, including processing [5–9], microstructure evolution [10–12], martensitic transformation behavior [6,13–15], mechanical properties [10,11] and SME [3,4]. As compared with the coarse-grained counterpart, the as-ECAP processed TiNi SMAs show lower transformation temperatures [14], better cycling stability [3,4,16] and shape recovery properties [3,17].

The microstructure of as-ECAP processed TiNi SMAs is usually characterized by the ultrafine grain size, non-equilibrium grain boundaries and high density dislocations. These specific features not only increase the critical stress for the slip of alloys, but also suppress the

martensitic transformation. This indicates that a proper annealing is essential to optimize the transformation and shape recovery properties by tailoring the microstructure. It has been previously reported that SME and superelasticity of the as-ECAP processed TiNi alloy can be improved by post-deformation annealing at 400 °C [18–20]. Martensitic transformation of as-ECAP processed TiNi alloy depends on the processing condition. KARAMAN et al [6] once observed the single-stage martensitic transformation in the $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy processed at 450 °C using a die with an angle of 90° and the two-stage $\text{B2} \rightarrow \text{R} \rightarrow \text{B19}'$ transformation upon cooling after annealing at a temperature higher than 300 °C for 1 min [6]. Our previous results showed that the two-stage $\text{B2} \rightarrow \text{R} \rightarrow \text{B19}'$ transformation was observed in the $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy processed at 450 °C for eight passes using a die with an angle of 120 ° [16]. In addition, from an application point of view, as the final process of fabrication of actuator based on TiNi SMAs, shape setting is usually carried out at 300–700 °C for different durations from several minutes to several hours depending on the dimensions of samples [21]. Therefore, it is necessary to further investigate the effect of annealing on the martensitic transformation of ECAP processed TiNi SMAs. In our previous results, the effect of annealing at a temperature range of 300–600 °C on microstructure and superelasticity of the as-ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy has been established [16,20]. Therefore, the purpose of present work is to continuously investigate the effect of annealing temperature on the martensitic transformation of as-ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy. The results are further discussed on the basis of microstructure evolution with annealing temperature.

2 Experimental

A $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy was investigated. The detailed ECAP processing has been given in our previous work [16]. After removing the surface oxide, the samples were sealed in vacuum quartz tubes, and then annealed at various temperatures from 300 and 600 °C for 30 min followed by quenching in water. The phase constitution was determined by X-ray diffraction (XRD) on a Panalytical X-pert'PRO diffractometer at room temperature using $\text{Cu K}\alpha$ radiation. Microstructure observation and selected area electron diffraction (SAED) were carried out on a Tecnai G2 F30 transmission electron microscope (TEM) operated at 300 kV with a double-tilt sample stage. The TEM foils were prepared by mechanical grinding, followed by twin-jet electropolishing using an electrolyte solution consisting of 95% acetic acid and 5% perchloric acid (volume fraction). Martensitic transformation was measured on a

Perkin-Elmer Diamond differential scanning calorimeter (DSC) at a constant heating/cooling rate of 20 °C/min. The transformation temperatures were determined as intersection of tangent lines from the DSC curves.

3 Results and discussion

Figure 1 shows the XRD patterns of differently treated samples. All of the patterns can be indexed as a mixture of B2 parent phase, $\text{Ti}_4\text{Ni}_2\text{O}$ phase and B19' martensite. It should be pointed out that the existence of R phase cannot be excluded because the (112) peak of R phase is very close to the (110) peak of B2 parent phase [22,23]. The formation of $\text{Ti}_4\text{Ni}_2\text{O}$ phase in Ni-rich TiNi alloys results from the introduction of oxygen during melting [24]. The appearance of B19' martensite is possibly related to the strain-induced martensite during ECAP [6]. With increasing the annealing temperature, the intensities of peaks corresponding to B19' martensite gradually decrease because the volume fraction of martensite decreases. This indicates that the strain-induced B19' martensite is unstable and can be restored by annealing. The strain-induced B19' martensite may be stabilized by the high density dislocations introduced during ECAP. During annealing, the recovery and recrystallization occur. As a result, the rearrangement and elimination of dislocations take place, leading to the reduction of volume fraction of B19' martensite with increasing the annealing temperature.

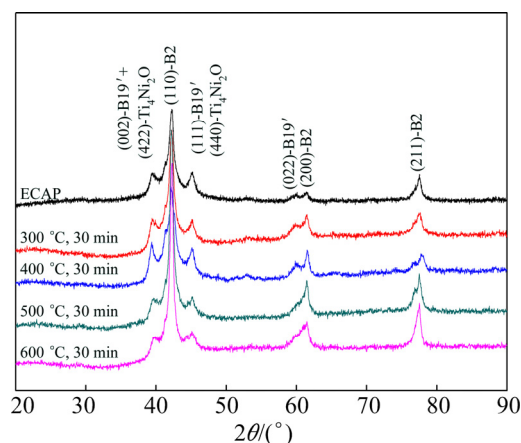


Fig. 1 XRD patterns of differently treated $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy

The R phase of the samples annealed at 300 and 400 °C was identified by SAED, and the results are shown in Fig. 2. The B2–R transformation start temperatures of other samples are below or very close to room temperature, as shown in Table 1. It is seen that the diffraction spots at 1/3 positions of the B2 reciprocal lattice are obvious, indicating the presence of R phase [25,26]. In addition, the diffraction spots corresponding to Ti_3Ni_4 phase are also visible in the

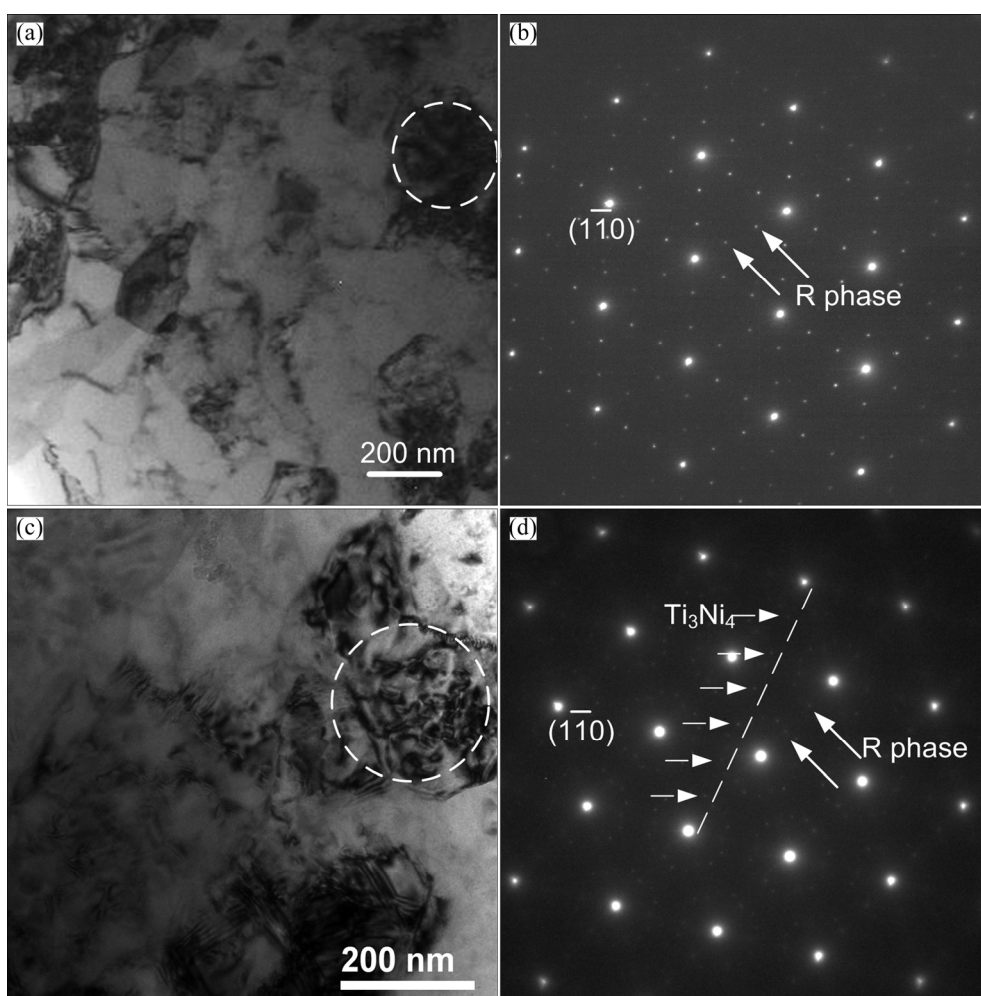


Fig. 2 TEM bright-field images (a, c) and SAED patterns of regions indicated by circles (b, d) of samples annealed at 300 °C (a,b) and 400 °C (c,d) for 30 min (incident beam is parallel to $[111]_{B2}$)

sample annealed at 400 °C [20].

Figure 3 shows the DSC curves of differently treated samples. During cooling, all the samples exhibit two-stage transformation. In order to identify the transformation sequence [27], partial DSC cycling technique was used. This method requires to heating to 80 °C, and holding for 2 min to obtain the parent phase state, and then cooling to a predefined temperature and holding for 2 min before heating. The results of partial DSC cycling are also shown in the insets of Fig. 3. It is seen that for the as-ECAP processed sample, the transformation hysteresis between peaks 1 and 3 is about 2 °C and the enthalpy is about −5 J/g upon cooling, thus this pair results from the reversible B2–R transformation, which is characterized by a small hysteresis due to its significantly small lattice deformation [28]. Therefore, the peak 2 corresponds to R→B19' transformation. The B2–R transformation induced by ECAP shows a wide transformation interval, which is different from that induced by aging. After annealing at 300 and 400 °C for 30 min, the transformation temperatures increase, as

shown in Figs. 3(b) and (c), respectively. A weak shoulder appears on the high temperature side of the heating curve, as indicated by the arrows, in which the transformation temperatures are the same as the reverse transformation temperature of R transformation during partial heating. This may suggest that this weak peak corresponds to R→B2 transformation. Therefore, it can be concluded that a two-stage B19'→R→B2 reverse transformation occurs in the above samples during heating. When the annealing temperature increases to 500 °C, the R phase transformation peak becomes sharper as compared with that of other samples. Upon cooling, a two-stage B2→R→B19' transformation occurs. Upon heating, a single-stage B19'→B2 occurs. When the annealing temperature increases to 600 °C, during cooling, a two-stage B2→R→B19' transformation occurs in the sample. However, the peaks 1 and 2 are very close, leading to the difficulty in separating from each other during partial DSC cycling. When cooled to the position between peaks 1 and 2, the transformation corresponding to peak 2 occurs in some

parts of the sample, as shown in Fig. 3(e). The temperature differences between peaks 1 and 3 and peaks 1 and 4 are 5 and 25 °C, respectively. This means that upon cooling, the peak 1 corresponds to B2→R transformation, the peak 2 corresponds to R→B19'; upon heating, the peak 3 corresponds to R→B2, and the peak 4 corresponds to B19'→B2. In the full cycle, the reverse transformation occurs in a single-stage B19'→B2 manner. In the present work, M_s represents the forward martensitic transformation start temperature, M_p represents the forward martensitic transformation peak temperature and M_f represents the forward martensitic

transformation finish temperature; A_s represents the reverse martensitic transformation start temperature, A_p represents the reverse martensitic transformation peak temperature and A_f represents the reverse martensitic transformation finish temperature; R_s represents the B2→R transformation start temperature, R_p represents the B2→R transformation peak temperature and R_f represents the B2→R transformation finish temperature; R_{As} represents the reverse B2→R transformation start temperature, R_{Ap} represents the reverse B2→R transformation peak temperature and R_{Af} represents the reverse B2→R transformation finish temperature. Table 2

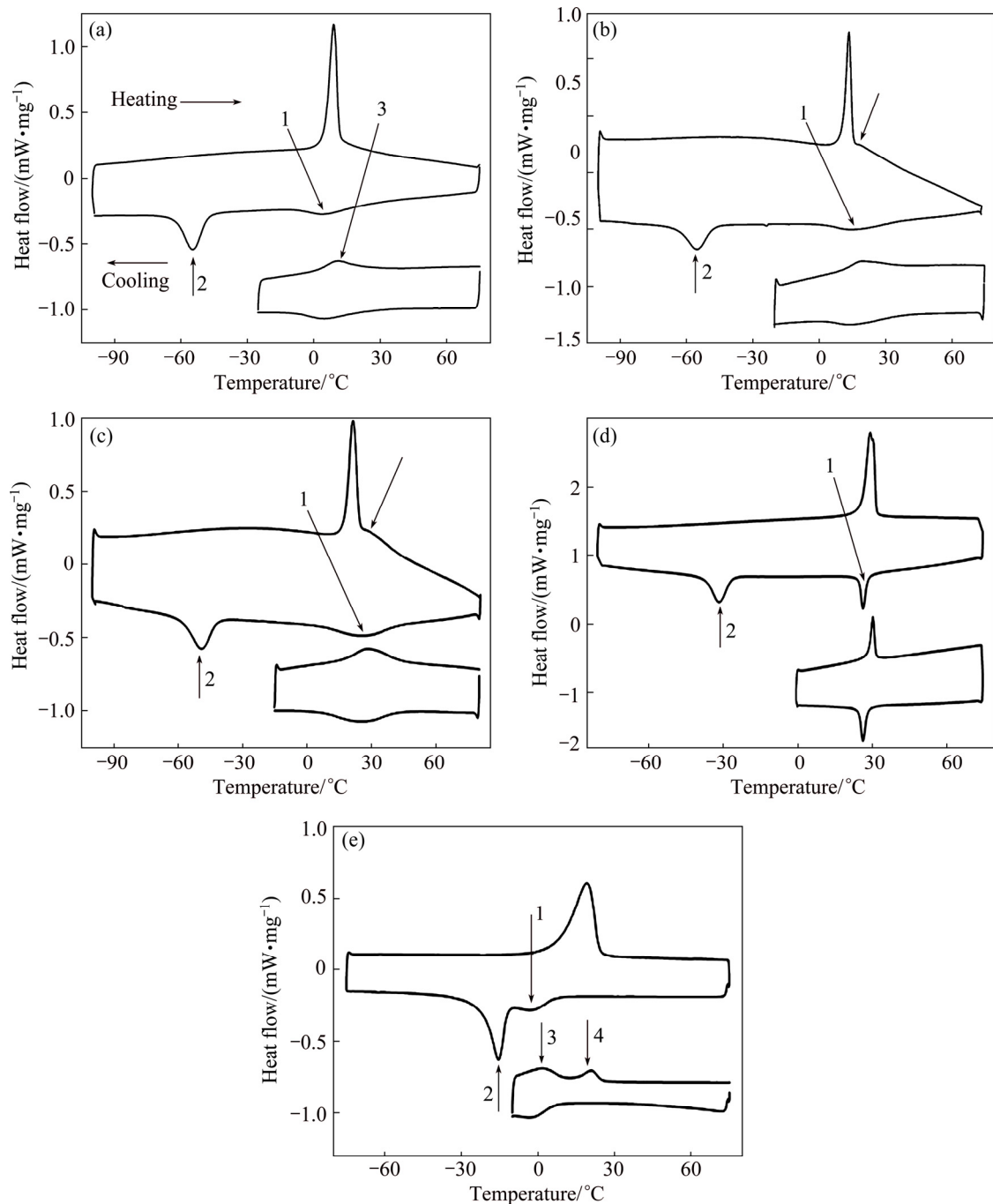


Fig. 3 DSC curves of alloys as-ECAP processed (a) and subsequently annealed at 300 °C (b), 400 °C (c), 500 °C (d) and 600 °C (e) for 30 min

Table 1 Transformation temperatures of samples as-ECAP processed and annealed at different temperatures

Sample	Transformation temperature/°C											
	M_s	M_p	M_f	A_s	A_p	A_f	R_s	R_p	R_f	R_{As}	R_{Ap}	R_{Af}
As-ECAP processed	−48	−55	−63	5	9	12	21	6	−9	3	11	32
Annealed at 300 °C	−48	−55	−64	11	14	16	34	16	2	9	19	40
Annealed at 400 °C	−43	−50	−59	17	21	24	41	25	7	14	28	46
Annealed at 500 °C	−27	−32	−38	26	29	32	28	26	22	28	30	32
Annealed at 600 °C	−11	−15	−23	5	19	25	5	−4	−10	−	2	10

Table 2 Transformation sequences of samples as-ECAP processed and annealed at different temperatures

Sample	Transformation sequence	
	Cooling	Heating
As-ECAP processed	B2→R→B19'	B19'→R→B2
Annealed at 300 °C	B2→R→B19'	B19'→R→B2
Annealed at 400 °C	B2→R→B19'	B19'→R→B2
Annealed at 500 °C	B2→R→B19'	B19'→B2
Annealed at 600 °C	B2→R→B19'	B19'→B2

summarizes the transformation sequences in the as-ECAP processed sample and the samples annealed at different temperatures. The transformation temperatures related to B2→R transformation and its reverse transformation were determined from the partial DSC cycling results, as shown in the inset of Fig. 3. According to the above results, all of the samples can be divided into two groups, the first group includes the as-ECAP processed sample and the samples annealed below 400 °C and the second group includes the samples annealed at 500 and 600 °C.

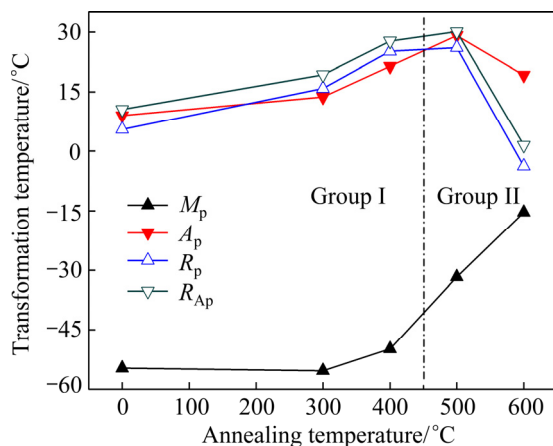
The two-stage transformation which occurs in the ECAP-processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy can be ascribed to the grain refinement and a large number of dislocations introduced during ECAP [14]. The similar transformation behavior was also observed in the cold-rolled TiNi alloys [29–31]. It should be emphasized that such a two-stage transformation was not observed in the ternary TiNi-based alloys processed by ECAP, including $\text{Ti}_{42.2}\text{Ni}_{49.8}\text{Hf}_8$ [4], $\text{Ti}_{50.3}\text{Ni}_{33.7}\text{Pd}_{16}$ [17] and $\text{Ti}_{44}\text{Ni}_{47}\text{Nb}_9$ [32] alloys. This suggests that the two-stage transformation is compositional dependence. In addition, KARAMAN et al [6] once reported that single-stage transformation occurs in the ECAP-processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy. This may result from the difference in the processing parameters. The B2→R transformation observed in as-ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy shows a wider interval (about 42 °C) than that induced by aging [27]. This is different from the results reported by KHELFAOUI and GUÉNIN [31] in which for $\text{Ti}_{50.4}\text{Ni}_{49.6}$ alloy, the B2→R transformation kept sharp and the interval of transformation from R phase to martensite was enlarged after cold rolling and annealing. The

present result is consistent with the previous results reported by ZHANG et al [13] in which it was attributed to the grain refinement and energy accumulation introduced by ECAP. However, the results obtained by WAITZ et al [33] does not support the above hypothesis. They prepared $\text{Ti}_{49.7}\text{Ni}_{50.3}$ alloy with a grain size of 160 nm by annealing the amorphous alloy and found that the interval of B2→R transformation was the same as that observed in coarse-grained one [33]. This indicates that grain refinement does not take a dominant role in determining the transformation interval. From a thermodynamic point of view, the transformation interval upon cooling is determined by the elastic strain energy. The lattice defects introduced during ECAP may interact with the interface between R phase and parent phase, thus increase the elastic strain energy. Table 3 summarizes the microstructure evolution of differently treated $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy [16,20]. It is seen that when the annealing temperature is below 500 °C, the grain size of samples does not change obviously and the dislocation density decreases with increasing the annealing temperature. The dependence of dislocation density on the annealing temperature is supported by the reported results [6,18,31]. For example, KARAMAN et al [6] reported that annealing at 450 °C may considerably reduce the dislocation density in the ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy. KHELFAOUI and GUÉNIN [31] reported that for the cold rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$ alloy, the recovery occurs after annealing at a temperature range from 265 to 385 °C. SHAHMIR et al [18] also reported that when $\text{Ti}_{49.8}\text{Ni}_{50.2}$ alloy processed by ECAP at room temperature was annealed at 400 °C, the dislocation density decreased with increasing the annealing time from 0 to 30 min. Correspondingly, when the sample is annealed at 500 °C, the interval of B2→R transformation significantly decreases, as shown in Fig. 3. This further suggests that the widening of B2→R transformation observed in the ECAP processed TiNi alloys is mainly related to the lattice defects. When the annealing temperature increases to 600 °C, the grain size obviously increases due to the recrystallization, but the interval of B2→R transformation also increases, which should be further investigated.

Table 3 Microstructure evolution of differently treated $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy

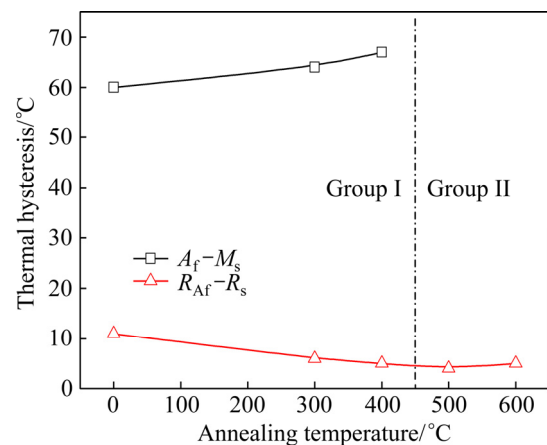
Sample	Average grain size/ μm	Precipitate	Dislocation
As-ECAP processed	0.29 ± 0.02	—	Dislocation density
Annealed at 300 °C	0.29 ± 0.02	—	decreases with increasing the annealing temperature
Annealed at 400 °C	0.3 ± 0.02	Ti_3Ni_4	
Annealed at 500 °C	0.4 ± 0.03	—	
Annealed at 600 °C	3.0 ± 0.15	—	Recrystallization

Figure 4 shows the effect of annealing temperature on the transformation temperature. It is seen that the transformation temperatures show different dependences on the annealing temperature. For the first group samples, all of the transformation temperatures increase with increasing the annealing temperature. For the second group samples, with increasing the annealing temperature, M_p increases, but A_p , R_p and R_{Ap} decrease, which is quite similar to the results reported in cold-worked $\text{Ti}_{50.4}\text{Ni}_{49.6}$ alloy [31]. Several influencing factors should be responsible for the dependence of transformation temperature on the annealing temperature, including grain size, dislocation and precipitation of Ti_3Ni_4 phase, as shown in Table 3. When the annealing temperature is less than 500 °C, the grain size increases and the dislocation density decreases with increasing the annealing temperature. Both the increased grain size and decreased dislocation density favor the transformation by reducing the transformation resistance [34,35]. When the sample is annealed at 400 °C, the Ti_3Ni_4 precipitates form, which also contributes to the elevation of transformation temperatures due to the depletion of Ni content in the matrix. When the annealing temperature increases to 600 °C, the recrystallization occurs, resulting in the increase of grain size and the decrease of dislocation density. This should be responsible for the

**Fig. 4** Effect of annealing temperature on transformation temperatures of as-ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy

increase of martensitic forward transformation temperatures (M_s , M_p and M_f). As compared with the sample annealed at 500 °C, the sample annealed at 600 °C shows a wider transformation interval upon heating, which means that the change of elastic energy of the former is smaller than that of the latter [36]. From a microstructural point of view, the sample annealed at 600 °C contains many very small grains with the size of several hundred nanometers [20]. Following Ref. [31], such very small grains may exhibit some internal stress, which increase the elastic strain energy and then reduce the reverse transformation temperatures. The detailed transformation temperatures are listed in Table 1.

Figure 5 shows the effect of annealing temperature on the transformation hysteresis of ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy. For the first group samples, the transformation hysteresis is defined as the difference between A_f and M_s of $\text{R} \leftrightarrow \text{B19}'$ transformation. The transformation hysteresis of as-ECAP processed sample is about 60 °C. When the annealing temperature is below 400 °C, the transformation hysteresis slightly increases with increasing the annealing temperature. As compared with that of the coarsen-grained sample, the enlarged transformation hysteresis is related to the lattice defects introduced during ECAP. For the second group samples, it is impossible to determine the transformation hysteresis because of the absence of two-stage reverse transformation upon heating. After annealing, the hysteresis of $\text{B2} \rightarrow \text{R}$ transformation ($R_{Af} - R_s$) slightly decreases and then keeps almost constant.

**Fig. 5** Effect of annealing temperature on transformation hysteresis of as-ECAP processed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloy

4 Conclusions

1) Upon cooling, the as-ECAP processed and annealed $\text{Ti}_{49.2}\text{Ni}_{50.8}$ alloys show $\text{B2} \rightarrow \text{R} \rightarrow \text{B19}'$ two-stage forward transformation. Upon heating, when the annealing temperature is less than 400 °C, the samples show $\text{B19}' \rightarrow \text{R} \rightarrow \text{B2}$ two-stage reverse transformation;

when the annealing temperature is higher than 500 °C, the samples show B19'→B2 single-stage reverse transformation.

2) The B2–R transformation of as-ECAP processed sample is characterized by wide interval. This is possibly related to the dislocations introduced during ECAP.

3) When the annealing temperature is less than 400 °C, the transformation temperatures increase with increasing the annealing temperature. When the annealing temperature is higher than 500 °C, the martensitic transformation temperatures increase, but the B2–R transformation temperature and reverse transformation temperatures decrease with increasing the annealing temperature.

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退火温度对等径角挤压处理 Ti_{49.2}Ni_{50.8}合金马氏体相变的影响

张殿涛^{1,2}, 郭宝^{1,2}, 佟运祥^{1,2}, 田兵^{1,2}, 李莉^{1,2},
郑玉峰^{2,3}, Dmitry-V GUNDEROV⁴, Ruslan-Z VALIEV⁴

1. 哈尔滨工程大学 超轻材料与表面技术教育部重点实验室, 哈尔滨 150001;
2. 哈尔滨工程大学 材料科学与化学工程学院 生物医学材料与工程研究中心, 哈尔滨 150001;
3. 北京大学 工学院 材料科学与工程系, 北京 100871;
4. Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, Ufa 450000, Russia

摘 要: 利用 X 射线衍射分析(XRD)、透射电子显微观察(TEM)与差示扫描量热分析(DSC)研究退火处理对等径角挤压 Ti_{49.2}Ni_{50.8} 合金马氏体相变行为的影响。经等径角挤压及后续退火处理的 Ti_{49.2}Ni_{50.8} 合金在室温下由 B2 母相、Ti₄Ni₂O 相与 B19' 马氏体相组成。冷却过程中试样均表现出 B2→R→B19' 两步相变。加热过程中, 退火温度不超过 400 °C 的试样呈现 B19'→R→B2 两步相变; 退火温度高于 500 °C 的试样呈现 B19'→B2 一步相变。等径角挤压过程中引入的位错导致 R 相变的相变区间变宽。

关键词: TiNi 合金; 等径角挤压; 马氏体相变; 退火温度

(Edited by Mu-lan QIN)