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Microstructure evolution in nanocrystalline NiTi alloy produced by HPT

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ABSTRACT

A slightly Ni-rich nano-NiTi alloy, deformed by high-pressure torsion (HPT) was investigated. By HPT, almost complete amorphization of initial B2 NiTi is obtained. Crystallization and microstructure evolution during isothermal treatment were investigated by differential scanning calorimetry (DSC) and transmission electron microscopy.

The DSC signals observed during continuous heating experiments indicate an unusually large separation between the crystallization and the growth stages. A detailed analysis of the evolution of the enthalpy release upon annealing reveals reproducibly non-monotonous trends with annealing time that cannot be explained solely by growth of crystalline volume fractions. The size of nanocrystals increases dramatically after annealing for 5 h. The effective activation enthalpies for stress relaxation (along with crystallization) and grain growth were estimated at 115 and 289 kJ/mol, respectively. The results are discussed with respect to the intricate interdependencies between synthesis and thermal processing pathways and the evolution of the nanoscale microstructure.

1. Introduction

The nearly equiatomic intermetallic compound NiTi has drawn much interest for its ability to be used in technological applications, because of its unique combination of thermal shape memory effect, superelasticity and good damping properties [1–5]. This alloy has many interesting service applications, particularly in the field of biomedical technology such as dental archwires, bone staples, endoscopic instruments, stents and surgical retractors [6].

Recently, bulk nanocrystalline NiTi alloy (grain size > 50 nm) was elaborated to a high-tech material, showing enhanced shape memory behavior and superelasticity with an ultra high recovery stress [7,8]. High pressure torsion (HPT) is one of the methods that allow obtaining nano-structured materials with new and unique properties and small grain size [9]. Combining HPT and subsequent annealing treatments one can tune the grain size and as a result the properties of the material can be controlled [10–12]. One prominent example is the size effect that can significantly shift the transformation from the cubic B2 high temperature phase to the monoclinic B19′ martensite; grains with a size less than 50 nm can even lead to the complete suppression of the transformation [13,14].

The present study aims to analyze the crystallization and the growth transformation kinetics and to investigate the microstructure evolution during annealing of amorphous NiTi alloy produced by HPT, using differential scanning calorimetry (DSC) and transmission electron microscopy (TEM).

2. Experimental details

2.1. Material

In the present study, a NiTi alloy with a composition of $Ni_{50.6}Ti_{49.4}$ (at.%) was used. This material was provided by the Institute of Physics of Advanced Materials, Ufa State Aviation TU, Russia. The initial rod with a diameter of 21 mm was water quenched from 1073 K. The discs cut from the quenched rod were subjected to HPT under a pressure of 5 GPa to a true logarithmic strain of 6. The as-prepared material was in the form of discs with diameters of 20 mm and thicknesses of about 0.8 mm. For the present study, discs with a diameter of 4.5 mm were used, cut from the as-processed disc by the spark erosion technique in Institute of Material Physics, Münster.

We have to note that the present investigation is not focused on the martensitic transformation behavior. The slightly Ni-rich NiTi alloy was chosen since its martensitic transformation temperature is quite low [15]. In the material under investigation, the martensite start and finish temperatures are 312 K and 293 K, respectively. This fact suggests a small (if any) effect on the DSC signal for the present measurements well above 400 K.

2.2. Characterization

Calorimetric measurements were performed by differential scanning calorimetry (Diamond DSC, Perkin-Elmer) under Ar atmosphere. A DSC scan was recorded in the temperature interval from 323 K to 723 K with heating rate 10 K/min, Fig. 1a. The total heat release ΔH_{total} was measured, as shown in Fig. 1a. The reproducibility of the signal was proven on different samples and it was found that $\Delta H_{total} = 38.6 \pm 1.7$ J/g. A set of subsequent DSC scans was then applied to determine the heat release during isothermal annealing (ΔH_{iso}) at 563 K as a function of annealing time. The following measurements were performed:

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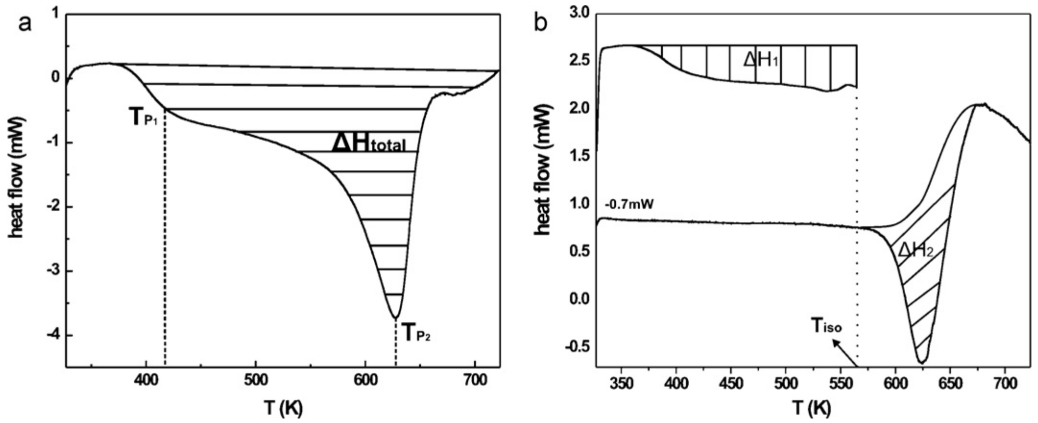

Fig. 1. (a) DSC curve for continuous heating from 323 K to 723 K, ΔH_{total}, and (b) DSC signals of the step-wise annealing treatment which includes a continuous heating from 323 K to 563 K, ΔH_1, annealing at 563 K for the given time followed by cooling down to 323 K and subsequent heating from 323 K to 723 K, ΔH_2. The DSC curve for ΔH_2 is shifted for convenient comparison.

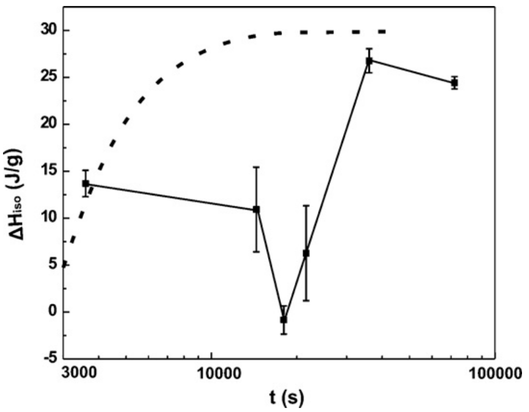

Fig. 2. Heat release ΔH_{iso} during isothermal annealing at 563 K vs. annealing time t (the heating rate 10 K/min), the solid line represents a guide to the eye. The dashed line sketches the expected behavior of ΔH_{iso}.

(1) Samples were continuously heated to the annealing temperature of 563 K and the heat release during this heating (ΔH_1) was measured, Fig. 1b.
(2) The samples were then annealed for different times at 563 K followed by cooling down to 323 K.
(3) Finally the same samples were heated from 323 K to 723 K and the heat release (ΔH_2) during this scan was measured, Fig. 1b.

The heat release ΔH_{iso} during isothermal annealing is calculated in the following way:

$$\Delta H_{iso} = \Delta H_{total} - (\Delta H_1 + \Delta H_2)$$

For each sample, two identical DSC runs were carried out. The second run was used as a baseline, which was then subtracted from the first run to obtain the irreversible part of the measurement signal and thus to account for the device function.

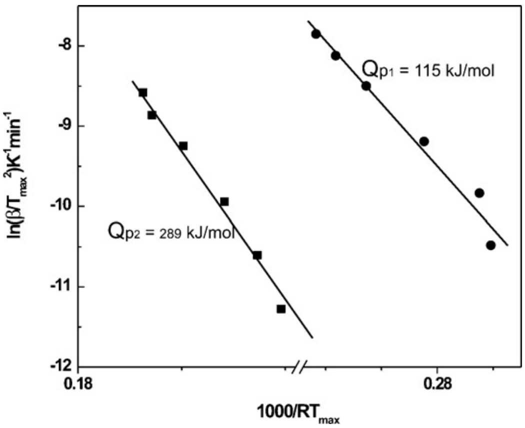

Fig. 4. Kissinger plot for the stress relaxation and the grain growth of the NiTi alloy after HPT, T_{p1} and T_{p2} in Fig. 1, respectively.

The TEM measurements were performed on as-prepared and thermally treated samples using a Zeiss Libra FE200 and a FEI Techai F20, transmission electron microscope. Specimens for transmission electron microscopy (TEM) were prepared by electropolishing using a solution of HNO_3 (65%) and CH_3OH in the ratio of 1:2 by volume. The electrolyte was cooled to −20 °C and the voltage applied for thinning was 10 V.

3. Results and discussion

The microstructure evolution of HPT deformed NiTi alloy during annealing at 563 K for 1–20 h is investigated by the combination

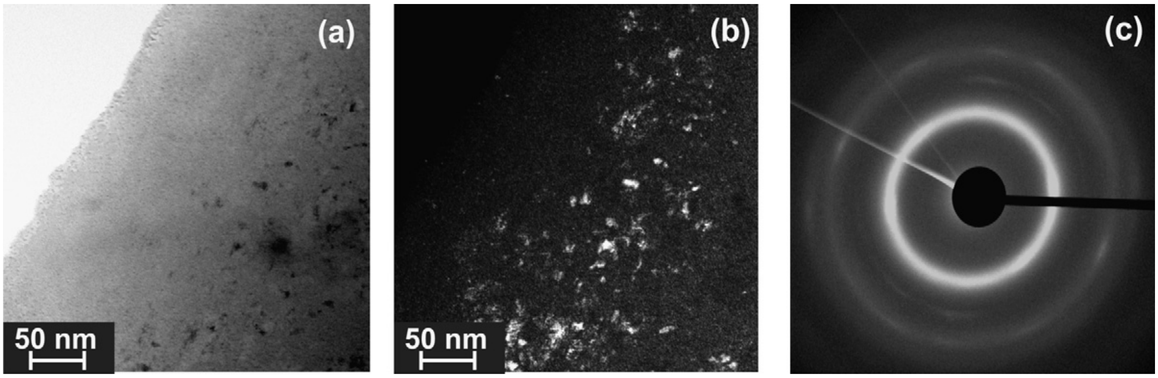

Fig. 3. Microstructure of the as-prepared NiTi alloy after HPT (a) bright field image, (b) dark field image, and (c) selected area electron diffraction.

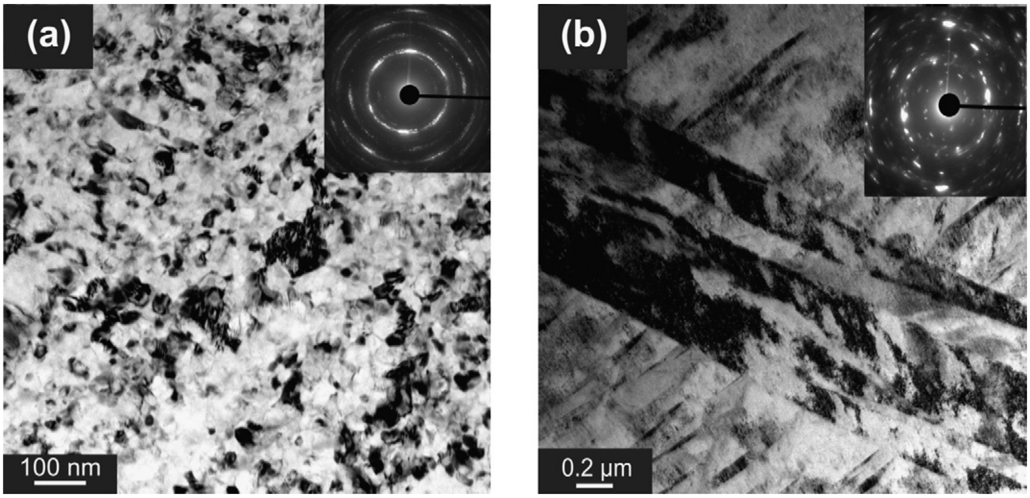

Fig. 5. Microstructure evolution of the NiTi alloy (a) after annealing at 563 K for 5 h followed by cooling down to 323 K and then heating from 323 K to 723 K; (b) after annealing at 563 K for 10 h followed by cooling down to 323 K.

of calorimetric and TEM study. The direct determination of the heat release during the isothermal annealing in DSC is not sufficiently accurate, since the signal is rather weak, develops sluggishly and the calorimetric sensitivity is proportional to the heating rate. Therefore, the above described procedure has been applied to determine ΔH_{iso}.

The values of ΔH_{iso}, are plotted in Fig. 2 as a function of the isothermal annealing time (t). The data obtained from this analysis shows a pronounced minimum at $t = 5$ h annealing duration, and become saturated at $t > 10$ h. If only one process (most likely, grain growth) would give rise to the DSC signal, a monotonous change of ΔH_{iso} is expected, the dashed line in Fig. 2. Such an asumption contradicts definitely to the trend experimentally observed.

Our recent study on the same material shows that after annealing at 563 K for 1 h, the material has a crystalline fraction along with amorphous bands [16] and significant grain growth occurs at $T > 623$ K. We suggest that increasing of the annealing time from 1 h to 5 h at 563 K does not increase the crystalline fraction due to a reverse amorphization process. This process is driven by the highly defective state of the residual crystalline matrix and only after defect annihilation/recovery a pronounced grain growth starts. Solid state amorphization during heat treatment of ball milled powders of nearly equiatomic NiTi was already suggested [17] to explain the structure changes accompanying relaxation. Chemical disorder, lattice and point defects contribute largely to the specific features of the crystal to amorphous transformation [18].

Fig. 3 shows that the as-prepared samples consist of both a minority nanocrystalline and a majority amorphous phase after HPT, where the structure of the crystalline fraction corresponds to the austenite (B2) phase. The size of the nanocrystalline grains is extremely small with average diameters of about 5–15 nm.

It has been shown [16] that during continuous heating from 323 K to 723 K with a heating rate 10 K/min, the stress relaxation along with crystallization starts at $T = 373$ K and the peak of the heat release for the grain growth appears at $T = 626$ K [16]. Our previous study [16] on the same material indicates that crystallization in the material starts at 373 K and continues up to 623 K. There is no separate peak which could definitely be attributed to crystallization. Therefore, the heat release ΔH_1 in Fig. 1b is due to the stress relaxation along with crystallization. To determine the effective activation energy of the stress relaxation (along with crystallization) and the grain growth, NiTi samples were heated from 323 K to 723 K at different heating rates ranging from 5 to 80 K/min and the Kissinger analysis [19] was applied. For the definition of the respective temperatures T_{p1} and T_{p2}, the reader is referred to Fig. 1. The activation enthalpies for stress relaxation (along with crystallization) and grain growth were determined at $Q_{\text{p1}} = 115$ kJ/mol and $Q_{\text{p2}} = 289$ kJ/mol, respectively, in Fig. 4. The value of Q_{p1} may be related to the motion of deformation-induced vacancies in grain boundaries. This interpretation correlates with the experimental measurements of grain boundary diffusion in NiTi [20,21]. The value of Q_{p2} exceeds considerably the measured activation enthalpies for both Ni and Ti bulk diffusion in NiTi [21–23]. This circumstance indicates the occurrence of far more complex processes, probably simultaneous grain growth and ordering.

Fig. 5a shows that the sample, firstly annealed at 563 K for 5 h, then cooled down to 323 K and finally heated from 323 K to 723 K with heating rate 10 K/min, is completely crystalline with an average grain size of 30 nm in the austenite phase. The grain growth took place during the second run of DSC.

Furthermore, on increasing the annealing time from 5 h to 20 h, there is an increase in the heat release. TEM data in Fig. 5b shows that the grain size is the range of micrometers, if the sample is annealed at 563 K for 10 h and then cooled down to 323 K with a cooling rate of 100 K/min. Also in Fig. 5b few needle-like features are observed, which is the typical feature of the presence of the martensite phase in the material; this is also reflected by the diffraction pattern, shown in Fig. 5b. It is well known that for the transformation from the cubic B2 high temperature phase to the monoclinic B19′ martensite grains size should be more than 50 nm. Below this size, the martensite phase might be completely suppressed [13,14]. This means that in the present study, the increase in the heat release during isothermal annealing at 563 K for more than 5 h is mainly due to grain growth. We also observed the martensite phase through the SAED pattern (Fig. 5b), when the sample was annealed at 563 K for 10 h followed by cooling with a cooling rate of 100 K/min. Hence 5 h annealing duration is the transient time at 563 K, below which there is apparently no significant grain growth due to interference by stress relaxation, crystallization and reverse amorphization. Short-range ordering [24] can also affect the relaxation effects in initially highly deformed NiTi phase.

4. Conclusion

The nanocrystallization of HPT deformed NiTi is studied during isothermal annealing at 563 K for different time intervals. One can tailor the properties of NiTi by obtaining a nanocrystalline structure, depending on the degree of the HPT deformation, temperature and the time of the subsequently annealing treatment. The effective activation energy related to stress relaxation (along with crystallization) and grain growth is 115 kJ/mol and 289 kJ/mol, respectively. It indicates the occurrence of far more complex processes, probably simultaneous grain growth and ordering. 5 h annealing time at 563 K seems to be the transient time, below which grain growth is hindered by a concurrent process.

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