

PHASE EVOLUTION IN Ni-48 AT.% TI SHAPE MEMORY ALLOY PREPARED BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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Abstract

In Ni rich Ni-Ti alloys, various phases such as hexagonal Ni₃Ti, cubic NiTi₂ and rhombohedral Ni₄Ti₃ appear during heat treatment. The presence of these precipitates affects the shape memory effect and superelasticity in an important manner. In this paper we present a study of the phase evolution during annealing of the Ni-48 at.% Ti shape memory alloy elaborated by self-propagating high-temperature synthesis (SHS). Morphology and crystallography of the phases were examined by means of light metallography, scanning electron microscopy (SEM), neutron and X-ray diffraction, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Besides the phases mentioned in the literature, a Ni-rich phase with the composition near Ni₃Ti₂ stoichiometry and having a cubic symmetry was found. This phase develops from Ni₄Ti₃ particles during slow (furnace) cooling from the temperature of 1000 °C. Its particles have the form of thin platelets coherent with the (B2) NiTi matrix. The orientation relation is either cube-to-cube, [111]_P || [115]_{B2} and (1-10)_P || (1-10)_{B2} or [011]_P || [011]_{B2} and (1-10)_P || (1-41)_{B2}.

Keywords: NiTi shape memory alloy, neutron diffraction, phase analysis, light and electron microscopy

1. INTRODUCTION

NiTi alloy with approximately equimolar composition is a well-known shape memory material. The most commonly applied techniques in industrial production of NiTi alloy are melting metallurgy processes: vacuum induction melting (VIM) [1] and vacuum arc re-melting (VAR) [2]. In VIM and VAR of Ti-containing alloys, there is a serious danger of a strong contamination of the melt due to high reactivity of molten titanium. Therefore, special zirconia (ZrO₂) or yttria (Y₂O₃) bulk or coated crucibles have to be used [3]. However, even these materials contaminate the molten NiTi alloy partially, causing the presence of oxide inclusions. A promising alternative to these melting metallurgy production routes is powder metallurgy (PM). However, the application of conventional PM processes using NiTi alloy powders is complicated due to their poor compressibility and sinterability [1]. A different and simple production technology is reactive sintering. In general, reactive sintering is a densification process, where initial elemental components in powder form are transformed to a compact product via thermally-activated chemical reactions. Since the intermetallics-forming reactions are strongly exothermic, the heat evolved by the reaction sustains and propagates the reaction through the reaction mixture. Therefore the process is called Self-propagating High-temperature Synthesis (SHS) [4]. The purpose of this paper is to characterise the phases formed in a Ni-48 at.% Ti shape memory alloy elaborated by SHS.

2. EXPERIMENTAL

Cylindrical shape green bodies 12 mm in diameter and 10 mm in height were prepared by uniaxial cold pressing of the blends of 52 at.% of Ni powder (> 99.8% purity, particle size < 10 μ m) and 48 at.% of Ti powder (> 99.8% purity, particle size < 10 μ m) under pressure of 320 MPa. Self-propagating high-temperature synthesis (SHS) was performed by heating the powder compacts in evacuated silica ampoules for 5 min at



1100 °C. Samples of the alloy were annealed at 1000 °C for 12 hours and then quenched into ice water without breaking the capsule. Alternatively, slow (furnace) cooling was employed. Quenched samples were also isothermally aged at 720 °C for 3 and 10 h. The phase analysis of the alloy was carried out by means of neutron diffraction at room temperature on the instrument MEREDIT, using neutron beam with wavelength of 0.14618 nm. Data refinements and phase analysis were performed with full pattern fitting method using FullProf software [5]. Alternatively, the phase analysis was carried out also by X-ray diffraction (XRD) method using PANalytical X'Pert Pro diffractometer (CuK α radiation). The XRD patterns were processed and evaluated by PANalytical X'Pert HighScore Plus software with PDF-2 database. The morphology and crystallography of the phases were examined by means of light microscope Zeiss Neophot 32 after polishing by colloidal silica and/or electropolishing in the solution of 5% HClO₄ in ethanol. Alternatively, scanning electron microscope (SEM) TESCAN FERA equipped with electron back-scattering diffraction (EBSD) system and energy dispersive X-ray spectrometer (EDS) EDAX was used. Transmission electron microscopy standard 3 mm samples were prepared by slicing the alloy by slow speed diamond saw, grinding to 60 μ m thickness, dimple polishing and final ion beam thinning using Gatan PIPS 691 device. The observation of thin foils was carried out at 200 kV using JEOL 2000 FX electron microscope with an EDS Bruker.

3. RESULTS AND DISCUSSION

3.1. As sintered condition

The microstructure of the alloy in the as sintered condition is shown in **Fig. 1**. There are numerous dendrites of the NiTi₂ phase embedded in the NiTi matrix (**Fig. 1a**). The dendrites are quite long, 50 to 100 µm thick, having secondary arm spacing (SDAS) of 5 to 10 µm. When isolated they have sometimes Chinese script form (**Fig. 1b**). According to the neutron diffraction phase analysis, the volume fraction of the NiTi₂ phase (space group: *Fd-3m* (227), a = b = c = 1.13232(18) nm, $\alpha = \beta = \gamma = 90^{\circ}$) is about 17 %. The phase fraction of the B2 ordered NiTi matrix (space group: *Pm-3m* (221), a = b = c = 0.300478(14) nm, $\alpha = \beta = \gamma = 90^{\circ}$) is only 39 %, because the alloy contains also an important fraction (44 %) of the precipitates of the rhombohedral phase Ni₄Ti₃ (space group: *R-3* (148), a = b = 1.12704(20) nm, c = 0.50981(15) nm, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$). However, its particles are very fine and thus they can be observed only by means of the transmission electron microscope (**Fig. 2**).



Fig. 1 Dendrites of the NiTi₂ phase in the NiTi matrix of the as sintered alloy (electrolytical polishing):
(a) Light micrograph, (b) SEM SE micrograph of the dendrite in the Chinese script form. The same microstructure was found also in the alloy quenched from 1000 °C after 12 h annealing





Fig. 2 TEM micrographs of the Ni₄Ti₃ phase in the as sintered condition: (a) Fine particles imaged in centered dark field in the spot marked by an arrow in the diffraction diagram in the inset on the right. The inset on the left shows the same region tilted to the [111] NiTi matrix zone axis (spots B2) which is coincident with the [0001] zone axis of the Ni₄Ti₃ precipitate (spots P). The spots of the Ni₄Ti₃ phase marked by crosses are in the twinning relationship with the plane of the symmetry (110)_{B2}. (b) Coarser particles imaged in bright

field. The inset shows the diffraction diagram of one of the Ni₄Ti₃ particles tilted to the [10-11] zone axis coincident with the [102] crystal zone of the B2 NiTi matrix

3.2. Annealed and quenched condition

After 12 h annealing of the alloy at 1000 °C followed by ice water quenching, the morphology and distribution of the NiTi₂ phase remains unchanged (light and SEM micrographs are the same as in the case of **Fig. 1** recorded for the as sintered condition). In a similar way, the volume fractions of NiTi₂ and Ni₄Ti₃ phases are nearly unaffected (18 and 47 %, respectively). The most important difference with respect to the as sintered state is coarsening of the fine Ni₄Ti₃ precipitate (**Fig. 3a**). Insets of electron diffractions in **Figs. 2a** and **3a** show, that the orientation relationship of the precipitates (P) of the rhombohedral phase Ni₄Ti₃ within the (B2) NiTi matrix is $[0001]_P || [111]_{B2}$, and $(11-20)_P || (12-3)_{B2}$.



Fig. 3 TEM micrographs of the Ni₄Ti₃ phase in the alloy quenched from 1000 °C: (a) Fine Ni₄Ti₃ precipitate coarsened (dark field). The inset shows corresponding diffraction diagram in the [111] NiTi matrix zone axis.
(b) Somewhat coarser particles of the Ni₄Ti₃ phase on the grain boundary surrounded by precipitate free zones (bright field)



In fact, there are two sets of precipitate diffraction spots forming a hexagonal pattern, the second ones (marked by crosses) are in the twinning relationship with the plane of the symmetry $(110)_{B2}$. Taking account of the symmetry, there are several variants of the precipitate-matrix orientations. The dark field micrograph in back of the **Fig. 3a** shows one set of the Ni₄Ti₃ particles in bright contrast, the dark veins inside the particles are antiphase boundaries. In the same micrograph other variants of Ni₄Ti₃ phase give only residual contrast, somewhat darker than the background matrix. One of these darker sets is in the twinning relation with bright particles (vertical mirror plane). Bright field micrograph in **Fig. 3b** shows somewhat coarser particles of the Ni₄Ti₃ phase on the grain boundary surrounded by precipitate free zones.

3.3. Slow cooled condition

Slow furnace cooling from 1000°C leads to the decomposition of the Ni₄Ti₃ phase. According to neutron diffraction phase analysis, the alloy contains only 20 % NiTi₂ phase and 80 % NiTi matrix. However, light and electron metallography, as well as X-ray diffraction reveal other phases, namely hexagonal Ni₂Ti group $P6_3/mmc$ (194)) compounds. Particles or laths of the Ni₂Ti phase are well visible in bright contrast in the SEM backscattered electron signal in Fig. 4a (arrows B). On the other hand, the dendrite arms (A) of the phase NiTi₂ containing low amount of nickel appear black. Other particles (labeled C in Fig. 4a, a detailed view in Fig. 4b) have shape of thin irregular platelets 2 to 5 µm in size. The SEM EDS analysis gives the ratio of Ni : Ti in at.% in these particles in the range from 1.37 to 1.47, thus close to Ni_3Ti_2 stoechiometry (Ni : Ti = 1.5). The phase Ni₃Ti₂ was reported e.g. by Nishida, Wayman and Honma [6], according to TEM diffraction analysis it is monoclinic (a = 0.441 nm, b = 0.882 nm, c = 1.352 nm, $\gamma = 89.3^{\circ}$) [7]. From **Fig. 4b** it can be seen that coarser particles of this phase are situated often between the NiTi₂ phase and the matrix, in several cases they surround the dark NiTi₂ dendrites completely, indicating that they form from NiTi₂ phase and NiTi matrix by a peritectoid reaction NiTi₂ + NiTi \rightarrow Ni₃Ti₂. Thin platelets of this phase were examined by means of TEM and selective area electron diffraction. The results of this analysis are summarized in Fig. 5. In the upper left corner of the micrograph in Fig. 5a there are two of the particles perpendicular to the electron beam and remaining ones with various orientations are imaged edge on. Figs. 5b to 5f show selective area electron diffraction patterns in several crystal zone axes. It can be seen that the particles are coherent with the matrix, they have a cubic symmetry (a = 0.874 nm) and cube-to-cube precipitate-matrix orientation (Figs. 5b to 5e). Alternatively, orientations [011]_P || [011]_{B2} and (1-10)_P || (1-41)_{B2} (not shown here) or [111]_P || [115]_{B2} and (1-10)_P || (1-10)_{B2} (Fig. 5f) were also observed.



Fig. 4 SEM BSE micrographs of the alloy after slow cooling from 1000°C, which led to the precipitation of other phases: (a) general view, A - NiTi₂, B - Ni₂Ti, C - Ni₃Ti₂ phase, (b) detail of fine plate-like particles of the Ni-rich cubic phase with the composition close to Ni₃Ti₂ stoichiometry



Fig. 5 (a) TEM micrograph of the fine plate-like particles of Ni-rich cubic phase (Ni₃Ti₂) corresponding to **Fig. 4b**, (b) to (f) electron diffraction patterns of the matrix and the precipitate in several orientations

3.4. Annealing at 720 °C

The quenched alloy was also isothermally annealed at 720 °C; the resulting microstructures are shown in **Fig. 6**. After 3 h annealing, the medium bright Ni₃Ti₂ phase shows only lath morphology (**Fig. 6a**), while after 10 h it is partially transformed into randomly distributed platelet morphology (upper left part of **Fig. 6b**).



Fig. 6 SEM BSE micrographs of the alloy after 12 h annealing at 1000 °C, ice water quenching and isothermal annealing at 720 °C: (a) 3 h anneal, (b) 10 h anneal. Dark NiTi₂, medium bright Ni₃Ti₂ and bright Ni₂Ti phases are visible in the grey NiTi matrix (for the phase descriptions see also **Fig. 4**)



When compared to the slow (furnace) cooled sample (Fig. 4), there is apparently a lower amount of the bright Ni_2Ti phase.

4. CONCLUSION

Morphology and crystallography of the phases in the Ni-48 at.% Ti shape memory alloy elaborated by selfpropagating high-temperature synthesis (SHS) was characterized by means of light metallography, scanning electron microscopy (SEM), neutron and X-ray diffraction, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The main results can be summarized as follows:

- The volume fraction of the NiTi₂ phase (about 20%) remains practically unaffected by long term annealing (12 h) at 1000°C. This annealing leads only to the coarsening of the Ni₄Ti₃ precipitates.
- Besides the phases mentioned in the literature, i.e. NiTi, NiTi₂, Ni₂Ti, Ni₃Ti, Ni₄Ti₃, monoclinic Ni₃Ti₂, a Ni-rich phase with the composition near Ni₃Ti₂ stoichiometry and having a cubic symmetry (*a* = 0.874 nm) was found.
- This phase develops from Ni₄Ti₃ particles during slow (furnace) cooling from the temperature of 1000 °C. Its particles have the form of thin platelets coherent with the (B2) NiTi matrix.
- The precipitate-matrix orientation relation is either cube-to-cube, $[111]_P \parallel [115]_{B2}$ and $(1-10)_P \parallel (1-10)_{B2}$ or $[011]_P \parallel [011]_{B2}$ and $(1-10)_P \parallel (1-41)_{B2}$.

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