

Proceedings of the International Symposium on Physics of Materials (ISPMA 14), September 10–15, 2017, Prague

Microstructure of Ni–48 at.%Ti Alloy Prepared from Powder and by Conventional Metallurgy

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Microstructure of the samples of the alloy Ni–48 at.%Ti prepared from elemental powders by self-propagating high-temperature synthesis is compared to that of the same alloy cast by conventional vacuum induction melting from bulk metals. Scanning and transmission electron microscopy observations show differences in the phase structure. Besides NiTi matrix, both materials contain also NiTi₂, Ni₂Ti, Ni₃Ti₂, Ni₃Ti, and Ni₄Ti₃ phases. Slow furnace cooling after long term annealing at 1000 °C leads to the transformation of the Ni₄Ti₃ phase into the Ni₈Ti₅ phase in the self-propagating high-temperature synthesis material. In the conventionally cast alloy, the Ni₈Ti₅ phase was not found.

DOI: [10.12693/APhysPolA.134.765](https://doi.org/10.12693/APhysPolA.134.765)

PACS/topics: 81.05.Bx, 81.20.Ev, 87.64.Ee

1. Introduction

NiTi alloys with approximately equimolar composition are well known functional materials exhibiting shape memory effect and pseudoelasticity, which make them attractive for various applications in robotics and automotive, aerospace and biomedical industries [1]. Both the shape memory effect and pseudoelasticity are due to reversible transformation from the high-temperature parent phase (austenite — β) with a $B2$ ($P\bar{m}3m$) structure to the low-temperature martensitic phase with a monoclinic structure $B19'$ ($P2_1/m$). In Ni-rich NiTi alloys, the phase transition temperatures (PTT) is lowered by about 20 °C per added 0.1 at.% Ni [2] and it can also be altered by precipitation, since several secondary phases, Ni₄Ti₃, Ni₃Ti₂ or Ni₃Ti, can form [3]. From the above-mentioned phases, i.e. metastable Ni₄Ti₃, Ni₃Ti₂ and equilibrium Ni₃Ti, the only particles that influence PTT are coherent Ni₄Ti₃ precipitates, inducing strain fields and decrease of Ni concentration in the surrounding matrix [4]. Another equilibrium phase which is frequently present in NiTi shape memory alloys is NiTi₂ which is formed during solidification at 984 °C [5]. Oxygen atoms are taken up by the Ti₂Ni phase and form thermodynamically stable oxygen-rich Ti₂Ni particles which are described using the

formula Ti₂NiO_x (an intermetallic phase with dissolved oxygen) or Ti₄Ni₂O (oxide phase) [6]. The oxide Ti₄Ni₂O is crystallographically very similar to Ti₂Ni, it is practically impossible to be distinguished from Ti₂Ni by X-ray diffraction (XRD) [7]. A new metastable phase Ni₈Ti₅ has been recently observed in the Ni–4 at.% Ti alloy prepared from elemental powders by self-propagating high-temperature synthesis (SHS) and subsequent annealing at 1000 °C for 12 h, followed by slow furnace cooling to room temperature [8]. The phase forms micrometer-sized precipitates within NiTi matrix. The structure of Ni₈Ti₅ was determined from precession electron diffraction tomography data using dynamical refinement approach. It has trigonal symmetry $R\bar{3}m$ ($a = 12.24(5)$ Å, $c = 15.33(5)$ Å) with the structure related to the structure of Ni₄Ti₃ phase from which it is formed during slow cooling [9].

The aim of this work is to compare the microstructure of an alloy Ni–48 at.%Ti prepared from elemental powders by self-propagating high-temperature synthesis (SHS) to that of the alloy conventionally cast (CC) after vacuum induction melting from bulk metals, in order to find if the Ni₄Ti₃ phase transforms to the Ni₈Ti₅ one also in this material.

2. Experimental details

Two small ingots (≈ 30 g, 12 mm in diameter) of a Ni–48 at.% Ti alloy were prepared by different processing routes, conventional vacuum induction melting from bulk

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metals and by SHS. The latter started by preparing compacts by uniaxial cold pressing of the blends of 52 at.% of Ni powder ($> 99.8\%$ purity, particle size $< 10\ \mu\text{m}$) and 48 at.% of Ti powder ($> 99.8\%$ purity, particle size $< 10\ \mu\text{m}$) under pressure of 320 MPa. SHS was performed by heating the powder compacts in evacuated silica ampoules for 5 min at 1100°C . Microstructural observations were carried out by means scanning electron microscope JEOL JSM 5510LV equipped with iXRF 500 energy dispersive X-ray spectroscopy analyzer. X-ray diffraction (XRD) phase analysis was performed using PANalytical X'Pert Pro diffractometer. Standard 3 mm transmission electron microscopy (TEM) samples were prepared by electrolytic polishing (Struers Tenupol 5, 5°C , 15 V) in a 10% solution of H_2SO_4 in methanol. Their observation was carried out at 200 kV in a JEOL JEM 2000FX transmission electron microscope equipped with Bruker energy dispersive X-ray spectroscopy analyser and CCD camera Veleta.

3. Results and discussion

3.1. As-sintered/as-cast condition

The microstructure of the materials in the initial as-sintered/ as cast condition is shown in the backscattered electron micrographs in Fig. 1. In the alloy prepared by SHS there are numerous dendrites of the NiTi_2 phase which appear dark. Many of them are 15 to $30\ \mu\text{m}$ in size, but on the right side there is a vertical one longer than $100\ \mu\text{m}$ (Fig. 1a). There are also many bright particles in dendrite-like regions about $15\ \mu\text{m}$ in size or decorating grain boundaries, apparently more rich in Ni than the matrix. On the other hand, the conventionally cast (CC) alloy is more homogeneous, the amount of the NiTi_2 phase is considerably lower, its particles are in general much smaller, either globular or thin elongated up to $5\text{--}10\ \mu\text{m}$ in size. There are several reasons for such a difference: (i) probably it is the grain size (up to $10\ \mu\text{m}$) of the initial powders of Ni and Ti used for SHS, which is comparable to the size of most of the dendrites ($15\ \mu\text{m}$), (ii) the SHS process is quite fast, it is completed in several seconds for samples of the size of tens of mm, and so there is not much time for diffusion to homogenize the composition, (iii) Ti is reactive and so the initial powder contains a thin oxide layer on the surface. During the SHS reaction, oxygen dissolves in the NiTi_2 and stabilizes it to form a more stable NiTi_2O_x compound [7]. About 3 wt% of oxygen was found by EDS in SEM in SHS alloys even in vacuum or argon or nitrogen atmospheres [11]. The stability of the NiTi_2 (NiTi_2O_x) phase in the SHS alloy is evident also from the long time 12 h annealing at 1000°C , i.e. at the temperature where NiTi_2 should dissolve [5]. After fast cooling from 1000°C , the same microstructure of the alloy was observed [8].

Figure 2 shows transmission electron micrographs of both SHS and CC alloys in the initial condition and after annealing $1000^\circ\text{C}/12\ \text{h}$ followed by slow furnace cooling. At the fine scale, in both materials there are precipitates

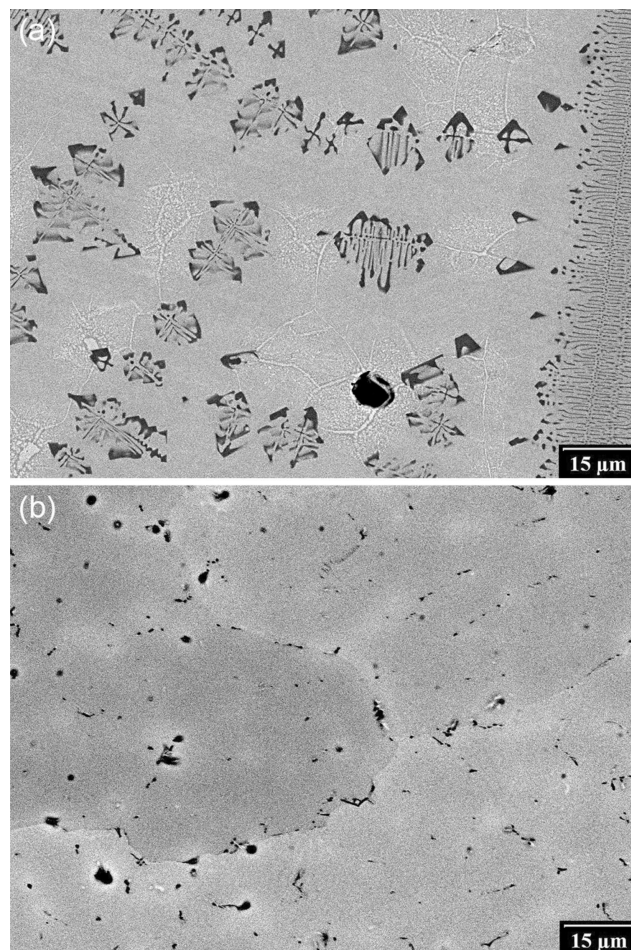


Fig. 1. SEM backscattered electron micrographs: (a) SHS as sintered alloy, (b) CC alloy.

of the Ni_4Ti_3 phase. Its particles in the SHS alloy are coarser, up to $500\ \text{nm}$ in diameter [8], but there are also regions with finer ones (Fig. 2a), in the CC alloy they are tiny, 2 to $5\ \text{nm}$ in size (Fig. 2b).

3.2. Annealed and slow cooled alloys

Slow furnace cooling of the materials from 1000°C led to different results. In the SHS prepared alloy it resulted in the transformation of the Ni_4Ti_3 phase to a new phase Ni_8Ti_5 , first reported in [8] as a cubic one, later confirmed by tomographic electron diffraction as having trigonal crystal lattice [9]. Particles of this phase, coherent with the matrix, have shape of thin irregular platelets $2\text{--}5\ \mu\text{m}$ in size with lenticular cross-section (Fig. 2c). On the other hand, in the CC alloy the size, shape and distribution of the precipitates is quite similar (Fig. 2d), but from electron diffraction it follows that it is still Ni_4Ti_3 phase, as it is shown in the inset of Fig. 2d. Its particles only coarsened, developed from tiny spherical particles in the as cast condition to their typical lenticular plate-like morphology, and they did not transform to Ni_8Ti_5 as in the SHS alloy.

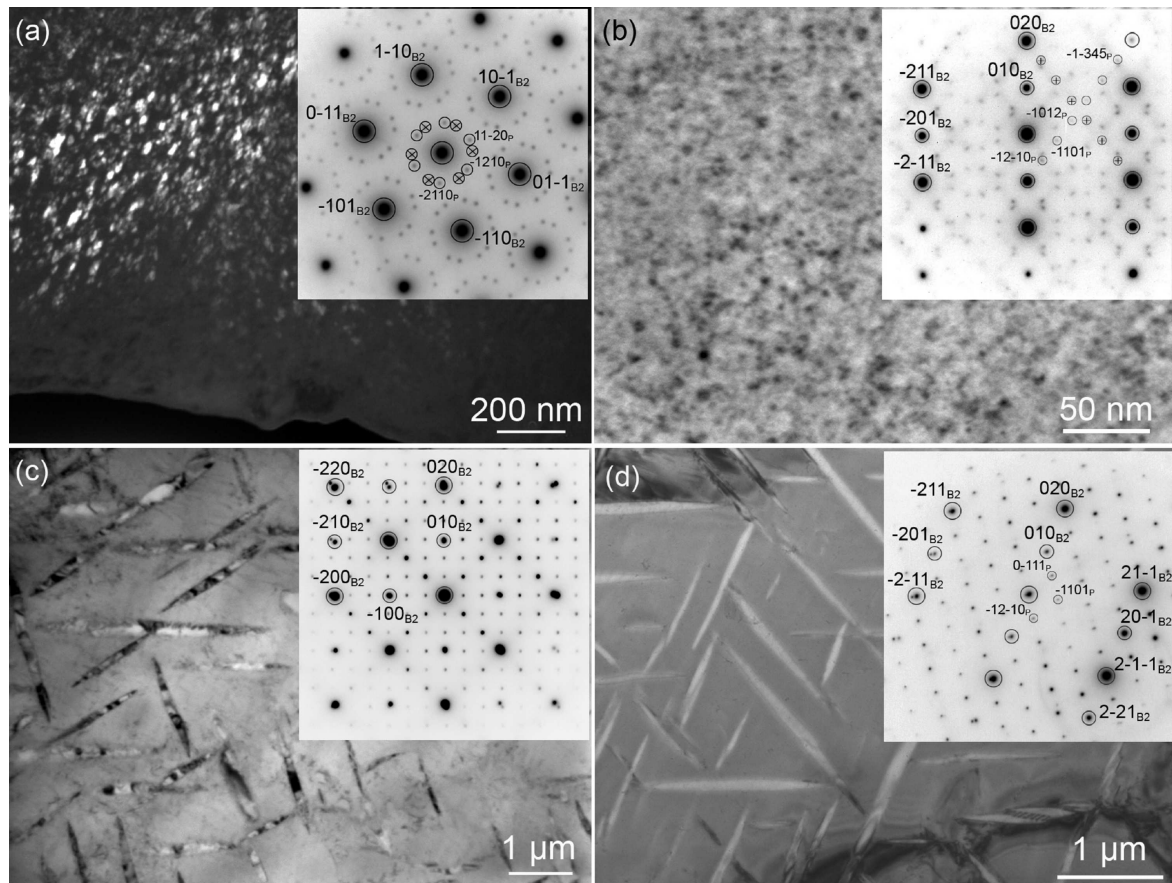


Fig. 2. TEM micrographs of the alloy in the as sintered/as cast condition (a,b), and after annealing 1000 °C/12 h with slow furnace cooling (c,d). The insets show diffraction patterns in zone axes of the $B2$ NiTi matrix: (a) [111], (b) [102], (c) [001]: (a) SHS sintered alloy — dark field of small Ni_4Ti_3 particles, (b) as cast alloy — bright field of tiny Ni_4Ti_3 particles; (a,b) two orientations of precipitates are observed (empty circles and crosses), which are related by the mirror plane $(010)_{B2}$, (c) platelets of Ni_8Ti_5 phase in furnace cooled SHS alloy, (d) morphologically similar Ni_4Ti_3 platelets in the furnace cooled cast alloy.

3.3. Annealing of the cast alloy

In order to try to find if there is a particular temperature range in which the Ni_4Ti_3 phase could transform to the Ni_8Ti_5 one, a series of annealing experiments of the CC alloy have been performed. First we used *in situ* TEM annealing at 450 and 550 °C, which showed only coarsening of Ni_4Ti_3 particles. Another attempt was *in situ* XRD isothermal heating experiments which failed on insufficient vacuum in the specimen chamber and rutile formation on the surface. In consequence we proceeded to annealing at 600 °C for 1 h and 10 h in quartz ampoule. The results of the XRD analysis are in Fig. 3. In the as cast condition, there were only peaks of the matrix NiTi and $NiTi_2$ phases. The signal of the nm size Ni_4Ti_3 particles is hidden by the 110 NiTi peak broadened due to mechanical polishing. After 1 h at 600 °C the Ni_4Ti_3 particles coarsened and their 121 peak is well visible. After 10 h at 600 °C, Ni_2Ti phase was also identified and later confirmed by TEM EDS analysis (Fig. 4a). By means of TEM, also particles of the high temperature Ni_3Ti_2 phase with $I4/mmm$ crystal structure (inset in Fig. 4b) were also observed. Coarse Ni_4Ti_3 particles

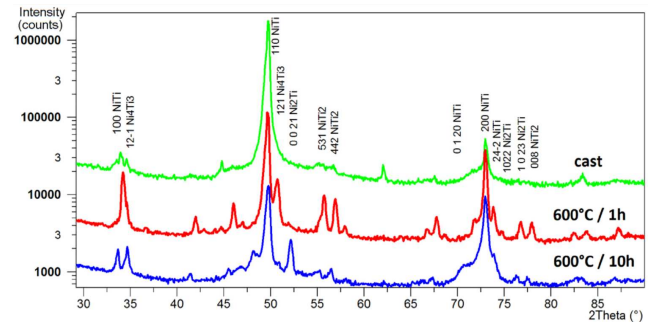


Fig. 3. XRD patterns of Ni-48 at.% Ti alloy in the as cast condition and after annealing at 600 °C for 1 h and 10 h.

with surrounding strain fields and numerous twins in the adjacent matrix were also frequently observed (not shown here). So the part of the volume fraction of the Ni_4Ti_3 phase transforms further to more stable Ni_3Ti_2 and Ni_2Ti phases [3], similarly as in the case of the SHS alloy annealed for 3 and 10 h at 720 °C [8]. In the CC alloy, transformation into Ni_8Ti_5 phase was not found.

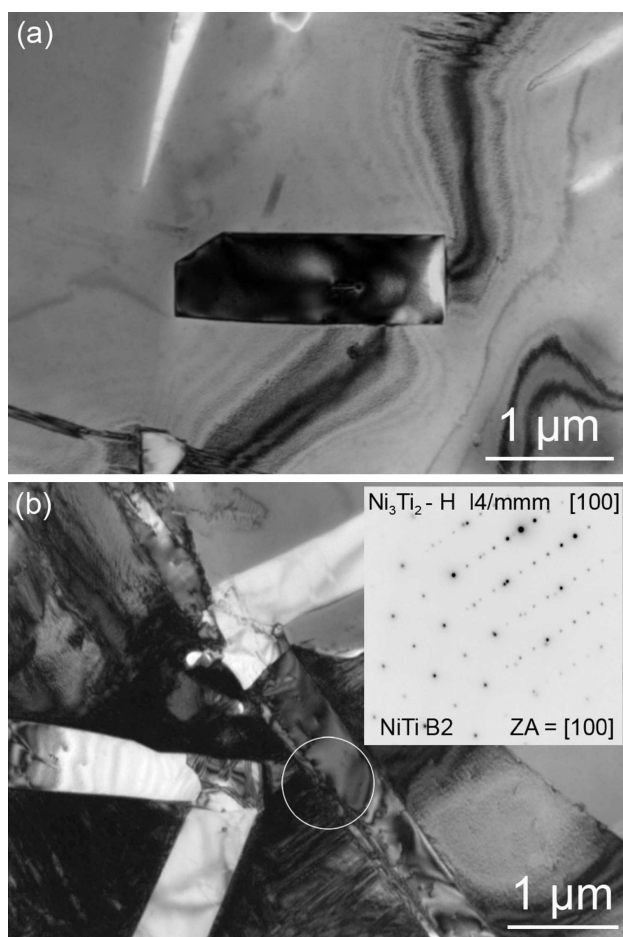


Fig. 4. TEM micrographs of the cast alloy after annealing 600 °C/10 h: (a) Ni_2Ti phase, (b) Ni_3Ti_2 — H phase, the inset shows diffraction pattern in the [100] zone axis, white circle indicating the position of the selective area aperture.

4. Conclusions

Microstructure of Ni–48 at.%Ti alloys prepared from elemental powders by SHS and by conventional vacuum induction melting was characterized with the following conclusions: (i) CC alloy contains lower amount of the NiTi_2 phase than the material prepared by SHS; (ii) fine precipitates of the Ni_4Ti_3 phase are present already in the as cast/as sintered condition; they are much finer

in the CC alloy, (iii) slow furnace cooling after long term annealing at 1000 °C leads to the formation of the Ni_8Ti_5 phase in the SHS material, while in the CC alloy morphologically similar particles of the Ni_4Ti_3 phase are formed instead; (iv) 10 h annealing at 600 °C of the CC alloy resulted in the formation of long thin particles of the Ni_3Ti_2 — H tetragonal phase ($I4/mmm$) and square particles of the Ni_2Ti phase; Ni_4Ti_3 further coarsened, (v) in the CC alloy, transformation into Ni_8Ti_5 phase was not found.

Acknowledgments

This research was carried out in the frame of the project No. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF, and of the Czech Science Foundation project 14-36566G.

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