

Properties of Ni-Ti-(Fe,Co,Al) Shape Memory Alloys Prepared by Self-Propagating High-Temperature Synthesis

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Shape memory, superelasticity and pseudoplasticity are the exceptional properties of Ni-Ti alloys, which are listed among SMAs (Shape Memory Alloys). The carrier of these properties is the intermetallic NiTi phase. In addition to this phase, the Ti₂Ni phase is always present, which is hard and brittle, and therefore it is undesirable in the Ni-Ti alloys. The aim of this work was to determine the influence of selected alloying elements (iron, cobalt and aluminium) in two different amounts (1 wt. % and 3 wt. %) on the microstructure, phase composition and amount of the Ti₂Ni phase, hardness and transformation temperature of Ni-Ti-X alloy. The samples examined were prepared by self-propagating high-temperature synthesis at sintering temperature of 1100 °C. By altering the selected elements, the Ti₂Ni phase was not reduced, on the contrary aluminium increased its amount. The Ni-Ti alloys alloyed with these three alloying elements proved to be harder. The phase transformations were observed only in the sample with 1 wt. % of aluminium at heating and cooling curves from differential scanning calorimetry.

Keywords: Powder metallurgy, reactive sintering, Ni-Ti-X alloy, shape memory

1 Introduction

The nickel-titanium alloys are widely used in shape memory applications where shape effects, superelasticity and pseudoplasticity are applied. These effects are caused by the phase transformation between the austenite (high-temperature cubic structure) and the martensite (low-temperature monoclinic structure). The impurities and change in the nickel-titanium ratio can lead to an undesirable shift of the phase transformation's temperatures. The powder metallurgy methods seem to be suitable and perspective for the production of the Ni-Ti shape memory alloys and other intermetallic compounds generally because the intermetallics can be characterized by poor casting properties and high melting point. In the case of the Ni-Ti alloys and other melt containing titanium, the high reactivity of the melt complicates the production by conventional melting metallurgy. The melt reacts with the melting crucible's material by vacuum induction melting (VIM) if the carbon crucible is used as usual and the secondary titanium carbide and Ti₄Ni₂O_x phases are formed during melting [1]. The carbon impurity can be suppressed by using a special melting crucible with zirconia (ZrO₂) and yttria (Y₂O₃) but the production price is rising [2]. The vacuum arc re-melting (VAR) produces Ni-Ti alloys with higher purity and without carbon impurities but to get ingots with a homogenous chemical composition it is necessary to repeat the VAR process at least four times [3, 4]. The reactive sintering – self-propagating high-temperature synthesis (SHS) is one of powder metallurgy techniques which enables to prepare easily the Ni-Ti alloys without impurities. This method is based on the preparation of the powder mixture in required proportions from metallic powders. The powder mixture is blended, cold compressed and heated to temperature, at which a strong exothermic reaction between nickel, titanium and eventually some alloying elements is initiated. The ignition temperature is intensively studied and there two are

two theories for the value of the ignition temperature. The first one claims that melting corresponding to the eutectic reaction at temperature of 942 °C initiates the SHS reaction (investigated by DSC analysis with heating rate of 20 °C.min⁻¹) [5]. The second opinion means that the exothermic reaction starts at approximately 890-900 °C (measured by optical pyrometer with the heating rate of 300 °C.min⁻¹) [6]. The initial temperature can be decreased more, there is an initial temperature of 640 °C after addition of aluminium into the Ni-Ti powder mixture [7]. Other studies describe the formation of the Ti₂Ni, NiTi and Ni₃Ti intermetallics during reactive sintering at a temperature range of 500 – 900 °C. It was found out that the Ti₂Ni phase is formed preferentially already at temperature of 500 °C while the NiTi and Ni₃Ti arise at temperature of 650 °C in addition to the Ti₂Ni phase. The formation of the Ni₃Ti phase contributes to the evolution of porosity during the reactive sintering of the Ni-Ti alloys. All reactions were determined to be diffusion-controlled mechanism below the temperature of 900 °C [6, 8]. The use of high heating rate, medium particle sizes of nickel and titanium powders and addition of alloying elements into the Ni-Ti powder mixture lead to suppress of formation the Ti₂Ni phase during reactive sintering [9-12].

This study is focused on the properties of the Ni-Ti46 alloy with addition of 1 and 3 wt. % of iron, cobalt and aluminium prepared by the self-propagating high-temperature synthesis. The influence of alloying elements on the microstructure, phase composition, mechanical properties and temperatures of phase transformations were evaluated.

2 Experimental

The tested samples were prepared by mixing and manual blending from elemental powders with the following purities and particles sizes – nickel (99.99 wt. %, <150 µm), titanium (99.5 wt. %, <44 µm), iron (99 wt. %, <212 µm), cobalt (~1 µm) and aluminium (<44 µm; 99.7 wt.

%). The alloying elements were added into the Ni-Ti46 wt. % mixture in the amount of 1 and 3 wt. % - the final chemical compositions of the samples are Ni53.5Ti45.5X1 and Ni52.4Ti44.6X3 in wt. % (labelled NiTiX1 and NiTiX3). The powder mixtures were compressed at a pressure of 450 MPa for 5 minutes using Lab-Test 5.250SP1-VM universal loading machine to cylindrical green bodies (12 mm in diameter). The compressed compacts in evacuated silica ampoules were inserted in preheated electric resistance furnace at a temperature of 1100 °C to perform reactive sintering with high heating of 300 °C.min⁻¹ and process duration of 20 minutes. The metallographic samples were prepared by grinding (sandpapers with silicon carbide abrasive elements), polishing by the diamond pastes D2 and D0.7 and etching in Kroll's reagent (10 ml HF, 5 ml HNO₃ and 85 ml H₂O). The microstructure was observed by the scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max 20 mm² SDD EDS analyser for the identification of the chemical composition of the individual phases. The phase composition of alloys was identified on the ground surfaces of the samples by the means of X-ray diffraction analysis (XRD) using PANalytical X'Pert Pro diffractometer with a copper anode. Area fraction of Ti₂Ni phase was evaluated by Lucia 4.8 image analysis software. Mechanical properties were

characterized by Vickers hardness test with a load of 10 kg. The differential scanning calorimetry (DSC) analysis of the prepared alloys was performed by using Setaram DSC 131 to determine the transformation temperatures in products. The measurements for the determination of the temperatures austenite start (A_S) and austenite finish (A_F) were carried out in the temperature range of -20 °C to 200 °C at a heating rate of 10 K min⁻¹, cooling from 200 °C to -5 °C for detecting the martensite start (M_S) and martensite finish (M_F) temperatures.

3 Results and discussion

The microstructures of the NiTiX1 and NiTiX3 (alloying elements were Al or Co or Fe) samples prepared by the SHS reaction using high heating (300 °C.min⁻¹) are showed at Fig. 1 and they are in a good agreement with the XRD analysis. Only the NiTi (cubic Pm-3m structure) and Ti₂Ni (cubic Fd-3m structure) phase are observable in all microstructures and the same phases were identified by the XRD analysis in the NiTiFe1, NiTiFe3, NiTiCo1 and NiTiCo3 alloys. The NiTi (monoclinic structure) was detected commonly with NiTi (cubic structure) in both samples alloyed by aluminium, the difference between the cubic and the monoclinic structure of the NiTi phase is not seen by the scanning electron microscope.

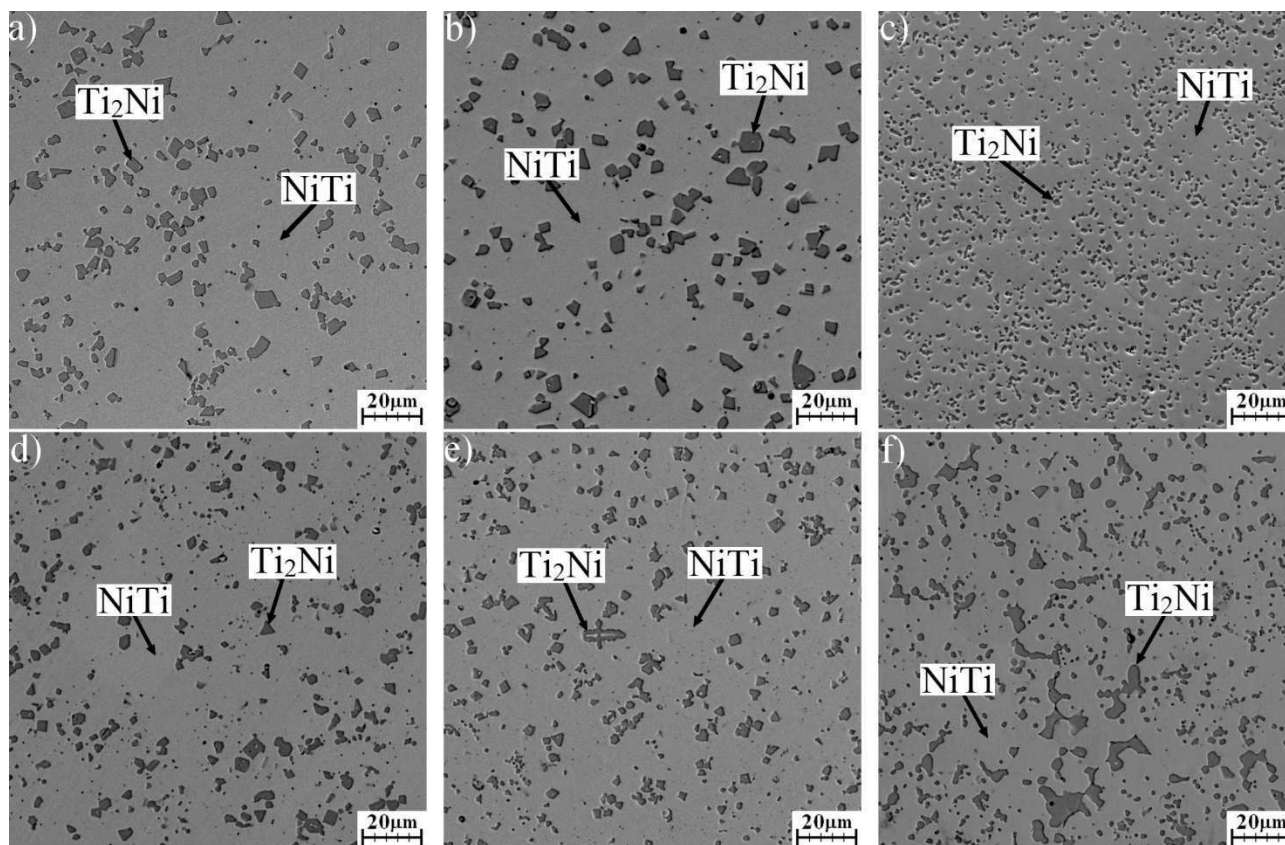


Fig. 2 Microstructures of the alloys: a) NiTiFe1, b) NiTiCo1, NiTiAl1, d) NiTiFe3, e) NiTiCo3 and f) NiTiAl3

The Ti₂Ni phase creates sharp particles (very similar shape like in our previous studies [13]) in the NiTi phase matrix and there is its content approximately 11-12 % of area fraction in the samples with the addition of iron and cobalt. The amounts of the Ti₂Ni phase in microstructures

are compared in Tab. 1. It is possible to see there that alloying by iron and cobalt also does not significantly change the amount of the Ti₂Ni phase in the microstructure in comparison with the binary Ni-Ti46 alloy and NiTiFe5 and NiTiCo5 alloys [13, 14]. The little variance

appeared in the samples with aluminium. The amount of the Ti_2Ni phase increases little by little with the increasing aluminium content in the alloy. There are 14.1 % in the NiTiAl1 and 18.1 % of area fraction of the Ti_2Ni phase in the NiTiAl3 against 13 % of Ti_2Ni in the binary Ni-Ti46 alloy. The huge increase of the Ti_2Ni phase to 32 % of the area fraction was found out after the addition 5 wt. % of aluminium into NiTi46 alloy in the previous study [13]. At the same time the change in shape of the Ti_2Ni is possible to watch with an increasing amount of aluminium in the alloy. The Ti_2Ni phase creates larger areas with rugged boundaries. Three wt. % of aluminium are not enough to form the Ni_4Ti_3 phase yet like in the NiTiAl5 alloy – it was not identified by the XRD and EDS analysis.

The chemical compositions of the individual NiTi and Ti_2Ni phase were investigated with an increasing amount of the added alloying elements. It was discovered that all alloying elements were dissolved easily in the NiTi phase. The NiTi phase contents approximately 1 wt. % of alloying elements more than the Ti_2Ni phase in the NiTiAl1 and NiTiX3 alloys. There are the differences smaller in the NiTiFe1 and NiTiCo1. The beginning of the trend with the decreasing amount of titanium in the Ti_2Ni phase in the NiTiAlx alloys is obvious, then there was determined only 57 wt. % of titanium in the Ti_2Ni phase in the NiTiAl5 alloy [13]. The summary of the chemical composition of the individual phases measured by the EDS analysis is placed in Tab. 1.

Tab. 1 Chemical compositions of individual phase and area fraction of the Ti_2Ni phase

Alloy	NiTi phase (wt. %)			Ti_2Ni phase (wt. %)			Area fraction of Ti_2Ni (%)
	Ni	Ti	X	Ni	Ti	X	
NiTiFe1	53.4	45.6	1.0	37.2	62.0	0.8	11.1±0.8
NiTiCo1	54.1	44.7	1.1	37.1	62.1	0.8	10.9±0.8
NiTiAl1	54.0	44.7	1.3	38.2	61.4	0.4	14.1±0.5
NiTiFe3	53.1	44.0	2.9	36.7	61.3	2.0	10.7±0.7
NiTiCo3	53.1	44.1	2.8	36.0	62.0	2.0	11.0±0.6
NiTiAl3	53.6	43.6	2.8	37.6	60.4	2.0	18.1±1.4

All the alloying elements increase the hardness of the sintered samples. Alloying by iron shows the greatest effect on hardness in the amount to 3 wt. %. The sample with aluminium was found out as the hardest after the addition of 5 wt. % of alloying elements. Iron and cobalt cause the increase of hardness by substitutional strengthening of the NiTi phase while the increase of hardness in the samples with aluminium can be caused by a combination of substitutional strengthening and larger areas of the hard Ti_2Ni phase. One wt. % of aluminium does not significantly change the hardness in contrast with iron and cobalt.

The DSC heating and cooling curves of the reactive sintered products were measured but the determination of the transformation temperatures was successful only in the NiTiAl1 alloy. It is probably that iron, cobalt and

more than 1 wt. % decrease the transformation temperatures below the used temperature range. These transformation temperatures ($A_S = 11.1$ °C; $A_F = 27.9$ °C; $M_S = 18.7$ °C; $M_F = -3.3$ °C) were curtailed in the NiTiAl1 alloy and they confirm the same effect of aluminium on transformation temperatures in the samples prepared by the self-propagating high-temperature synthesis and conventional melting metallurgy [15].

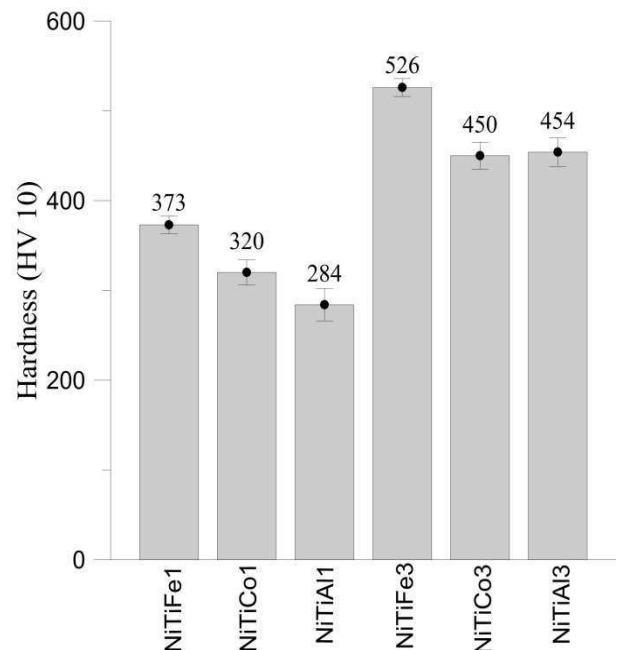


Fig. 2 Hardness of the Ni-Ti-X alloys prepared by SHS

4 Conclusion

The microstructures and the phase composition of the Ni-Ti-X alloys with a low addition (1 and 3 wt. %) of iron and cobalt are similar to the binary Ni-Ti46 alloy prepared by the self-propagating high-temperature synthesis. A small exceptions are the samples alloyed by aluminium, in which the area fraction of the Ti_2Ni phase increases and the shape of this phase is changed. Addition of iron, cobalt and aluminium increases the hardness of the Ni-Ti-X alloys. The temperature of the transformation temperature was measured in the NiTiAl1 sample successfully and it was found out that aluminium decreases these temperatures in the Ni-Ti alloys prepared by the self-propagating high-temperature synthesis.

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