

Effect of Zirconium, Niobium and Chromium on Structure and Properties of Ni-Ti Alloy

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This work deals with the possibility of modification of the phase composition and improvement of the properties of the NiTi alloy by alloying with other elements. After the production by conventional melting metallurgy as well as powder metallurgy, the Ni-Ti alloys contain in addition to the NiTi shape memory phase a lot of other phases, for example Ti₂Ni, Ni₃Ti, Ni₄Ti₃. Some of these phases can have an undesirable effect on the properties of the Ni-Ti alloy. A possible solution is the addition of alloying elements to destabilize these phases. The aim of this work is to describe the effect of Zr, Nb and Cr as alloying elements in the amount of 1 and 3 wt. % on microstructure, phase composition, hardness and transformation behavior of the Ni-Ti alloy produced by powder metallurgy using reactive sintering. Alloying by chromium leads to increase of hardness and microhardness of the NiTi phase whereas the addition of the alloying elements niobium and zirconium increases the temperatures of phase transformations.

Keywords: Ni-Ti alloys, Reactive sintering, Shape memory effect

1 Introduction

The Ni-Ti alloy belongs to the group of materials with shape memory. This alloy has found its application mainly due to the excellent properties associated with the shape memory effect. It is necessary to keep the ratio between nickel and titanium approximately equimolar. In the alloy there could exist many intermetallic phases – NiTi, Ti₂Ni, Ni₃Ti, Ni₄Ti₃ and Ni₃Ti₂ and Ni₈Ti₅ [1, 2]. The intermetallic phase NiTi is responsible for the ability of shape memory. In addition to this phase, there is always a Ti₂Ni intermetallic phase, which is undesirable because of its hardness and brittleness. In the NiTi phase, the phase transformation could be indicated between the high-temperature modification (austenite) and the low-temperature modification (martensite). It could be indicated by thermal energy or mechanical energy [3-5]. The superelasticity is the most important property of this alloy. The material is above the austenite finish temperature (austenite phase). After mechanical deformation austenite is changed to martensite. Martensite is not stable in these conditions and it is changed back to austenite [6, 7].

Manufacturing is difficult because of the need for the exact chemical composition of a product. It is necessary to keep the exact ratio between nickel and titanium because of the temperature of the phase transformation. For example 0.1 at. % of nickel could decrease the martensite start temperature for 10 °C. The problem is also with the reactivity of titanium. Titanium has a high affinity to oxygen, nitrogen and carbon, so it is necessary to do the production under vacuum or inert atmosphere. The most common techniques of production are vacuum induction melting (VIM) and vacuum arc remelting (VAR). In VIM, the ingot has a good homogeneity, but there is a danger of contamination due to the usage of a crucible. The crucible is made of graphite and it reacts with titanium and products carbide of titanium. In VAR, the crucible is made of copper, so there is less contamination, but the problem is with homogeneity [8, 9].

An alternative to melting metallurgy is powder metallurgy. The biggest advantage of this technique is the opportunity of making a product with an exact chemical composition. Reactive sintering method is used for the production of Ni-Ti alloys. The principle of this method is very easy. The powders of nickel and titanium are mixed in the exact chemical composition, then pressed by define pressure and heated up to the temperature of initiation the reaction between nickel and titanium. This temperature is lower than the melting temperature of the phase NiTi. This reaction is very exothermic. The propagation of heat is very fast and it causes the reaction in a whole bulk. This process runs in two stages. A slow diffusion part in which the temperature is lower than in the second part. The second part is faster and is called self-propagating high-temperature synthesis (SHS). The advantages of this method are low price and low energy for production, but the negatives of this method are uncontrollable porosity and an incomplete reaction of all elemental particles is possible [1, 10].

There are also the alternatives to reactive sintering such as hot isostatic pressing (HIP), spark plasma sintering (SPS) or metal injection moulding (MIM), but the reactive sintering powder metallurgy was chosen in this work [1, 10].

2 Experimental

The dependence of microstructure, hardness and temperatures of phase transformation are described in this work. The elemental powders with given purities and particle sizes (nickel: 99.99 wt. %, <150 µm; titanium: 99.50 wt. %, <44 µm; chromium 99 wt. %, <44 µm; niobium and zirconium 99 wt. %) were blended to the powder mixtures with chemical compositions of Ni_{52.4}Ti_{44.6}X₃ and Ni_{53.5}Ti_{45.5}X₁ where X represents alloying element. The powder mixtures were uniaxially cold compressed at a pressure of 450 MPa for 5 minutes to cylindrical green body samples using LabTest 5.250SP1-

VM universal loading machine. The reactive sintering was carried out in evacuated silica ampoules which were placed in the preheated electric resistance furnace at 1100 °C for 20 minutes. After cooling in air, the samples were ground by sandpapers with silicon carbide abrasive elements and polished by the diamond paste D2. The microstructure was etched in Kroll's reagent (10 ml HF, 5 ml HNO₃ and 85 ml H₂O). The phase composition was identified by X-ray diffraction (XRD) PANalytical X'Pert Pro diffractometer with a copper anode. 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 determination of chemical composition of individual intermetallic phases. The hardness of the samples was measured with a load of 10 kg (HV 10) and microhardness (using Microhardness tester FM-700) of the NiTi phase with a load of 10 g (HV 0.01). The transformation temperatures of sintered products (M_S martensite start, M_F martensite finish, A_S austenite start, A_F austenite finish) were measured by differential scanning calorimetry (DSC) from the temperature of -10 °C to 200 °C with the heating rate of 10 °C·min⁻¹.

3 Results and discussion

In the previous work, successful preparation of many intermetallics was investigated by powder metallurgy methods and specifically by reactive sintering. These

methods are used mainly for intermetallic compounds with poor casting properties, high melting temperature or in the case when the melt reacts with the material of melting crucible. The Ti-Al, Fe-Al, Ni-Ti based systems belong to the group of materials with problems described above and the research is focused currently on the description of the reaction mechanism between elemental powders and intermetallic phases, influence of sintering conditions like temperature, heating rate, used particles sizes of powders or addition alloying elements on properties of sintered products [11-15]. The low addition of alloying elements (1 and 3 wt. % of chromium, niobium and zirconium) does not change phase composition, the area fraction of the undesirable Ti₂Ni phase and generally microstructure considerably in comparison with the binary NiTi46 alloy. Only in the sample with chromium, there is a little decrease of the amount of the Ti₂Ni phase. According to XRD analysis, all sintered samples contain the NiTi phase (cubic structure) and the Ti₂Ni phase, in the samples with addition of niobium there is the NiTi phase with monoclinic structure moreover and all mentioned phases and the Ni₄Ti₃ phase were formed in the NiTiZr1 and NiTiZr3 alloys. The phase compositions, the area fraction of the Ti₂Ni phase and chemical compositions of the NiTi and Ti₂Ni phases measured by EDS are summarized in Tab. 1. The Ni₄Ti₃ phase was identified only by XRD in the NiTiZr samples but it was not observed in the microstructure in the NiTiZr samples, therefore its chemical composition is not placed in Tab. 1.

Tab. 1 Phase and chemical composition of reactive sintered NiTiX samples

Sample	XRD	Ti ₂ Ni area fraction (%)	EDS (wt. %)			
			Phase	Ni	Ti	X
NiTiCr1	NiTi (cubic), Ti ₂ Ni	11.7±0.4	NiTi	53.9	44.8	1.3
			Ti ₂ Ni	37.5	61.9	0.6
NiTiCr3	NiTi (cubic), Ti ₂ Ni	11.2±0.8	NiTi	53.8	44.6	2.6
			Ti ₂ Ni	36.7	61.9	1.4
NiTiNb1	NiTi (cubic), NiTi (monoclinic), Ti ₂ Ni	12.4±0.3	NiTi	54.1	44.9	1.0
			Ti ₂ Ni	38.0	61.7	0.3
NiTiNb3	NiTi (cubic), NiTi (monoclinic), Ti ₂ Ni	12.1±0.3	NiTi	53.0	43.9	3.1
			Ti ₂ Ni	37.7	60.0	2.3
NiTiZr1	NiTi (cubic), NiTi (monoclinic), Ti ₂ Ni, Ni ₄ Ti ₃	12.7±0.5	NiTi	53.9	44.9	1.2
			Ti ₂ Ni	38.2	60.8	1.0
NiTiZr3	NiTi (cubic), NiTi (monoclinic), Ti ₂ Ni, Ni ₄ Ti ₃	13.0±0.9	NiTi	53.2	43.5	3.3
			Ti ₂ Ni	37.5	60.3	2.2

Two intermetallic phases (NiTi and Ti₂Ni) were observed in microstructures. The differences in chemical composition of individual phases are well visible in Fig. 1 a-f which were taken in back-scattered electrons mode of SEM. From chemical compositions of phases it is evident that the alloying elements are dissolved in the NiTi phase preferably. The alloying elements zirconium and niobium substitute mostly titanium in intermetallic phases and only chromium by higher addition replaces nickel in the Ti₂Ni phase. The shape memory behavior was not detected in the samples with the addition of chromium. According to paper [16], the decrease of the temperature of the austenite-martensite phase transformation was expected. The disappearance of the transformation temperatures was mentioned in the case of the NiTiCr5 alloy prepared by reactive sintering [17]. However, the

austenite finish temperature (approx. 49 °C) was reported in another research [18]. It is a question why the reactively sintered NiTiCr samples do not show shape memory effects. It is possible that only 1.3 wt. % of chromium decreases the temperature of austenite finish below the temperature of -10 °C or chromium has another effect and it leads to a loss of shape memory effects in our experiments. The samples alloyed by niobium have the transformation temperatures higher than the NiTi46 alloy and these temperatures decrease with the increasing amount of niobium. The addition of zirconium causes the increase of the transformation temperature. The DSC curves of the Ni52.4Ti44.6Cr3 and Ni52.4Ti44.6Zr3 are shown in Fig. 2 and values for all samples which are assembled in Tab. 2.

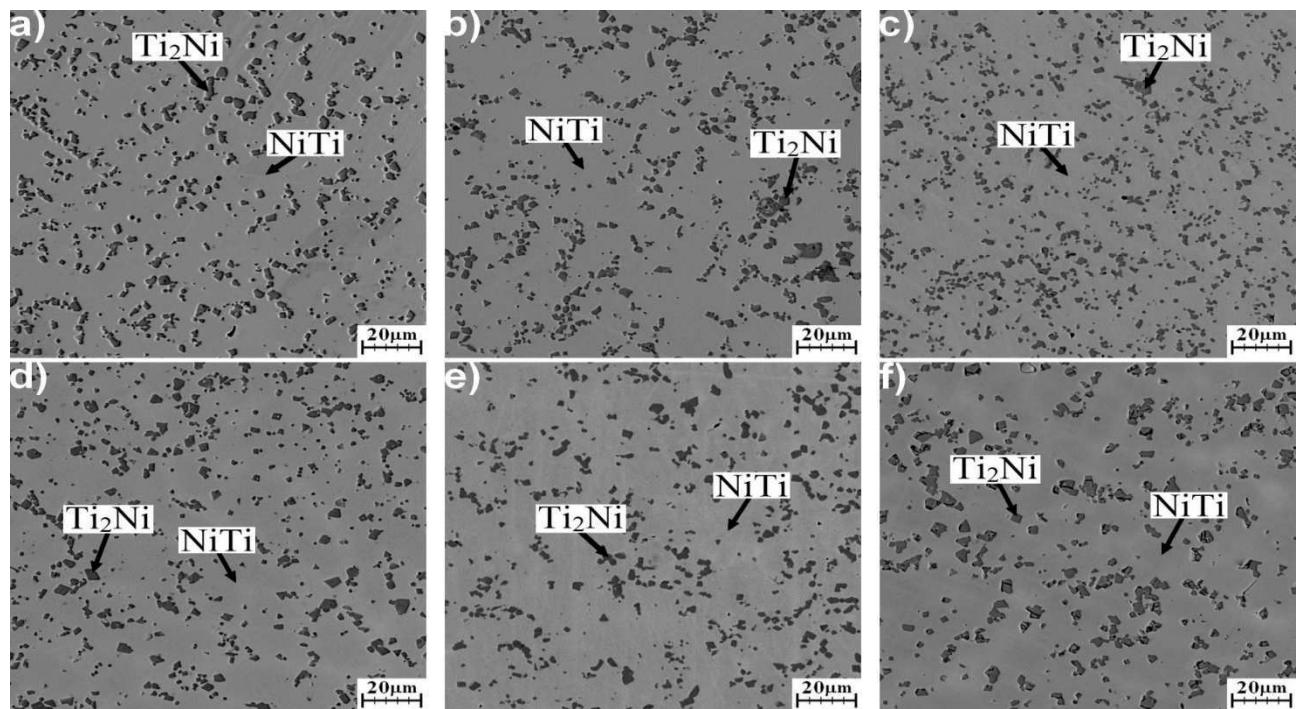


Fig. 1 Microstructures of a) NiTiCr1, b) NiTiCr3, c) NiTiNb1, d) NiTiNb3, e) NiTiZr1 and f) NiTiZr3 alloys

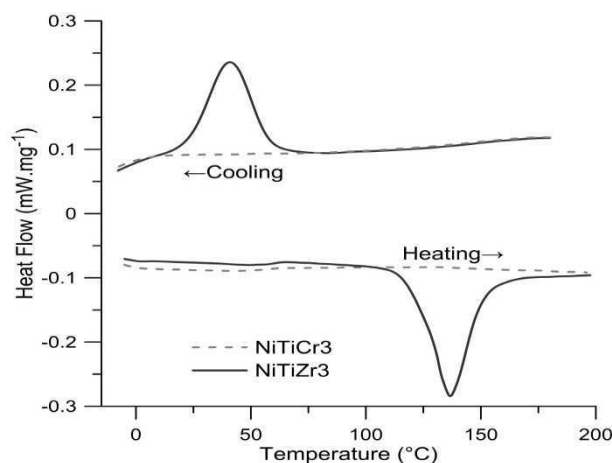


Fig. 2 DSC curves of Ni52.4Ti44.6Cr3 and Ni52.4Ti44.6Zr3 alloys

Tab. 2 Temperatures of phase transformations

Sample	A _S (°C)	A _F (°C)	M _S (°C)	M _F (°C)
NiTiNb1	81	132	51	-
NiTiNb3	73	114	23	-
NiTiZr1	102	148	68	15
NiTiZr3	111	156	56	13
NiTi46 [19]	56	86	21	-

The results of hardness (HV 10) and microhardness of the NiTi phase (HV 0.01) measurement are shown in Fig. 3. In Ni53.5Ti45.5Cr1 and Ni52.4Ti44.6Cr3 there is the clear increasing evolution of both values with increasing amount of chromium in the sample. When looking at the results of the NiTiCr3 alloy [17], there is comparable hardness of the NiTiCr3 and NiTiCr5 alloys and microhardness of NiTiCr alloys is still only increasing. The increase of microhardness of the NiTi phase slows down with the higher amount of chromium in the samples. In

case of samples alloyed by niobium and zirconium, there is a trend of hardness little ambiguous because after addition of 1 wt. %, hardness increases. However after 3 wt. % amount of the alloying elements, hardness decreases below the value of the binary NiTi46 [19]. The microhardness of the NiTi phase is decreasing only with the increasing amount of niobium and zirconium in the alloys. The decrease of the mechanical properties continues by addition of 5 wt. % [14, 17].

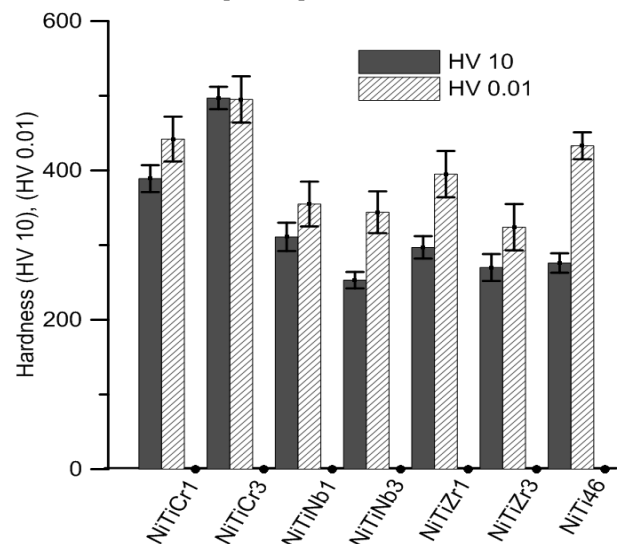


Fig. 3 Hardness and microhardness of NiTiX alloys

Generally, reactive sintering enables to prepare the ternary NiTiX alloys without contamination from the melting crucible like in VIM. The presence of the undesirable Ti₂Ni phase is the problem which appears by melting metallurgy and powder metallurgy too and the addition of ternary alloying elements does not solve it completely.

4 Conclusions

In this work, the influence of alloying elements (chromium, niobium and zirconium) was researched. The samples consist of the NiTi and Ti₂Ni phases. The only alloying element of chromium reduced the area fraction of the Ti₂Ni phase for 1.8 %, the decrease was negligible in case of other alloying elements. The disappearance of the shape memory effects represents the problem of the NiTiCr samples. On the contrary, using zirconium and niobium enables to manage the temperature of the phase transformation between the austenite and martensite structure of the NiTi phase. Mechanical properties – hardness and microhardness of the NiTi phase were increased by the addition of chromium. Niobium and zirconium decreased microhardness of the NiTi phase.

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