

PROPERTIES OF Ni-Ti-X SHAPE MEMORY ALLOYS PRODUCED BY ARC RE-MELTING

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Abstract

This paper deals with Ni-Ti46 and Ni-Ti-X wt. % alloys prepared by arc re-melting under argon protective atmosphere. The melting was repeated three times to obtain a homogenous chemical composition of samples. Niobium, vanadium and silicon were chosen as alloying elements and they were added into the alloy in an amount of 5 wt. %. Microstructure, phase composition, hardness and transformation behaviour were investigated parameters. Properties of cast alloys are compared with alloys of the same chemical composition prepared by powder metallurgy method – self-propagating high-temperature synthesis (SHS). Arc re-melting produced a more homogeneous microstructure with a lower content of the Ti₂Ni phase than powder metallurgy methods in case of Ni-Ti-X alloys. Quite a high amount of the secondary phase (a mixture of the Ni₂Ti, NiTi and Ti₂Ni phases) was created in the microstructure of Ni-Ti46 wt. % alloy. The addition of silicon caused an increase of transformation temperatures and hardness.

Keywords: Shape memory alloys (SMA), Nickel Titanium, Arc melting, Phase transformations

1 Introduction

Shape memory alloys have exceptional properties like superelasticity and One- and Two-ways shape memory effect. In approximately equimolar Ni-Ti alloy, these properties are ensured by the NiTi intermetallic phase. Shape memory effects are caused by the phase transformation between austenitic (high-temperature B2 cubic structure – type CsCl) and martensitic (low-temperature monoclinic B19' structure) phase. The temperatures of phase transformation are influenced by the nickel-titanium ratio (transformation temperature decreases with increasing nickel content), alloying elements and presence of impurities. Alloying elements such as iron, cobalt, manganese, chromium, aluminium and vanadium can reduce the transformation temperature and stabilize the austenite phase. On the contrary, the transformation temperatures can be increased by the addition of hafnium, zirconium, platinum and palladium [1]. Alloying by hafnium - Ni49.4Ti38.6Hf12 alloy (at. %) - increases the transformation temperature martensitic start (M_s) to 468 K (195 °C) [2]. Shape memory effect can also be found in some other alloys, e. g. Cu-Zn-Al, Co-Ni-Al and Au-Cd [3].

Ni-Ti alloys are most often produced by melting processes Vacuum Induction Melting (VIM) and Vacuum Arc Re-melting (VAR). Because of high reactivity of melt, the production process

is conducted under vacuum. Stirring and mixing of the melt is ensured by electrodynamic forces and the resulting products do not have problems with the homogeneity of the chemical composition [4]. The material of the crucible has a significant influence on the quality and purity of the product. Crucibles based on MgO and Al₂O₃ oxides are not suitable because they contaminate the melt with oxygen. From the oxide materials, crucible made of CaO [5] or coated by zirconia [6] may be used, they had evidenced little interaction with the Ni-Ti melt. Graphite crucibles are used the most commonly, being cheap compared to other materials. With increasing temperature and duration of melting, the amount of carbon absorbed into the melt increases. During solidification, TiC particles are formed and concentration of nickel increases. When a fresh crucible is used and Ni-pellets are in a direct contact with the crucible, then the first ingot shows a high carbon concentration. Other ingots in the same crucible have a lower content of carbon because the TiC layer is created there which acts as a diffusion barrier. A reduction of carbon concentration in ingots can be achieved by precluding the direct contact of nickel and carbon crucible. In the published study [7] it was achieved by Ti-disk cladding. The amount of carbon to 200-500 ppm in the melt should not have an effect on the shape memory characteristics [4]. The method of vacuum arc re-melting, the second manufacturing process used in production of commercial Ni-Ti alloys, enables to get an alloy with a higher purity because there is no contamination of the melt with the material of the crucible. Melting and solidification occur in a water-cooled copper crucible. The VAR's ingots usually contain up to 200 ppm carbon [8]. The disadvantage of this procedure is the ability to obtain only a small volume of melt and heterogeneity of the chemical composition of the product. The ingot must be re-melted more times to get a homogenous chemical composition [4]. During solidification, undesirable phases can be formed. It is the Ti₂Ni phase which is stabilized by oxygen [9]. Other possible phases present in microstructure are Ni₄Ti₃, Ni₃Ti₂ and Ni₃Ti. The Ni₄Ti₃ and Ni₃Ti₂ are thermodynamically metastable and by the appropriate thermal treatment they can be converted to Ni₃Ti. The Ti₂Ni and Ni₃Ti phases are thermodynamically very stable and their removal from the structure of Ni-Ti alloys is problematic [10]. Nowadays the fabrication of Ni-Ti alloys powder metallurgy methods are studied intensively [11, 12, 13].

This work is focused on properties of Ni-Ti shape memory with addition of an alloying element and it compares the influence of the alloying elements on Ni-Ti alloys prepared by melting and powder metallurgy methods.

2 Experimental materials and methods

The samples with the chemical composition of Ni_{51.3}Ti_{43.7}X₅ wt. % alloys (labelled NiTiX₅) were cast by arc melting in the Edmund Bühler MAM-1 furnace under argon atmosphere from pure elements (99.95 wt. % purity). The samples were re-melted three times to obtain a homogeneous state. Silicon, niobium and vanadium were chosen as promising alloying elements for the change of properties of Ni-Ti alloys. The metallographic samples were prepared by grinding using sandpapers with silicon carbide abrasive elements and polishing by diamond pastes. The microstructure was observed after etching in Kroll's reagent (10 ml HF, 5 ml HNO₃ and 85 ml H₂O). The microstructure was studied by light metallographic microscope Olympus PME3 and the scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max 20 mm² SDD EDS analyser. The phase composition of the alloys was identified on ground surfaces of the samples by the means of X-ray diffraction analysis (XRD) using PANalytical X'Pert Pro diffractometer with a copper anode. The area fraction of the Ti₂Ni phase was measured by Lucia 4.8 image analysis software. Differential scanning

calorimetry (DSC) analysis of prepared alloys was performed by using Setaram DSC 131 to determine the transformation temperatures (martensite start M_s , martensite finish M_f , austenite start A_s , austenite finish A_f) in products. The measurement was carried out between temperatures $-10\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$ with heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Hardness and microhardness were measured by Vickers method with the load of 10 kg (HV 10) and 10 g (HV 0.01).

3 Results and discussion

Figs. 1, 2, 3 and 4 present microstructures of the Ni-Ti46, NiTiV5, NiTiNb5 and NiTiSi5 alloys acquired by scanning electron microscope in a mode of backscattered electrons. Only the NiTi phase (chemical composition Ni54.5Ti45.5 in wt. %) and mixture of NiTi, Ti_2Ni and Ni_2Ti phases were observed in the microstructure of the Ni-Ti46 alloy and it is in a good agreement with XRD analysis (see phase compositions of samples in **Tab. 1**). The alloy NiTiV5 (in **Fig. 2**) demonstrates a microstructure with visible NiTi (chemical composition Ni53.4Ti44.2V2.4 in wt. %) and Ti_2Ni phases (Ni38.6Ti54.7V6.7 in wt. %). The phase composition is created only by cubic NiTi phase and there occurred an extra Ni_4Ti_3 phase in contrast with the Ni-Ti46 alloy. The mixture of NiTi, Ti_2Ni and Ni_2Ti phases takes approximately 41.2 % of area fraction in Ni-Ti46 alloy and NiTiV5 alloy is consisted of 9.6 % area fraction of the Ti_2Ni phase. The summary of XRD results is presented in **Tab. 1**.

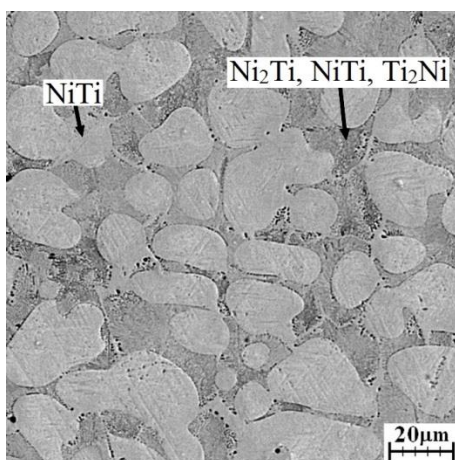


Fig. 1 Microstructure of Ni-Ti46 alloy

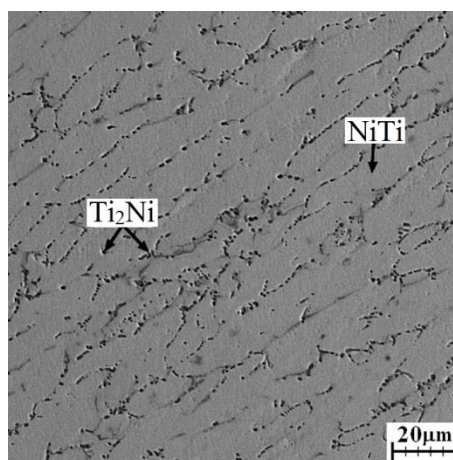


Fig. 2 Microstructure of NiTiV5 alloy

Table 1 Phase composition of Ni-Ti46 and Ni-Ti-X alloys prepared by arc re-melting

Alloy	Phase composition
Ni-Ti46	NiTi (cubic), NiTi (monoclinic), Ti_2Ni , Ni_2Ti
NiTiV5	NiTi (cubic), Ti_2Ni , Ni_4Ti_3
NiTiNb5	NiTi (cubic), Ti_2Ni , TiNb
NiTiSi5	NiTi (cubic), NiTi (monoclinic), Ti_2Ni , Ni_4Ti_3 , $\text{Ni}_3\text{Ti}_2\text{Si}$

Nearly half amount of this undesirable phase, area fraction, of the Ti_2Ni phase of 4.6 % was formed in the microstructure of the NiTiNb5 alloy. The microstructure is composed by niobium-

rich areas (white areas in **Fig. 3**) commonly with NiTi (Ni52.6Ti43.4Nb4.0 in wt. %) and Ti₂Ni phases. The niobium-rich areas (with chemical composition Ni40.5Ti38.4Nb21.4 in wt. %) were identified by XRD analysis as the TiNb phase where niobium is substituted by nickel. The most diverse phase composition was obtained by arc re-melting of NiTiSi5 alloy. Apart from cubic and monoclinic modifications of the NiTi phase (Ni52.1Ti43.3Si4.6 in wt. %) and Ni₄Ti₃ phase, the mixture of Ti₂Ni phase and nickel titanium silicide (Ni39.9Ti50.5Si9.6 wt. %) were identified by XRD analysis. But only the NiTi and mixture of Ti₂Ni and Ni₃Ti₂Si phases are visible in **Fig. 4**. The Ni₄Ti₃ phase is usually present in the form of fine precipitates in the NiTi matrix [13, 14]. Area fraction of Ti₂Ni and Ni₃Ti₂Si phases of 6.1 % was determined by image analysis in this alloy.

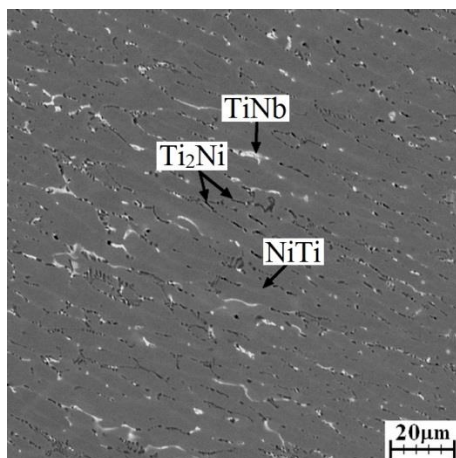


Fig. 3 Microstructure of NiTiNb5 alloy

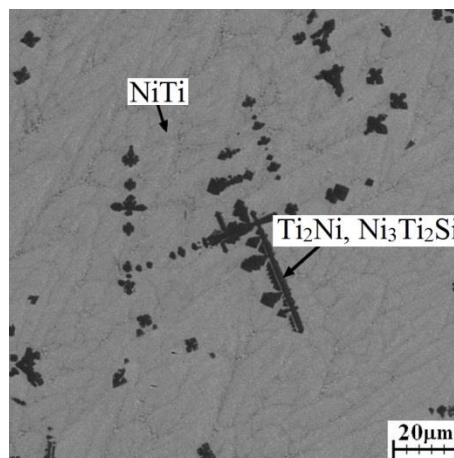


Fig. 4 Microstructure of NiTiSi5 alloy

If we compare microstructures and phase compositions (mainly amount and morphology of the Ti₂Ni phase) with the same chemical compositions alloys prepared by powder metallurgy methods, there are some similarities and some differences. There are not so big differences in phase composition, but minor amount of residual nickel or titanium can stay in samples after SHS reaction. The arc re-melting produces Ni-Ti-X alloys with lower amount of the Ti₂Ni phase in each case (the exception is the binary Ni-Ti alloy where the mixture of Ni₂Ti, NiTi and Ti₂Ni phases as secondary phase was created and takes a larger area fraction) than powder metallurgy methods like SHS reaction and spark plasma sintering. It is very interesting that the basic Ni-Ti46 alloy produced by arc re-melting contains the higher amount of the mixture of Ni₂Ti, NiTi and Ti₂Ni phases than other Ni-Ti-X alloys produced by arc re-melting, whereas if the alloys are produced by powder metallurgy ways, the Ni-Ti46 alloy has the lowest amount of the Ti₂Ni phase at all [15]. The big change between the preparation ways came in the shape of Ti₂Ni phase particles, which have polygonal and sharp shape after SHS reaction and it creates large areas along sintered powder's boundaries after spark plasma sintering [16]. The exception is the NiTiSi5 alloy because the mixture of Ti₂Ni and Ni₃Ti₂Si phases create the same dendrites during SHS reaction and arc re-melting [17].

DSC analysis of casting products found big differences in transformation behaviour between samples. During heating there were detected some thermal effects, which are connected with the transformation of martensite to R-phase, which is subsequently transformed to austenite. This phenomenon occurred in NiTiV5, NiTiNb5 and Ni-Ti alloys. In these alloys, the temperatures of

martensite finish (M_F) were not determined because the finish of the martensitic transformation takes place at lower temperatures than $-10\text{ }^{\circ}\text{C}$ during cooling. The addition of silicon into Ni-Ti alloy caused the increase of temperatures of the austenitic a martensitic transformation and the R-phase was not formed. It is well known that increase of the transformation temperatures and also stabilizing of martensitic phase can be done by alloying of Ni-Ti alloy by expensive alloying elements like platinum, palladium, zirconium and hafnium [1,2]. In this work it has been found that it is possible due to use cheaper alloying element - silicon. The transformation temperatures are summarized in **Tab. 2**.

Table 2 Properties of Ni-Ti46 and Ni-Ti-X alloys prepared by arc re-melting

Alloy	As [$^{\circ}\text{C}$]	R-phase [$^{\circ}\text{C}$]	Af [$^{\circ}\text{C}$]	Ms [$^{\circ}\text{C}$]	Mf [$^{\circ}\text{C}$]	HV 10	HV 0,01
Ni-Ti46	7	49	70	13	-	179 $\pm$ 5	240.5 $\pm$ 12.0
NiTiV5	6	34	54	19	-	220 $\pm$ 12	303.0 $\pm$ 9.8
NiTiNb5	22	36	72	10	-	177 $\pm$ 7	200.2 $\pm$ 8.7
NiTiSi5	40	-	67	72	105	531 $\pm$ 15	395.4 $\pm$ 14.9

Mechanical properties were evaluated by measurement of hardness with a load of 10 kg and of hardness of NiTi matrix with a small load of 10 g. Values of hardness are presented in **Tab. 2**. The influence of alloying elements on hardness is similar to the samples prepared by SHS reaction. Hardness is decreased by niobium whereas much higher hardness was measured in NiTiSi5 alloy probably due to fine particles of silicides microstructure, which can cause the strengthening of NiTi phase matrix or substitutional strengthening of NiTi phase by silicon. The Ni-Ti46 and NiTiV5 alloys have approximately same values of hardness after SHS reaction, by preparation method of arc re-melting vanadium causes the increase of hardness [15].

4 Conclusions

The properties of Ni-Ti46 wt. % alloy prepared by arc re-melting were studied in this paper. At the same time influence of alloying elements silicon, vanadium and niobium on Ni-Ti alloy was investigated. It was found that the effect of silicon on transformation behaviour of Ni-Ti appears to be significant because the silicon stabilizes the martensitic structure of NiTi phase and also it can replace very expensive alloying elements like platinum and palladium. The cast Ni-Ti-X alloys contain lower amount of the Ti_2Ni phase than the alloys of the same chemical compositions prepared by powder metallurgy methods.

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