

## PHASE FORMATION IN NiTiAl10 POWDER MIXTURE DURING HEATING TO 1100 °C

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### Abstract

In this paper the comparison of NiTiAl10 wt. % with the binary NiTi46 wt. % prepared by powder metallurgy was researched. The method of combustion synthesis was carried out under following conditions: sintering temperature of 800 °C and 1100 °C and heating rate approx. 300 °C.min<sup>-1</sup>. The addition of aluminium to NiTi46 wt. % powder mixture completely changed the temperature of combustion synthesis and phase evolution during sintering. The reactions into Ni-Ti-Al powder mixture started below the melting temperature of aluminium and the new phases were formed in the material. The process of reactive sintering was studied by differential thermal analysis using the heating rate of 30 °C.min<sup>-1</sup> and 100 °C.min<sup>-1</sup>. A combination of induction furnace and optical pyrometer. The addition of aluminium influenced microstructure significantly and increased the hardness of samples.

**Keywords:** Self-propagating high-temperature synthesis, Powder metallurgy (PM), Differential thermal analysis (DTA), Intermetallics

### 1 Introduction

The shape memory effects and superelasticity occur in the Ni-Ti alloy due to the NiTi intermetallics phase. This phase exists in two structure modifications. The low-temperature structure called martensite (monoclinic) and high-temperature structure – austenite (cubic). The shape memory properties are caused by diffusion-less phase transformation between austenite and martensite structures [1]. The powder metallurgy routes seem to be perspective a way of production intermetallics or special materials with high mechanical properties in general. The reactive sintering – combustion and self-propagating high-temperature synthesis [2, 3], hot isostatic pressing [4], mechanical alloying and spark plasma sintering [5-7] belong to important methods. In the Ni-Ti binary system, the reaction starts by the formation of the Ti<sub>2</sub>Ni phase after annealing for 24 hours at the temperature of 500 °C. The NiTi and Ni<sub>3</sub>Ti phases were observed after annealing at 650 °C. The reactions are probably diffusion-controlled and the reaction scheme is presented in [8].

The high exothermic self-propagating high-temperature between nickel and titanium particles is initiated at the temperature of  $\alpha \rightarrow \beta$  Ti (approx. 882-890 °C) [5] or around the temperatures of 942 and 984 °C when the liquid phase due to eutectic and peritectic transformation is formed [9, 10]. The lower temperature of initiation is supported by high heating rate because the

intermetallic phase layers around particles boundaries formed during heating by a low rate can act as a barrier. In the same way, the SHS reaction was blocked in the spark plasma sintering technique. The diffusion layers on the particles surface separated the unreacted nickel and titanium and blocked SHS reaction, even though the high heating rate ( $300\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ) was applied by spark plasma sintering [11]. The change of reaction mechanism comes with the aluminium addition into Ni-Ti powder mixture. Aluminium is the component, which brings the liquid phase to the Ni-Ti-Al system at  $660\text{ }^{\circ}\text{C}$  by melting of aluminium or at  $640\text{ }^{\circ}\text{C}$  by Ni-Al eutectic melt formation. During heating of Ni-Ti-Al powder mixture, the first onset peak of reaction at  $596\text{ }^{\circ}\text{C}$  by use of  $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  the heating rate was observed and the phase composition consisted of unreacted Ni, Ti and Al and nickel aluminides  $\text{Ni}_2\text{Al}_3$  and  $\text{NiAl}_3$ . The other  $\text{Al}_3\text{Ti}$ , Al,  $\text{AlNi}_3$ ,  $\text{Ti}_2\text{Ni}$  and NiTi intermetallic phases were formed during heating to the temperature of  $910\text{ }^{\circ}\text{C}$ . The exothermic reaction occurs at  $942\text{ }^{\circ}\text{C}$  which corresponds with the eutectic transformation in the binary Ni-Ti powder mixture. The NiTi and other Ni-Ti-Al ternary phases are formed in dependence on the amount of aluminium in the sample [12].

This work compares the reaction mechanism of NiTi46 and NiTiAl10 wt. % powder mixture by use of  $30$  and  $100\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , microstructures, phase compositions and hardness of the samples sintered at  $800$  and  $1100\text{ }^{\circ}\text{C}$ .

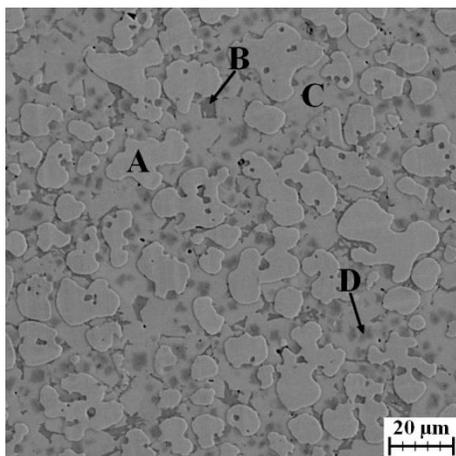
## 2 Experimental materials and methods

The elemental powders with particle size and purity (nickel:  $<150\text{ }\mu\text{m}$  99.99 wt. %; titanium:  $<44\text{ }\mu\text{m}$ , 99.5 wt. %; aluminium:  $<44\text{ }\mu\text{m}$  99.7 wt. %), were blended into powder mixtures NiTi46 wt. % and Ni48.6Ti41.4Al10 wt. % (labelled NiTi46 and NiTiAl10). The powder mixtures were uniaxially compressed at room temperature at a pressure of  $450\text{ MPa}$  for 5 minutes using LabTest 5.250SP1-VM universal loading machine. The SHS reaction was carried out in evacuated silica ampoule in electric resistance furnace preheated to  $800$  and  $1100\text{ }^{\circ}\text{C}$  (sintering duration 20 minutes and heating rate approx.  $300\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ). The metallographic samples were prepared by mechanical grinding and polishing and etched in Kroll's reagent (10 ml HF, 5 ml  $\text{HNO}_3$  and 85 ml  $\text{H}_2\text{O}$ ). The microstructure and chemical composition were studied by the scanning electron microscope TESCAN VEGA 3 LMU equipped with the OXFORD Instruments X-max  $20\text{ mm}^2$  SDD EDS analyser. The phase compositions of the alloys were identified on ground surfaces of the samples using X-ray diffraction (XRD) PANalytical X'Pert Pro diffractometer with a copper anode. The reaction mechanism was studied using differential thermal analysis (DTA) SETSYS Evolution – 1750 device in a temperature range from  $50$  to  $1200\text{ }^{\circ}\text{C}$  with the heating rate of  $30\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  in an argon atmosphere. The initial temperature of SHS reaction by the heating rate of  $100\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  was discovered by the use of induction furnace with argon atmosphere and optical pyrometer. The mechanical properties were investigated by hardness measurement with a load of  $10\text{ kg}$ .

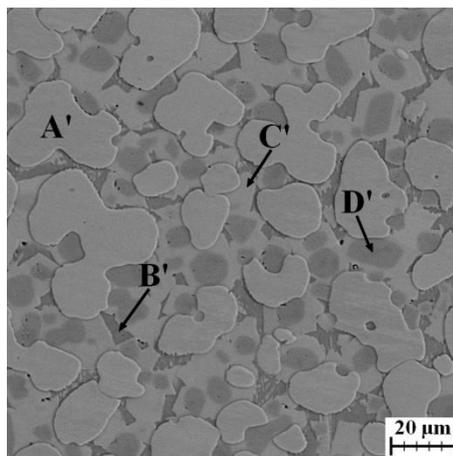
## 3 Results and discussion

The conditions of self-propagating-high temperature synthesis were investigated as sintering temperature, heating rate and particle sizes of used elemental powders in previous studies [2, 10, 13-15]. The sintering temperature of  $1100\text{ }^{\circ}\text{C}$ , the possibly highest heating rate and middle particle sizes were chosen to limit the formation of the  $\text{Ti}_2\text{Ni}$  phase. The sintering temperature of  $800\text{ }^{\circ}\text{C}$  shows the possibility to use lower sintering temperature in the NiTiAl10 alloy and to reveal possible differences in the properties of NiTiAl10 sample sintered at a higher temperature

than the peritectic point at 984 °C and lower than the  $\alpha \rightarrow \beta$  Ti transformation at 882 °C in Ni-Ti system. The microstructures of NiTi46 alloys sintered at 800 °C and 1100 °C were discussed in these studies [2, 16]. There are only unreacted nickel and titanium particles bordered with the  $Ti_2Ni$ , NiTi and  $Ni_3Ti$  intermetallic layers in NiTi46 sintered at 800 °C whereas the same powder mixture sintered at 1100 °C is composed of the NiTi phase matrix with the  $Ti_2Ni$  phase. The individual phases were confirmed by XRD analysis and their chemical compositions correspond with Ni-Ti phase diagram. The microstructures of the NiTiAl10 alloys heated to 800 °C and 1100 °C are shown in **Fig.1** and **Fig. 2**. The difference in the microstructures of NiTiAl10 alloys using two sintering temperatures is minimal in comparison with NiTi46 samples.



**Fig. 1** The microstructure of NiTiAl10 alloy sintered at 800 °C



**Fig. 2** The microstructure of NiTiAl10 alloy sintered at 1100 °C

**Table 1** Chemical composition (EDS) of NiTiAl10 samples

Sample	Area	Ni (wt. %)	Ti (wt. %)	Al (wt. %)
NiTiAl10 800 °C	A	58.4	28.5	13.1
	B	32.5	56.4	11.1
	C	38.5	54.4	7.2
	D	38.3	53.4	8.3
NiTiAl10 1100 °C	A'	59.3	28.1	12.6
	B'	31.2	58.5	10.2
	C'	37.9	56.1	5.9
	D'	37.3	55.9	6.9

The same phases (NiTi,  $Ti_2Ni$  and ternary  $AlNi_2Ti$ ) were identified according to XRD analysis in both the NiTiAl10 alloys. The microstructures are created by four areas with different chemical compositions (**Table 1**) and it is clear that the phases can contain various amount of aluminium and thus the structures of the phases are a little bit deformed. Hardness was measured

with following results: NiTi46\_800 °C = 56±2 HV, NiTi46\_1100 °C = 276±12 HV, NiTiAl10\_800 °C = 675±20 HV and NiTiAl10\_1100 °C = 697±21 HV. The low value of hardness was expected due to not completely reacted NiTi46 sample. The increase of hardness after addition of aluminium was expected due to the formation of more intermetallic phases as well. The increase of hardness after aluminium addition was described in [17, 18]. It was caused by stabilization of the hard Ti<sub>2</sub>Ni phase and substitution strengthening of the NiTi phase. The hardness difference between NiTiAl10 sintered at 800 and 1100 °C can be caused by the promoted formation of phases (higher amount of fine aluminides could be formed) due to easier diffusion at a higher temperature. The reaction mechanism was described by DTA analysis (Fig. 3) and by measuring the temperature profile using an optical pyrometer (Fig. 4).

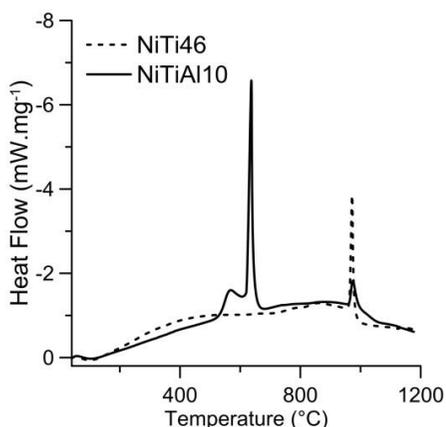


Fig. 3 DTA heating curve with a heating rate of 30 °C.min<sup>-1</sup>

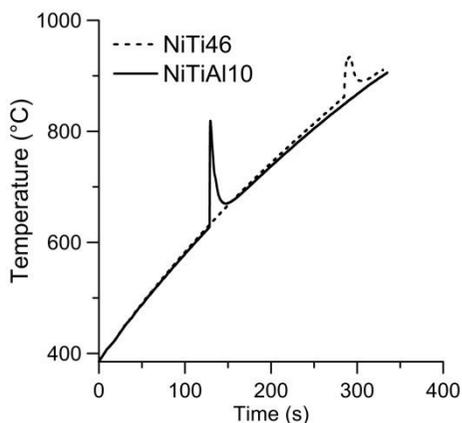


Fig. 4 Heating curve recorded by optical pyrometer with a heating rate of approx. 100 °C.min<sup>-1</sup>

The diffusion-controlled formation of the Ti<sub>2</sub>Ni phase was observed below the temperature of 882 °C, and the SHS reaction is initiated close to this temperature at approx. 948 °C by the use of 30 °C.min<sup>-1</sup> heating rate (Fig. 3). In the NiTiAl10 powder mixture, there are three exothermic peaks. The first one in the temperature range of 525 – 610 °C represents the formation of nickel aluminides (Ni<sub>2</sub>Al<sub>3</sub> and NiAl<sub>3</sub>) similarly as in binary Ni-Al system [19]. Its presence was confirmed by XRD analysis (Fig. 5) at the samples annealed 20 minutes at 610 °C and quickly cooled in water.

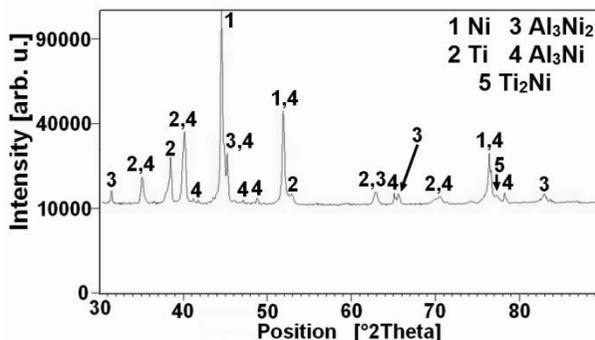


Fig. 5 The diffraction pattern of NiTiAl10 sintered at 610 °C and quickly cooled in water

The second peak with an onset temperature of 620 °C and peak maximum at 637 °C is caused by the main exothermic reaction of the formation of intermetallic phases. The heat from the first exothermic reaction could lead to the local formation of melt and the initiation of SHS reaction. The residue of unreacted nickel and titanium reacts at 960 °C – the third exothermic effect. The similar reaction mechanism was described in [12] using heating rate of 20 °C.min<sup>-1</sup>. The two first reactions go together by heating with the rate of 100 °C.min<sup>-1</sup>, see the heating curve recorded by an optical pyrometer. The initiation temperature of SHS reaction was detected at 863 °C. It is below the temperatures reported previously when the initial temperature of 882 °C was found out [5]. The lower temperature could be measured due to the different way of heating into induction furnace. The similar research was carried out focused on the change of sintering mechanism after addition of alloying elements into Ni-Ti powder mixture, but none of the alloying elements (magnesium, carbon, zirconium) influenced the reaction during heating in the same way as aluminium [20].

#### 4 Conclusions

The results of this work are in agreement with previous works dealing with sintering of powder mixtures with similar Ni-Ti-Al chemical compositions. The differences were showed in sintering mechanism between Ni-Ti and Ni-Ti-Al system. The decrease of SHS reaction close to the eutectic temperature in Ni-Al system was confirmed and in case of local overheating due to the exothermic formation of nickel aluminides, the SHS reaction can be initiated at approx. 620 °C depending on the used heating rate.

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