FORMATION OF Ni-Ti INTERMETALLICS DURING REACTIVE SINTERING AT 800–900 °C

OBLIKOVANJE NiTi INTERMETALNIH ZLITIN MED REAKTIVNIM SINTRANJEM PRI 800–900 °C

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In this work the formation of intermetallics in the Ni-Ti system by reactive sintering at 800–900 °C was studied. The mechanism and kinetics of the reactions, which led to Ni-Ti phases, were determined by thermal analysis, in-situ XRD and the application of an experimental model consisting of nickel-plated titanium. It was found that the formation of Ni-Ti phases below the transformation temperature of titanium is controlled by diffusion. Above this temperature, the reactions switch to the rapid Self-propagating High-temperature Synthesis (SHS) mode.

Keywords: reactive sintering, powder metallurgy, NiTi

V delu je bil raziskan nastanek intermetalnih zlitin v sistemu NiTi pri reaktivnem sintranju na 800-900 ° C. S termično analizo, XRD-in situ analizo in uporabo eksperimentalnega modela, nikljanega s titanom, sta bila določena mehanizem in kinetika reakcij, ki sta vodila k NiTi fazam. Ugotovljeno je bilo, da je tvorba NiTI faze pod transformacijsko temperaturo titana, nadzorovana z difuzijo. Nad to temperaturo se reakcije spremenijo na hitro rastoči temperaturno -sintezni način (SHS).

Ključne besede: reaktivno sintranje, metalurgija prahov, NiTi

1 INTRODUCTION

The Ni-Ti alloy called nitinol, in approximately equimolar proportions, is the most widely known shape-memory alloy. The shape-memory effect in this alloy is connected with the transformation between high-temperature cubic austenite and low-temperature monoclinic martensite.[1,2] For the practical application of these alloys, superelasticity is very important. This phenomenon occurs when the NiTi alloy is deformed slightly above the martensite → austenite transformation temperature. Deformation induces the formation of the martensite phase, which is continuously transformed to austenite during unloading. Due to this phenomenon, this alloy behaves like an enormously elastic material.[1,2] In addition, the NiTi alloy is also a corrosion-resistant material.[3] Due to its exceptional properties, the NiTi alloy is applied in both medical (dental implants, stents, scaffolds)[4,5] and technical applications (actuators, robotics, etc.).[6–8]

The most commonly applied techniques in the industrial production of nitinol alloy are melting metallurgy processes – vacuum induction melting (VIM) and vacuum arc remelting (VAR).[9,10] In the VIM of Ti-containing alloys there is a serious danger of a strong contamination of the melt due to the high reactivity of molten titanium.[11] The VAR technique makes it possible to prepare alloys of higher purity, but there is a problem with homogeneity. To obtain a sufficiently homogenous product, the VAR process has to be repeated even more than 4 times.[10] This implies that it is costly and relatively problematic to obtain a NiTi shape-memory alloy. If a simple production technology would be developed, the NiTi alloy could be more frequently applied, not only in specific areas requiring the shape-memory effect, but also in other technical branches as a corrosion-resistant alloy. It will be beneficial for European economy, because this alloy does not contain any elements listed as critical raw materials.[12]

A promising alternative to melting metallurgy production routes is powder metallurgy (PM). A simple non-conventional PM production technology is reactive sintering. In general, the reactive sintering is a densification process, where initial components in powder form are transformed to a compact product via thermally-activated chemical reactions.[13] These reactions are mostly exothermic when intermetallics are formed. The route from powders to the compact usually contains powder blending, cold pressing and sintering.[13,14] When pure powders and an efficient protective atmosphere are

applied, a high-purity product is obtained due to the limited contact of the compressed reaction mixture with the crucible or support during the process.

The reactive sintering process of many intermetallics, including the Ni-Ti alloy, proceeds in two stages: a lower-temperature diffusional stage and a rapid high-temperature process called Self-propagating High-temperature Synthesis (SHS).[13–15]

In the case of the reactive sintering of NiTi alloy, the following mechanism is proposed in the literature. During heating to 900 °C, the slow diffusional formation of three intermetallics (Ti_2Ni, NiTi and Ni_3Ti) proceeds. In our previous paper we found that traces of the Ti_2Ni phase start to form already at 471 °C, being followed by NiTi and Ni_3Ti at 632 °C.[16] The transformation of α-Ti to β-Ti takes place as the temperature increases and after that the β-Ti rapidly saturates with nickel. When the temperature exceeds 942 °C, a liquid phase is formed from the solid solution of nickel in β-Ti by eutectic transformation and thus ignites the SHS reaction.[15] However, in our previous paper about the optimization of the conditions for the reaction synthesis of the NiTi shape memory alloy the structure corresponding to the SHS reaction was observed already after heating to 900 °C, being very similar to the material processed at 1100 °C.[17]

This paper aims to explain how it is possible to initiate the SHS reaction in NiTi alloy at 900 °C. To prove it, the mechanism and kinetics of the Ni+Ti reactions were studied by thermal analysis, in-situ XRD analysis and an experimental model.

2 MATERIALS AND METHODS

As mentioned above, the structure appearing to result from SHS reaction was observed in the NiTi alloy already at 900 °C using a heating rate of approximately 300 °C/min,[17] even though other references state that the SHS reaction is triggered by the melt formation by eutectic reaction at 942 °C. To prove the possibility to initiate the SHS reaction under these conditions and to describe the reaction mechanism, the following steps were carried out:

- Thermal analysis during heating from room temperature to approximately 1200 °C with the heating rate of approximately 300 °C/min. The heating rate was the same as in our previous paper, where the structure corresponding to the SHS reaction was observed after the process at 900 °C.[17]
- In-situ XRD analysis during heating from the laboratory temperature to 900°C with the heating rate of 60 °C/min. The heating rate was limited by the capabilities of the device.
- Description of mechanism and kinetics of the Ni-Ti phases' formation at 800 °C and 900 °C using an experimental model.

- Reactive sintering of Ni-Ti samples at 800 °C and 900 °C with the heating rate of 300 °C/min.

Experimental material for thermal analysis and in-situ XRD was prepared by blending of nickel powder (particle size < 150 μm, > 99.99 % purity, supplied by Aldrich) and titanium powder (particle size <44 μm, > 99.5 % purity, supplied by Alfa Aesar). Green bodies with a cylindrical shape of 10 mm in diameter and approximately 5 mm in height were prepared by uniaxial cold pressing of the powder blends under a pressure of 630 MPa using LabTest 5.250SP1-VM universal loading machine.

Thermal analysis was carried out during heating in the induction furnace from room temperature to 900 °C with the heating rate of approximately 300 °C/min. An optical pyrometer (Optris P20 2M) was used to record the temperature profile of the reaction.

In-situ XRD analysis (Cu-K_α radiation) was carried out during heating from laboratory temperature to 900 °C in a helium atmosphere with a heating rate of 60 °C/min.

An experimental model was established and successfully applied in our previous works in the Fe-Al, Fe-Al-Si and Ti-Al-Si systems.[18,19] In the mentioned papers, the experimental model consisted of an iron or titanium sample submerged in molten aluminium or Al-Si alloy. The aim of these experiments was to describe the kinetics of the formation of intermetallics in these particular alloys systems, because directly in reactive sintering process it is not possible. In the present work a model (Ni-Ti diffusion couple) consisting of a titanium bulk sample coated with nickel was applied. The nickel-plated titanium simulates the interaction between the compressed titanium and nickel powder particles. The galvanic nickel plating was carried out at 60 °C in a Watts's bath containing 300 g/L $NiSO_4.7H_2O$, 40 g/L $NiCl_2$ and 40 g/L H_3BO_3 using a current density of 10 A/m to the final thickness of approximately 20 μm. Before galvanic plating, titanium samples were sandblasted with alumina for 10 min, pickled in 35 % HCl at 60 °C for 12 min and activated in 35 % HCl at 20 °C for 15 s. The coated samples were annealed for 30–180 min in evacuated and sealed silica ampoules at 800 °C. At 900 °C, the experiment was stopped after <120 min, because the whole thickness of the nickel coating reacted to form Ni-Ti phases. The heating rate during the experiments was approximately 300 °C/min. The phase composition of the obtained multilayer systems was identified by the X-ray diffraction (XRD) method using PANalytical X'Pert Pro diffractometer (Cu-K_α radiation). PANalytical X'Pert HighScore Plus software with the PDF-2 database was used to process and to evaluate the XRD patterns. The microstructure of intermetallics' layers was examined with a TESCAN VEGA 3 scanning electron microscope equipped with OXFORD Instruments X-max EDS SDD 20 mm² detector (SEM-EDS). Samples were mechanically ground, polished and etched using modified Kroll's reagent (10 mL HF, 40 mL HNO_3

and 50 H_2O) before the microstructure observation. Image analysis was carried out by the means of ImageJ software in order to determine the thickness of the intermetallics' layers. A process controlling the formation of intermetallics was determined by fitting the layer thickness with a parabolic growth equation. When a process is controlled by diffusion of species through a reaction product, it is generally described by the parabolic law, written as Equation (1):

$$d = \sqrt{k_p \cdot t} \qquad (1)$$

where d is the layer thickness (μm) and t represents the annealing duration (s).[20]

3 RESULTS AND DISCUSSION

The temperature profile during heating of the compressed powder mixture of nickel and titanium was recorded using an optical pyrometer. During heating in an induction furnace by the rate of nearly 300 °C/min, the temperature increased almost linearly up to approximately 880 °C (**Figure 1**). After that, the increase of the slope, i.e., the heating rate, can be observed. This increase can be probably be attributed to the initiation of the strongly exothermal SHS reaction. This temperature corresponds well with the transformation of titanium from hexagonal (hcp) structure to cubic (bcc) one.[21] After achieving approximately 940 °C, the slope of the curve increases even more rapidly, probably due to the formation of a liquid phase by the eutectic transformation in the Ni-Ti system (942 °C).[21] The liquid medium supports the SHS reaction by increasing the diffusion rate of the reactants. The maximum temperature achieved by the reactions was 1137 °C. This indicates that the sample was partially molten due to eutectic
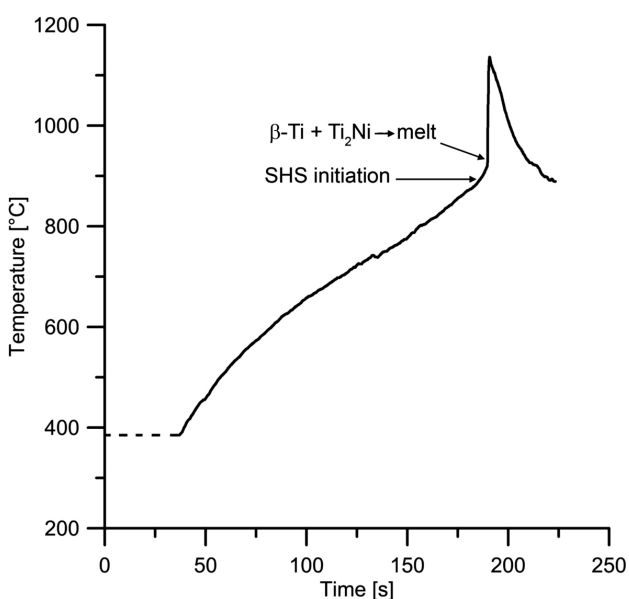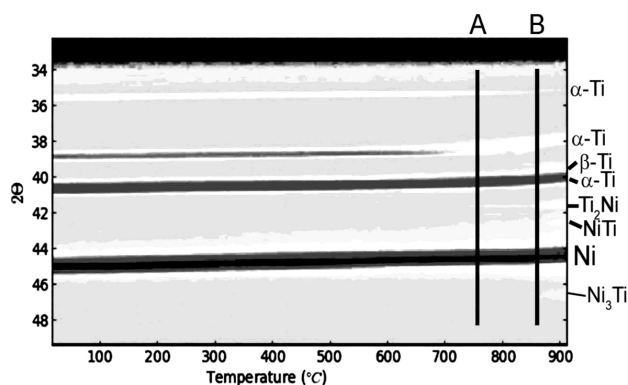
reactions at 942 °C and 1118 °C, but did not exceed the melting point of the NiTi phase (1310 °C).[21] It can be expected that the temperature at the reaction front can be even higher, but the heat is quickly transferred to the rest of the sample and therefore the overall temperature of the sample is lower.

The in-situ XRD analysis during heating of the compressed powder mixture from the room temperature to 900 °C with a rate of 60 °C/min (**Figure 2**) shows the continuous shift of the diffraction lines of nickel and titanium to lower angles with increasing temperature. This phenomenon is caused by the thermal expansion of the powders. In addition, the phase transformation of hexagonal α-Ti to cubic β-Ti can be observed around the temperature expected according to the Ni-Ti phase diagram (882 °C).[21] In addition to this phase transformation, the weak diffraction lines of the Ti_2Ni (cubic structure Fd$\bar{3}$m)[21] and NiTi (austenite, cubic structure Pm$\bar{3}$m)[21] phases start to be visible at approximately 750 °C. The intensity of the lines of the Ti_2Ni phase increase very rapidly, when a temperature of approximately 880 °C is achieved (**Figure 2**). This increase is immediately followed by the rapid formation of NiTi (austenite, cubic structure Pm$\bar{3}$m)[21] and Ni_3Ti (hexagonal P6$_3$/mmc)[21]. It implies that the SHS reaction between nickel and titanium is initiated by the transformation of titanium to its cubic allotropic modification. It forms the Ti_2Ni phase, which then reacts with nickel and/or the Ni_3Ti phase to form NiTi (austenite). The same phases' formation sequence was also observed for the diffusion stage of the reactive sintering process during long-term annealing at 500–650 °C. It implies that Ti_2Ni forms preferentially and it cannot be avoided in both low-temperature diffusion process, as well as during SHS mode.

To be able to describe the kinetics of the formation of intermetallics, the experimental model simulating the interaction between compressed nickel and titanium particles was applied. The model consisted of a bulk titanium sample covered by a nickel layer of approximately 20 μm in thickness. The model samples were

Figure 1: Heating curve of Ni-Ti compressed powder mixture (heating rate of approx. 300 °C min⁻¹, recorded by optical pyrometer)
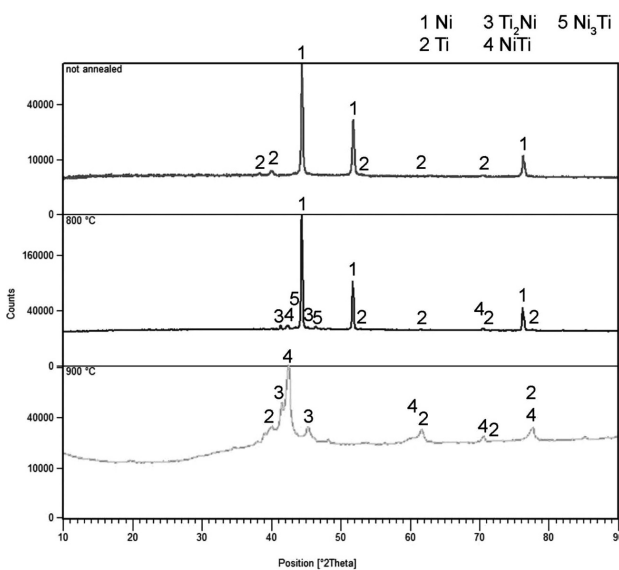

Figure 2: Variation of XRD intensities of NiTi46 (in mass fractions, (w/%)) compressed powder mixture during heating from room temperature to 900 °C (heating rate of 60 °C min⁻¹)
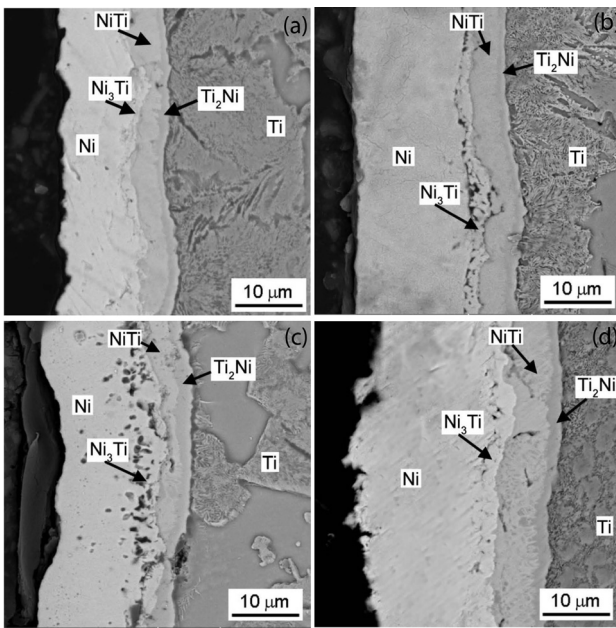
Figure 3: Microstructure of Ni-Ti model samples annealed at 800 °C for: a) 30 min, b) 60 min, c) 120 min and d) 180 min

annealed at 800 °C and 900 °C and the thickness of formed layers of intermetallics was measured to describe the difference between in the mechanism and kinetics of the Ni+Ti reactions below and above the $\alpha \rightarrow \beta$ transformation temperature in titanium. During annealing at 800 °C, the layers of Ti_2Ni, NiTi and Ni_3Ti are formed between the titanium and nickel coating (**Figure 3a** to **3d**). The presence of these phases was confirmed by the XRD (**Figure 4**) and local EDS analysis (**Table 1**). While the XRD analysis revealed all present layers on the sample, the EDS analysis was used to identify the sequence of the layers between the reacting titanium and nickel. The dependences of the thickness of the Ti_2Ni

and NiTi layers on the process duration exhibit the parabolic shape (**Figure 5**). The calculated parabolic rate constants for all the samples indicate that the growth of these layers slightly slows down with the process duration (**Table 2**). The layer of Ni_3Ti (hexagonal $P6_3/mmc$)[21] phase starts to grow after 60 min of annealing and then it follows the parabolic law. The formation of the Ni_3Ti phase is probably the reason why the growth of the NiTi and Ti_2Ni layers decelerates during longer annealing. As the Ni_3Ti phase grows, NiTi and/or Ti_2Ni are consumed, as well as nickel. The results confirm that during the diffusion stage, the process starts with the formation of Ti_2Ni and NiTi layers, followed by Ni_3Ti after longer annealing duration. Almost the same shape of the kinetic curves was also observed during annealing at 650 °C in our previous paper, where the formation of Ni-Ti intermetallics was studied during long-term annealing at 500-650 °C.[16]

Table 1: Chemical composition (EDS) of layers observed after annealing of model samples at 800 °C for 120 min

Phase	Content (in amount fractions, (a/%))	
	Ti	Ni
Ni	4.0±0.2	96.0±0.2
Ti_2Ni	65.7±0.6	34.3±0.6
NiTi	51.4±0.4	48.6±0.4
Ni_3Ti	27.9±1.8	72.1±1.8
Ti	98.4±0.2	1.6±0.2

Annealing at 900 °C leads to the layers of Ti_2Ni and NiTi (**Table 3, Figure 4**), which grow slightly more rapidly up to 60 min (**Figure 6a**) than at 800 °C (**Figure 5**). However, the thickness of the NiTi phase layer is very non-uniform. After 60 min, the thick layer of Ni_3Ti (hexagonal $P6_3/mmc$) phase arises in the structure. The
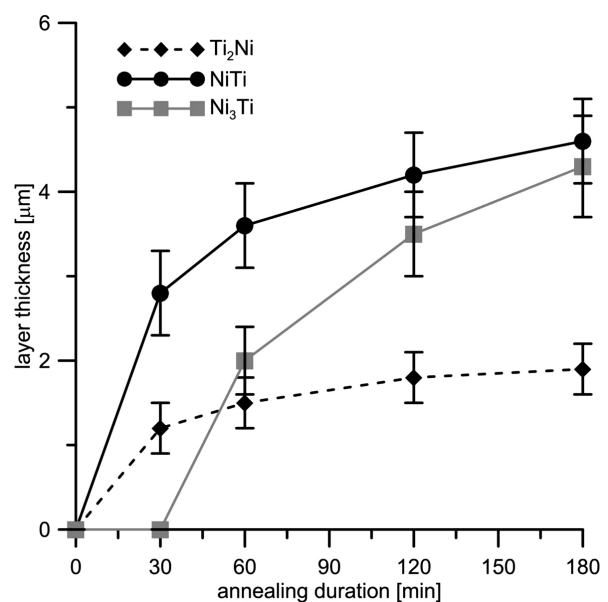
Figure 5: NiTi, Ti_2Ni and Ni_3Ti layer thickness on model samples vs. duration of annealing at 800 °C

Figure 4: XRD patterns of model samples annealed at 800 °C and 900 °C

Table 2: Parabolic rate constant of the formation of Ti_2Ni, NiTi and Ni_3Ti layer vs. annealing duration at 800 °C

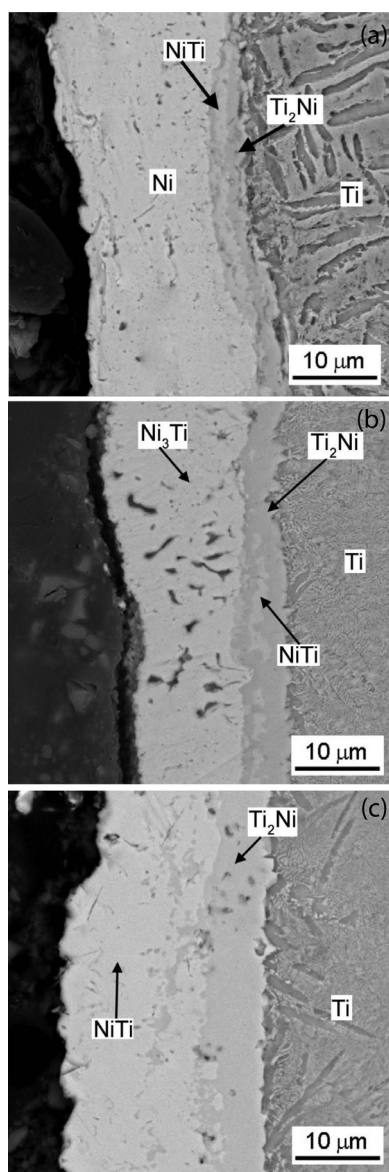| Annealing duration (min)	Parabolic rate constant of the growth of layers (×10⁻⁴ μm s⁻¹)		
	Ti_2Ni	NiTi	Ni_3Ti
30	8.0	43.6	0
60	6.3	36.0	11.1
120	4.5	24.5	17.0
180	3.3	19.6	17.1

Table 3: Chemical composition (EDS) of layers observed after annealing of model samples at 900 °C for 120 min

Phase	Content (in amount fractions, (a/%))	
	Ti	Ni
Ti_2Ni	66.8±0.5	33.2±0.5
NiTi	53.2±0.9	46.8±0.9
Ti	97.8±0.3	2.2±0.3

Figure 6: Microstructure of Ni-Ti model samples annealed at 900 °C for: a) 30 min, b) 60 min and c) 120 min

Ni_3Ti layer consumes almost the whole residual thickness of the nickel coating (**Figure 6b**). The Ni_3Ti layer is very porous, which confirms the previous results, where the Ni_3Ti phase was found to be a source of porosity.[16] When continuing the annealing, the Ni_3Ti phase disappears completely, since it reacts with Ti_2Ni in order to form a thick layer of NiTi phase (**Figure 6c**). The experiment was stopped after 120 min, because the whole layer was composed of NiTi and Ti_2Ni phases (**Figures 6c** and **7**). Calculated parabolic rate constants (**Table 4**) show that the formation of NiTi (austenite) and Ni_3Ti is not diffusion-controlled at 900 °C, because the constants vary strongly with the process duration. It confirms that the process runs in SHS mode.

Table 4: Parabolic rate constant of the formation of Ti_2Ni, NiTi and Ni_3Ti layer vs. annealing duration at 900 °C

Annealing duration (min)	Parabolic rate constant of the growth of layers (×10⁻⁴ μm s⁻¹)		
	Ti_2Ni	NiTi	Ni_3Ti
30	16.1	46.7	0
60	87.1	40.1	267.0
120	50.0	325.0	0

To prove the results of the experimental model, the real compressed powder mixtures were prepared and heated at 800 °C and 900 °C with a holding time of 120 min. The same heating rate as in the experimental model (approx. 300 °C/min) was applied. The sample prepared by heating at 800 °C is composed of unreacted nickel and titanium particles covered by layers of Ti_2Ni, NiTi and Ti_3Ti of very similar thickness like in the model system (**Figure 8a**). On the other hand, the sample reactively sintered at 900 °C is comprised of Ti_2Ni particles in a NiTi matrix. The morphology of the sample changed from cylindrical shape to irregular shape due to partial melting during the process (**Figure 9**). This indicates that
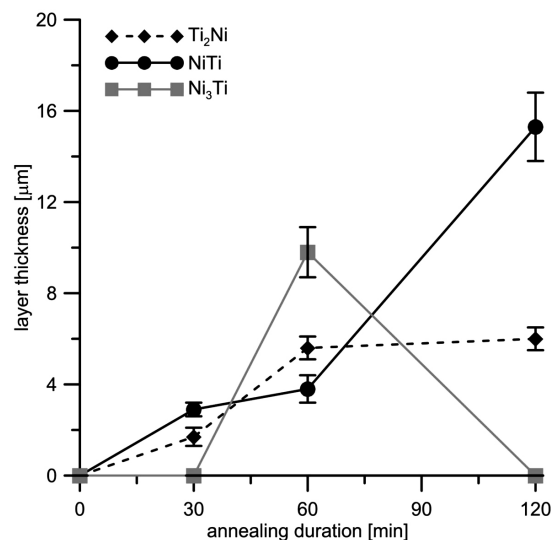
Figure 7: NiTi, Ti_2Ni and Ni_3Ti layer thickness on model samples vs. duration of annealing at 900 °C
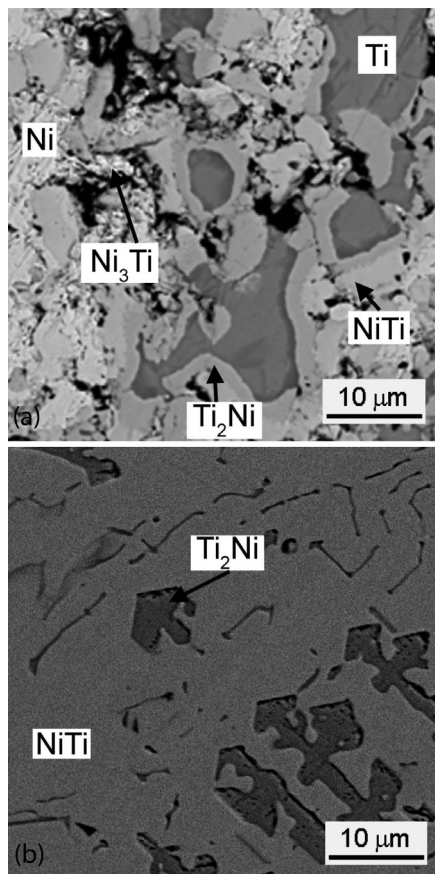
Figure 8: Microstructure of NiTi46 (in mass fractions, (*w*/%)) compressed powder mixtures reactively sintered at: a) 800 °C for 120 min and b) 900 °C for 120 min

during annealing of the powder mixture at 900 °C, enormous heat is evolved due to the SHS reaction.

The above-presented results show that the SHS reaction can be initiated immediately after exceeding the $\alpha \rightarrow \beta$ transformation temperature of titanium. It means that it is not necessary to achieve the melt formation by a eutectic reaction at 942 °C. In addition, the rapid SHS process is supported significantly when a high heating

rate is applied.[17] During rapid heating, the diffusion is strongly suppressed. Therefore, the SHS can be initiated by the reaction of solid particles of nickel and titanium, having a cubic structure, producing a mixture of cubic Ti₂Ni and NiTi phases at the end of the process.

4 CONCLUSIONS

In this work the mechanism and kinetics for the formation of Ni-Ti phases at 800 °C and 900 °C were studied. The results revealed that the rapid SHS reaction is initiated in the solid state by the $\alpha \rightarrow \beta$ phase transformation of titanium. Below this temperature, the growth of Ni-Ti intermetallics is controlled by diffusion of the reactants. Above this temperature, the rapid SHS reaction is initiated. It was proved with an experimental model, where a significant change in the rate constant of the formation of Ni-Ti intermetallics was observed at 900 °C, compared with 800 °C. It was confirmed by the change of the slope of the heating curve in thermal analysis, as well as by the in-situ XRD analysis, where a rapid increase of the intensity of the diffraction lines of Ni-Ti intermetallics was observed after exceeding approximately 880 °C. The SHS process starts with the formation of Ni_3Ti phase, which reacts with Ti_2Ni already present from diffusion stage and forms the NiTi shape-memory phase. The temporary formation of Ni_3Ti phase results in an increase of the materials' porosity.

Acknowledgement

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Figure 9: Morphology of NiTi46 (in mass fractions, (*w*/%)) compressed powder mixture reactively sintered 900 °C for 120 min

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