

## Characterization of a NiTiCu shape memory alloy produced by powder technology

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### Materials

#### ABSTRACT

**Purpose:** The main aim of presented work was to find a sintering conditions (temperature and time) for manufacturing of a Ni(1-X)Ti<sub>50</sub>CuX alloy (where X = 2; 3; 5; 10; 15; 20 and 25at%) by powder technology.

**Design/methodology/approach:** Various conditions of sintering considering temperature and time were applied to compacted powders. Sintering temperature varied from 850°C to 1100°C and sintering time was chosen from a range of 5 to 50 hours, respectively. Microstructure, structure, chemical composition and thermal behavior of sintered blends were studied by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction.

**Findings:** Homogenous alloys, containing lower addition of copper (less than 10 at%), were sintered at 940°C for 7 hours. For higher copper content (10-25at%) lower sintering temperature 850°C but longer sintering time was preferred (20 hours). The quality of the alloy was characterized by porosity and density. In sintered blends non-transformable phases Ti<sub>2</sub>(Ni,Cu) and (Ni,Cu)<sub>3</sub>Ti, which possess the crystal structure of Ti<sub>2</sub>Ni and Cu<sub>3</sub>Ti respectively, were found. Despite the fact that same sintering conditions lead to an increase of inhomogeneity all sintered alloys reveal the presence of the reversible martensitic transformation.

**Practical implications:** Obtained results allowed to optimize sintering condition for NiTiCu shape memory alloy manufacturing.

**Originality/value:** A NiTiCu shape memory alloy, with various content of copper, was successfully produced by powder metallurgy.

**Keywords:** Smart materials; Shape memory alloy; Powder metallurgy; Nickel titanium copper alloy

### 1. Introduction

NiTiCu alloys obtained by replacing a part of Ni atoms by Cu in the equiatomic NiTi alloy have attracted wide interest because of a variety of advantages in practical use. Copper addition, as a ternary alloying element, results in increasing the characteristic temperatures of the martensitic transformation, when compared to a binary NiTi alloy. Moreover, copper causes good stability of characteristic temperatures and good corrosion resistance, narrow transformation hysteresis and prevention of Ti<sub>3</sub>Ni<sub>4</sub> precipitation

[1-2]. Composition sensitivity of martensitic start temperature ( $M_s$ ) is also significantly reduced by Cu addition. Unfortunately, Cu addition, which exceeds 10 at%, spoils the alloy formability. This was the reason for application of a non-melting technology. Recently, intensive effort has been put to adopt the non-conventional production techniques such as powder metallurgy (PM), melt-spinning (MS) or twin roll casting (TRC) for manufacturing the NiTi-based alloys [3-5]. The main advantage of the powder metallurgy is avoiding typical thermomechanical treatment needed after conventional casting. However, powder metallurgy produces pores, which diminishes mechanical properties.

The main purpose of the study was to find a compromise between time and temperature of sintering process to get the homogenous alloy, which shows a reversible martensitic transformation.

## 2. Experimental procedure

### 2.1. Experimental method

The chemical composition was determined using energy-dispersive X-ray analysis (EDX) in a JEOL SM6480 microscope. In order to study thermal behavior of the martensitic transformation modulated differential scanning calorimeter (MDSC) – TA Instrument 2000 was used. Parameters of the forward and reverse martensitic transformation such as: enthalpy of transformation, start ( $M_s$ ,  $A_s$ ) and finish ( $M_f$ ,  $A_f$ ) as well as maximum and minimum of the thermal peak were calculated using TA software.

Melting point of the compacted powder and temperature of allotropic transformation were determined using high temperature differential calorimeter (HTDSC) – TA Netzsch.

### 2.2. Compact and alloy production

Ni, Ti and Cu powder, with commercial purity (99.7%), was used as a starting material for producing NiTiCu shape memory alloys. Powders were weighted in proper proportions (Table 1) and mixed in a rotating mixer for 5, 24 and 48 hours.

Table 1

Nominal chemical composition and melting temperature ( $T_M$ )				
Symbol	Ti at%	Ni at%	Cu at%	$T_M$ [°C]
S1	50	48	2	1321
S2	50	47	3	1243
S3	50	45	5	1237
S4	50	40	10	1247
S5	50	35	15	1225
S6	50	30	20	1170
S7	50	25	25	1264

Compacts were prepared, at room temperature, in a form of cylinders with two diameters (10 mm and 7 mm) and 6 mm in height under a pressure of 800 MPa. Zinc oxide was used for matrix lubrication. Sintering was performed under flowing dry argon in a pre-evacuated horizontal tube furnace.

In respect to the allotropic transformation of titanium, which appeared at about 897°C, diffusion properties and melting temperature  $T_M$  (Table 1), the sintering temperature  $T_S$  was varied from 850°C to 1100°C. Consequently, heating of the powder mixture was done in two steps: first heating up to 600°C at 10°C/min and continued from 600°C up to  $T_S$  at 2°C/min. Also, total sintering time varied from 5 to 50 hours. The specimens were furnace cooled.

## 3. Results and discussion

### 3.1. Porosity and density

Despite the applied sintering technology, pores are inevitable components of the microstructure. They are classified as open or closed ones. Their diameter mainly depends on particle size and compacting/sintering condition.

The density of compacts was calculated from the ratio of volume ( $V$ ) and mass ( $m$ ). Figure 1 shows changes of the density versus chemical composition and applied sintering conditions. The density of copper (8.95 g/cm<sup>3</sup>) slightly differs from nickel (8.90 g/cm<sup>3</sup>). It results in a small increase of the theoretical density of NiTiCu alloy, when copper content is increased from 2 to 25 at%.

Also, green density increases with copper content increase. However, pores, which were introduced during compacting causes that the green density is about 15% lower when compare to the theoretical value. Sintering, independently of temperature and time, results in a decrease of the density with increasing copper content. The highest value of the density can be seen for sintering at 850°C for 10 hours and 940°C for 7 hours. Sintering at 850°C for 5 hours and 1100°C for 7 hours causes significant decrease of the density for every studied composition. Decrease of the density is closely related to increase of the porosity. The total porosity ( $P_T$ ) was calculated as an empty volume from the density as follows:

$$P_T = \left( \frac{1 - \rho}{\rho_T} \right) \cdot 100\% \quad (1)$$

where:  $\rho$  is the measured density and  $\rho_T$  - theoretical density for the studied alloys.

Figure 2 presents changes of the total porosity versus sintering condition. The porosity varies from 13 to 16% for green compacts. Consequently to the changes of the density, the porosity after sintering remains the lowest for the alloys with lower content of copper. Increase of the copper content and sintering temperature cause an increase of the porosity. This can be explained as follows. The diffusion of copper atoms in titanium is several times higher than diffusion of nickel atoms in titanium. Also, the diffusion ratio of copper and nickel atoms in titanium is higher than titanium in copper or nickel. As a consequence, titanium particles create a base for an alloy, where first copper atoms diffuse-in and second – nickel. In this manner, the volume of the pores increases. Using this mechanism, pores with smaller size can be created at the border between titanium particles and copper/nickel. Increase of the sintering temperature intensifies the diffusion while the average size of the pore also increases.

Open porosity was characterized by a ratio between volume of open pores ( $P_O$ ) to the volume of total pores from a formula:

$$\chi = \left( \frac{P_O}{P_T} \right) \cdot 100\% \quad (2)$$

Volume of open pores was determined from the SEM images, taken on transverse and longitudinal cross-sections of the cylindrical compacts, as an average volume of pores distributed on intersection with outer surface of the cylinder. Calculated values show that independently of chemical composition about 78 – 89% volume of pores is concentrated at the surface of the cylinder, whereas the rest of them are randomly distributed inside the blends.

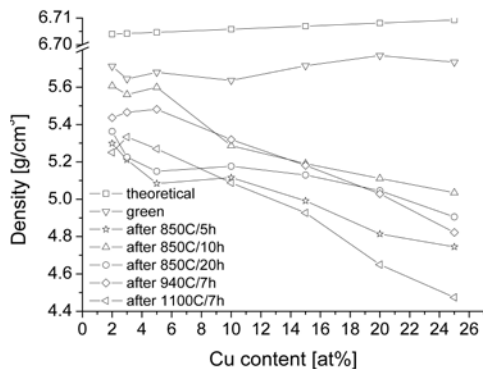


Fig. 1. Changes of the density versus chemical composition and sintering conditions

### 3.2. Homogeneity and martensitic transformation

Generally, in equiatomic NiTi alloy parent phase B2 usually transforms to a monoclinic B19' structure. Exception is two-step transformation, where additional R-phase appears and the sequence of transformation changes to:  $B2 \leftrightarrow R \leftrightarrow B19'$ . Thermal hysteresis of the transformation  $B2 \leftrightarrow B19'$  is relatively broad with its width between 30 and 60 degrees, whereas for  $B2 \leftrightarrow R$  never exceeds 10 degrees.

Addition of Cu up to 7at% does not change the sequence of the martensitic transformation and, similar to Ni-Ti alloy, the parent phase transforms to monoclinic martensite B19'. However, when the copper content increases from 7at.% to 15at%, the transformation occurs in two steps:  $B2 \leftrightarrow B19 \leftrightarrow B19'$ . Moreover, exceeding copper content over 15at% the martensitic transformation again proceeds in one step but the final product of the transformation is orthorhombic martensite B19. In case of  $B2 \leftrightarrow B19$ , the thermal hysteresis of the martensitic transformation becomes narrow and its value does not exceed 15 degrees. Also the homogeneity of the alloys has a significant influence onto thermal range of the martensitic transformation.

Two alloys, which differ in copper content: S2- 3at.% Cu and S6 – 20at.% Cu, are discussed here. Measurements of chemical composition were done in macro scale, where 50 points were taken for calculation. The chemical composition was calculated as an average value.

Figure 3 shows the DSC cooling/heating curves registered for alloys: S2 (3at% of Cu) and S6 (20at.% of Cu) after sintering in conditions, which resulted in a homogenous and – a completely inhomogeneous alloy respectively. For alloy S2, sintered at 940°C

for 7 hours, DSC curves reveal only one thermal peak on cooling and heating at 65,9 and 90,2, respectively. The range of the martensitic transformation ( $A_f - M_f$ ) equals 55,5 degrees and thermal hysteresis ( $A_f - M_s$ ) is about 33 degrees. Such a relatively wide hysteresis suggests that the parent phase transforms directly to the martensite B19'.

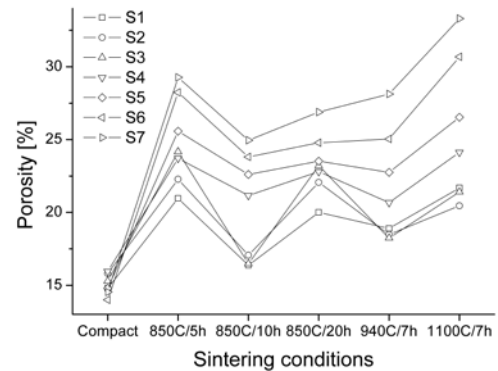
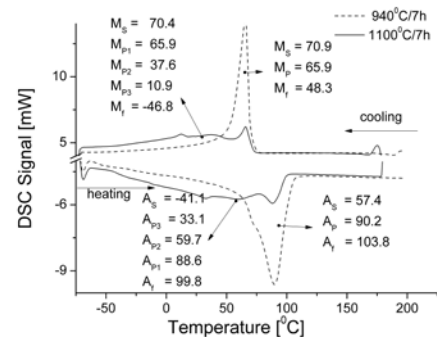


Fig. 2. Changes of the porosity versus sintering condition

A completely different thermal behavior is measured for the same chemical composition but sintered at 1100°C for 7 hours. First, it can be observed that thermal peaks during cooling and heating moved towards lower temperatures.

a)



b)

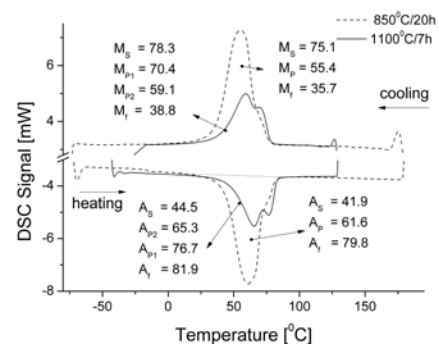


Fig. 3. Comparison of DSC cooling/heating curves registered for sample sintered in various conditions: S2 (a) and S6 (b)

Second, instead of one peak, three peaks were found on cooling as well as on heating. The range of the martensitic transformation increased to 150 degrees whereas width of the thermal hysteresis almost did not change (29,4 deg). However, higher sintering temperature produces a non-transformable phase rich in titanium  $Ti_2(Ni,Cu)$ , which has the same type of the crystal structure as the  $Ti_2Ni$  phase. It significantly decreases its content in the parent phase. In consequence, transformation temperatures moved to lower -temperatures. This was proven by measurement of the chemical composition (Fig. 4a). Figure 4 shows the distribution of the elements along the applied sintering conditions for the sample S2. In order to analyze the homogeneity or inhomogeneity, a standard deviation was marked as a vertical bar. It has been clearly seen that a distribution of alloying elements, close to the nominal composition, was obtained in samples sintered at  $940^{\circ}C$  for 7 hours and  $850^{\circ}C$  for 20 hours. However, the sintering condition:  $850^{\circ}C/20h$  causes a small increase of inhomogeneity, which is characterized by a higher values of the standard deviation. Also the value of the standard deviation calculated for sintering conditions:  $850^{\circ}C/50h$  and  $1100^{\circ}C/7h$ , significantly increases to 8% for Ni and Ti as well as for Cu up to 2%. High inhomogeneity of the samples, which containing low copper content, eliminates them as a shape memory material.

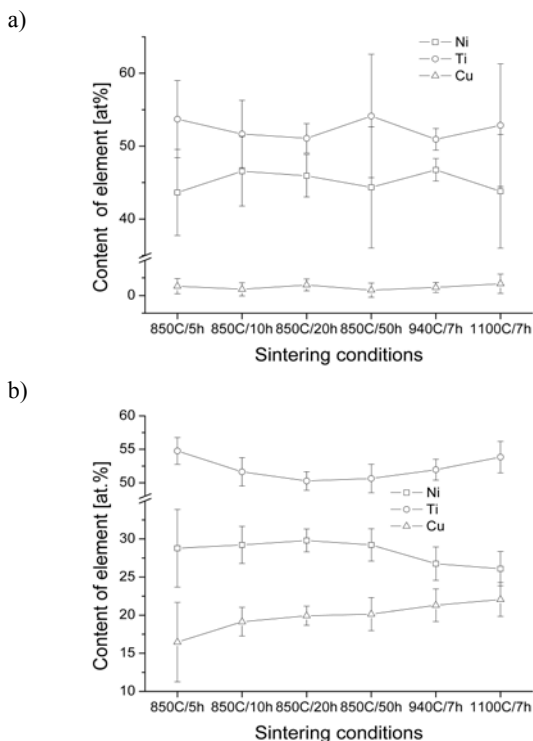


Fig. 4. Dependence of chemical composition distribution on sintering conditions for sample: S2 (a) and S6 (b)

Figure 3b compares DSC curves measured for sample S6, with copper content of 20at.%, sintered at  $850^{\circ}C$  for 20 hours and at  $1100^{\circ}C$  for 7 hours. Sintering at lower temperature, during prolonged time, results into one transformation peak on the cooling and heating curve. Thermal hysteresis of the martensitic

transformation is relatively narrow with its width of 5 degrees. It suggests that the parent phase reversibly transforms to the orthorhombic martensite B19. Similarly to that, sintering at  $1100^{\circ}C$  for 7 hours gives comparable width of the thermal hysteresis (4 deg). However, due to the inhomogeneity, high-temperature sintering leads to splitting of the thermal peak into two. Contrary to alloys with low-content of Cu, a non-transformable phase  $(Cu,Ni)_3Ti$ , which shows the same type of a crystal structure as the  $Cu_3Ti$  phase occurs. This phase causes local change of the chemical composition. The Ni and Cu content decreases in the B2 parent phase. As a consequence the characteristic temperatures of the martensitic transformation increase. The distribution of the elements can be seen in Figure 4b. The chemical composition for the sample S6, close to its nominal value, was obtained after sintering at  $850^{\circ}C$  for 20 and 50 hours. Shorter sintering time produces more homogenous material as well as less pores (25%). Prolongation of the sintering temperature to  $940^{\circ}C$  or  $1100^{\circ}C$  breaks up the homogeneity and a significant deviation from the nominal chemical composition was observed.

## 4. Conclusions

The porous Ni-Ti-Cu shape memory alloys have been successfully manufactured by powder technology. However, only a correct combination of sintering temperature and time leads to a homogeneous alloy. The results can be summarized as follows:

- For the alloy with low-content of copper (<5at.%) and constant titanium content (50at.%) a temperature of  $940^{\circ}C$  and a relatively short sintering time (7 hours) gives a homogenous regularly transformed material.
- The best sintering condition for NiTiCu alloy with high content (>10at.%) demands a lower sintering temperature of  $850^{\circ}C$  while extending the sintering time to 20 hours.
- The porosity in homogenous samples does not exceed 25%.
- The porous NiTiCu shape memory alloys reveal a similar reversible martensitic transformation when compared to dense material.

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