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NiTiCu shape memory alloy produced by powder technology

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Abstract

The main aim of presented work was to find the sintering conditions (temperature and time) for manufacturing of a $Ni_{(50-X)}Ti_{50}Cu_X$ alloy (where $X = 2$, 3, 5, 10, 15, 20 and 25 at%) by powder technology. Various conditions of sintering considering temperature and time were applied to compacted powders. Sintering temperature varied from 850 to 1100 °C and sintering time was chosen from a range of 5–50 h, 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. Homogenous alloys, containing lower addition of copper (less than 10 at%), were sintered at 940 °C for 7 h. For higher copper content (10–25 at%) lower sintering temperature 850 °C but longer sintering time was preferred (20 h). The quality of the alloy was characterized by porosity and density. In sintered blends non-transformable phases $Ti_2(Ni,Cu)$ and $(Ni,Cu)_3Ti$, which posses the crystal structure of Ti_2Ni and Cu_3Ti, 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. Obtained results allowed to optimize sintering condition for NiTiCu shape memory alloy manufacturing.

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_3Ni_4 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 [3–16]. The main advantage of the powder metallurgy is avoiding typical thermomechanical treatment needed after conventional casting. However, powder metallurgy produces pore, 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 Coulter Laser Scattering Particles Size Analyzer (CLSPSA) was applied to characterize the average diameter of initial and mixed powders. The microstructure of powders and sintered alloys was observed with a scanning electron microscope Jeol SEM 6480.

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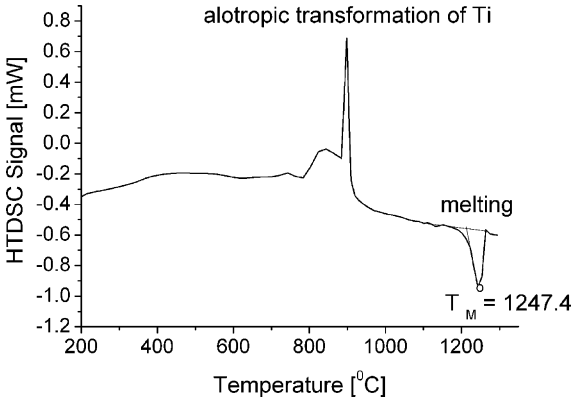

Fig. 1. HTDSC heating curve registered for sample S4.

In order to study thermal behavior of the martensitic transformation modulated differential scanning calorimeter (MDSC) – TA Instrument 2000 was used. Samples weighted 50–80 mg, were heated up to 200 °C and then cooled to −60 °C with cooling/heating rate of 10 °C/min. 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. Transformation temperatures were determined from thermal peaks using a slope line extension method.

Melting point of the compacted powder and temperature of allotropic transformation were determined using high-temperature differential calorimeter (HTDSC) – TA Netzsch. Samples were heated in two stages: from room temperature to 800 °C at 20 °C/min and then up to 1400 °C at 10 °C/min. An example of the HTDSC measurement is shown in Fig. 1.

The phase identification and structural parameters were established using the X-ray diffraction patterns obtained on the INEL diffractometer, equipped with curved position sensitive detector CPS120, Ge flat monochromator and a temperature attachment. The temperature device allows to register X-ray diffraction patterns from −100 to +120 °C [17]. Structure of the compacted powders and sintered alloys were studied using X-ray diffractometer Philips PW 1140 at room temperature with copper radiation ($\lambda_{K\alpha1}$ = 1.54056 Å and $\lambda_{K\alpha2}$ = 1.54435 Å).

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 h.

Compacts were prepared, at room temperature, in a form of cylinders with two diameters (10 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 885 °C, diffusion properties and melting temperature T_M (Table 1), the sintering temperature T_S was varied from 850 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 (Fig. 2). Also, total sintering time varied from 5 to 50 h. The specimens were furnace cooled.

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

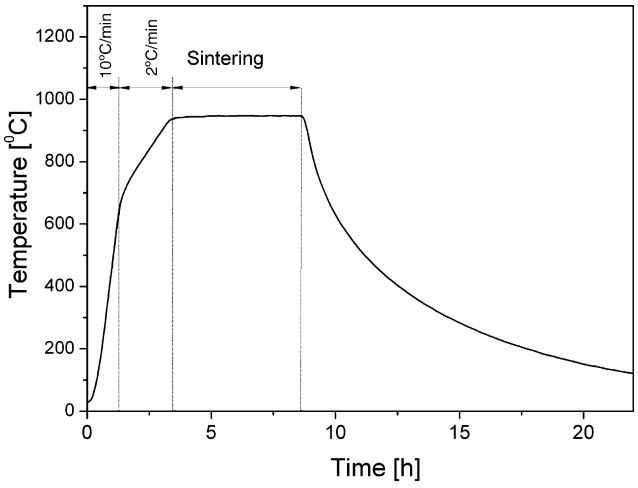

Fig. 2. An example of a plot of a temperature control during sintering.

3. Results and discussion

3.1. Powders characterization

The average particle size, determined from CLSPSA, for elemental Ni and Ti was 13 and 63 μm, respectively, and 105 μm for Cu. Fig. 3a shows the regular ball-shaped particles of elemental

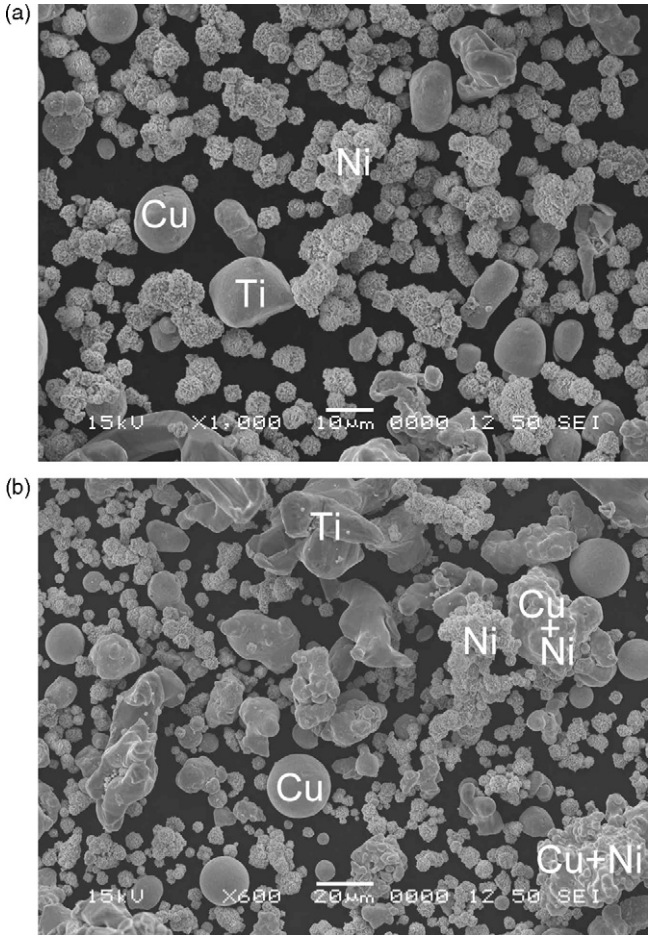

Fig. 3. SEM micrographs of powders mixture (sample S5) mixed: 5 h (a) and 48 h (b).