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EFFECT OF ELECTRIC CURRENT ON THE PRODUCTION OF NiTi INTERMETALLICS VIA ELECTRIC-CURRENT-ACTIVATED SINTERING

VPLIV ELEKTRIČNEGA TOKA PRI IZDELAVI INTERMETALNE ZLITINE NiTi S SINTRANJEM, AKTIVIRANIM Z ELEKTRIČNIM TOKOM

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This study focuses on investigating the fabrication of in-situ intermetallic NiTi composites from a powder mixture containing the mass fractions 50 % nickel powder and 50 % titanium powder. The elemental powders were mixed in the stoichiometric ratio corresponding to the NiTi intermetallic molar proportion of 1 : 1, ball-milled and uniaxially compressed under a pressure of 170 MPa. Sintering was then carried out for 15 min in a steel mold using the electric-current-activated sintering method. Electric-current values of 1000 A, 1300 A and 2000 A were used for the sintering while keeping the voltage in the range of 0.9 V to 1.2 V. The phases in the samples were analyzed with XRD and their Vickers hardness was measured as (701 ± 166) $HV_{0.05}$. Energy dispersive X-ray spectroscopy carried out with a scanning electron microscope (SEM-EDS) showed that the microstructures of the samples consist of different phases such as Ti, Ni_2Ti_3, $NiTi_2$, Ni_3Ti and TiO_2 as a function of electric current. The XRD analysis also supported the SEM-EDS results. The nano-indentation technique was used to determine the elastic modulus of different phases.

Keywords: NiTi intermetallics, electric-current-activated sintering (ECAS), nano-indentation

Ta študija je usmerjena v preiskavo in situ izdelave intermetalnega NiTi-kompozita iz mešanice prahov z masnima deležema 50 % niklja v prahu in 50 % titana v prahu. Obe vrsti prahu sta bili zmešani v stehiometričnem razmerju, ki ustreza molskemu razmerju NiTi 1 : 1, zmleti v kroglastem mlinu in enoosno stisnjeni pri tlaku 170 MPa. Petnajstminutno sintranje je bilo izvršeno v jeklenem kalupu s sintranjem, aktiviranim z električnim tokom. Pri sintranju so bili uporabljeni električni tokovi 1000 A, 1300 A in 2000 A, medtem ko je bila napetost v območju med 0,9 V in 1,2 V. Faze v vzorcih so bile določene z rentgenom (XRD) in izmerjena je bila trdota po Vickersu (701 ± 166) $HV_{0,05}$. Energijska disperzijska rentgenska spektroskopija (EDS), izvršena na vrstičnem elektronskem mikroskopu (SEM-EDS), je pokazala, da je mikrostruktura vzorcev sestavljena iz različnih faz, kot so Ti, Ni_2Ti_3, $NiTi_2$, Ni_3Ti in TiO_2, odvisno od električnega toka. XRD-analiza je podprla rezultate, dobljene s SEM-EDS. Elastični modul različnih faz je bil določen z nanovtiski.

Ključne besede: intermetalna zlitina NiTi, sintranje, aktivirano z električnim tokom (ECAS), nanovtiski

1 INTRODUCTION

To meet the increasing demand of the aerospace and automobile industries for lightweight structural materials suitable for high-temperature applications, researchers focus on lightweight and high-strength intermetallics.[1] Intermetallic compounds are promising materials for structural and non-structural high-temperature applications (heat resistance, corrosion resistance, electronic devices, magnets, super conductors).[2,3] Especially NiTi alloys are some of the most technologically important shape-memory alloys[4,5] which find extensive applications in the mechanical, medical, electronic, chemical and aerospace industries due to their excellent shape-memory effect, high erosion resistance, high damping capacity and biocompatibility. These properties make them suitable candidates for various engineering applications.[2–7] Nickel titanium is a near-equiatomic intermetallic exhibiting distinctive and desirable thermo-mechanical properties, namely, the thermal shape-memory effect and super elasticity.[8] Up to now, a number of processes including self-propagating high-temperature synthesis (SHS), thermal explosion, laser-melting deposition, casting and mechanical alloying techniques[2,5,9,10] have been used for manufacturing ıntermetallics. In the electric-current-activated/assisted sintering (ECAS) technique, a cold-formed compact obtained with uniaxial compression is inserted into a container heated by the passing electrical current. A sintering pressure of 50 MPa is applied and maintained throughout the sintering.[11] The present study aimed to determine the effect of the current on the production of a NiTi intermetallic from the Ni and Ti elemental powders.

2 EXPERIMENTAL PROCEDURE

2.1 Materials and methods

Powder materials from titanium (99.5 % purity, 35–44 μm) and nickel (99.8 % purity, 3–7 μm) were used as the starting materials to manufacture a NiTi intermetallic compound. The Ni and Ti powders were mixed in the stoichiometric ratio corresponding to the Ni-Ti phase diagram (**Figure 1**), in a molar proportion of 1 : 1.

The powder mixture was cold-pressed before the sintering to form a cylindrical compact in a metallic die under a uniaxial pressure of 170 MPa. Dimensions of a compact were 15 mm in diameter and 5 mm in thickness. The production of the NiTi intermetallic compounds was performed with the electric-current-activated sintering technique in an open atmosphere at 1000–2000 A for 15 min as shown in **Figure 2**. The process parameters are listed in **Table 1**.

Table 1: Process parameters for the samples
Tabela 1: Procesni parametri pri vzorcih

Sample code	*x*/%	Current (A)	Voltage (V)
NT1	50Ti-50Ni	1.000	0.9–1.2
NT2	50Ti-50Ni	1.300	0.9–1.2
NT3	50Ti-50Ni	2.000	0.9–1.2

After the sintering, the specimens were unloaded and air-cooled to room temperature. After metallographic preparations, the resulting microstructures and phase constitutions were characterized.

2.2 Characterization

The morphologies of the samples were examined with scanning electron microscopy (SEM-EDS) in terms of the resulting phases. An X-ray diffraction (XRD) analysis was carried out using Cu-K_α radiation with a wavelength of 0.15418 nm over a 2θ range of 10–80 °. The micro-hardness of the investigated samples was

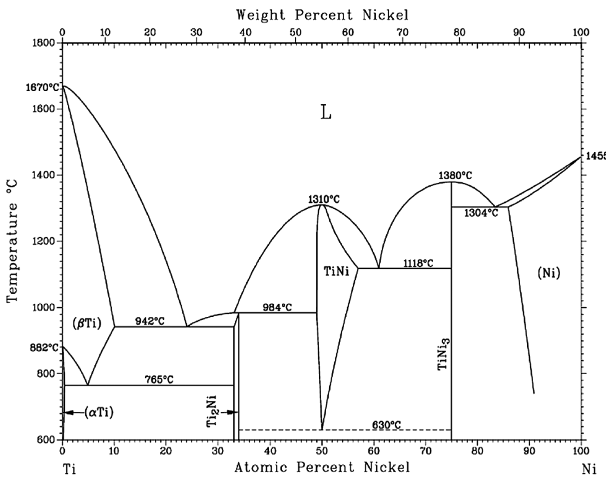

Figure 1: Ni-Ti phase diagram[3]
Slika 1: Fazni diagram Ni-Ti [3]

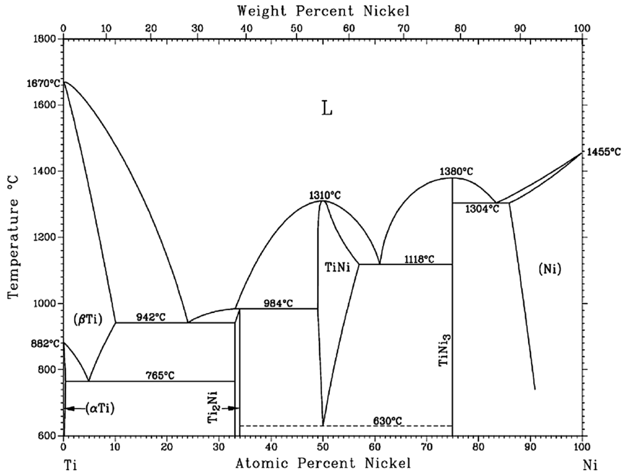

Figure 2: Schematic of electric-current-assisted sintering (ECAS) process
Slika 2: Shematski prikaz sintranja z električnim tokom (ECAS)

measured employing the Vickers-indentation technique with a load of 50 g using a Struers Duramin hardness instrument. For determining the elastic modulus of the samples, nano-indentation device DUH-211S by Shimadzu was used at a load of 98 mN and a dwell time of 10 s. The ImageJ programme was also used to determine the porosity of fractions of the samples.

3 RESULTS AND DISCUSSION

3.1 SEM-EDS analysis

The morphologies of the as-received Ni and Ti powders are shown in **Figure 3**. The metallic Ni-powder

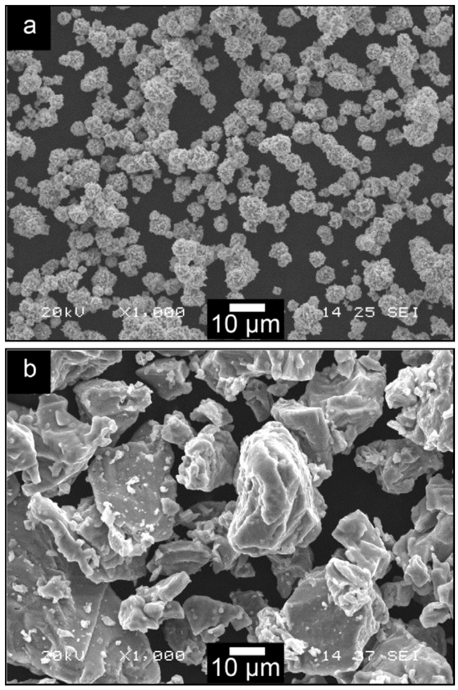

Figure 3: SEM micrographs of: a) Ni powder, b) Ti powder
Slika 3: SEM-posnetka prahov: a) Ni, b) Ti

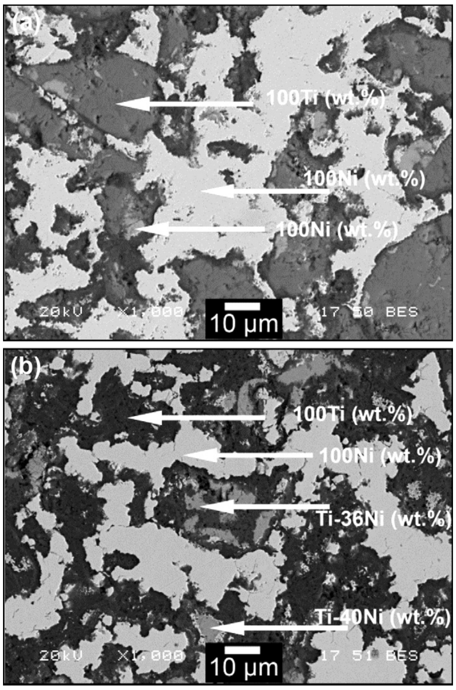

Figure 4: SEM-EDS analyses of: a) NT1, b) NT2 composites
Slika 4: SEM-EDS-analizi kompozitov: a) NT1, b) NT2

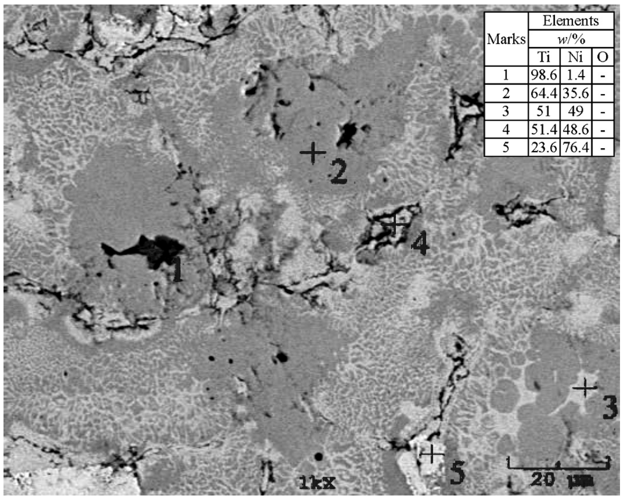

Figure 6: SEM-EDS analyses of NT3 composite
Slika 6: SEM-EDS-analize kompozita NT3

particles were generally spherical with a diameter of 4–7 µm. The Ti-powder particles had sharp corners and were less than 40 µm in size.

SEM-EDS analyses of the NT1 and NT2 intermetallic compounds are shown in **Figure 4**. The microstructure in **Figure 4a** shows that a low current intensity results in separately formed Ni and Ti areas. When increasing the values of the current for NT2 (**Figure 4b**), new phases like $NiTi_2$ (**Figure 1**) start to form, but these microstructures are still far from the stoichiometric composition of the main NiTi phase.

When increasing the current to 2000 A for the NT3 sample (**Figure 5**), the main phases in the microstructure such as NiTi, $NiTi_2$, Ni_3Ti are evident. Besides, there are also a small amount of the residual Ti phase and a small oxidation problem due to the open atmosphere. It can be inferred that a high current intensity leads to a high amount of intermetallic phases. According to the ImageJ image-analysis programme, a porosity of 0.2 % can be found in the microstructures.

As can be seen from the SEM and EDS analyses presented in **Figure 6**, the reaction of the NiTi-compound synthesis was not completed. It is assumed that the applied voltage was insufficient for a complete transformation of the NiTi phases during the sintering.

3.2 XRD analysis

The XRD analysis (**Figure 7**) shows that the main phase of the composite is $NiTi_2$. The NiTi phase is also seen as a small peak. Additionally, Ni_3Ti, Ti and TiO are the other phases existing in the NT3 composite. These results support the observations from the SEM-EDS analysis.

3.3 Hardness and the elastic modulus

The measured $HV_{0.05}$ hardness values for the NT1, NT2 and NT3 samples are (250 ± 27), (405 ± 71) and

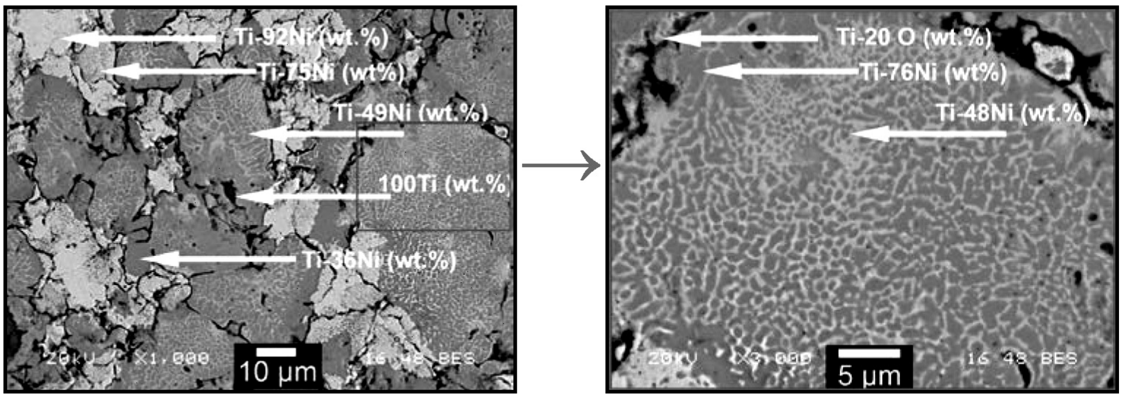

Figure 5: SEM-EDS analyses of NT3 composite
Slika 5: SEM-EDS-analizi kompozita NT3

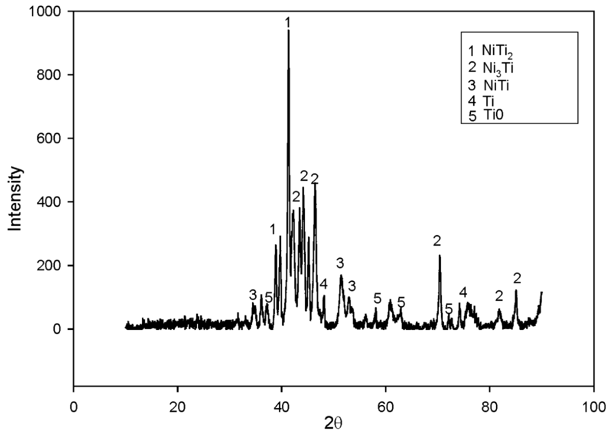

Figure 7: XRD analysis of NT3 sample
Slika 7: Rentgenogram vzorca NT3

(701.6 ± 166), respectively. The hardness values are in good agreement with the literature.[1,12] The elastic-modulus values for the NT1, NT2 and NT3 samples determined with the nano-indentation technique are (98.3 ± 9) GPa, (120 ± 23) GPa and (132 ± 25) GPa, respectively. Nano-indentation is an important technique for probing the mechanical behavior of materials at small-length scales.[13] The results for the elastic modulus cannot be compared to the literature because of the contrasting reported values.[14] However, the obtained value of 135 GPa is between the elastic-modulus values for the Ni and Ti materials.

4 CONCLUSIONS

The reaction of the NiTi-compound synthesis was not completed. It is inferred that the applied voltage was insufficient for a complete transformation of the NiTi phases. When increasing the current intensity from 1000 A to 2000 A, the fractions of intermetallic phases NiTi, $NiTi_2$ and Ni_3Ti increased as well. There was also a small amount of retained metallic Ti in the microstructure. The hardness of the intermetallic composites was increased from 250 HV to 701 HV by increasing the current intensity, due to the formation of higher amounts of the intermetallic phases. The elastic modulus of the composites was between the elastic-modulus values for the Ni and Ti materials.

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5 REFERENCES

[1] X. Songa et al., Microstructure and mechanical properties of Nb- and Mo-modified NiTi-Al-based intermetallics processed by isothermal forging, Materials Science & Engineering A, 594 (**2014**), 229–234, doi:10.1016/j.msea.2013.11.070

[2] N. Ergin et al., An investigation on TiNi intermetallic produced by electric current activated sintering, Acta Physica Polonica A, 123 (**2013**), 248–249, doi:10.12693/APhysPolA.123.248

[3] M. Farvizi et al., Microstructural characterization of HIP consolidated NiTi-nano Al_2O_3 composites, Journal of Alloys and Compounds, 606 (**2014**), 21–26, doi:10.1016/j.jallcom.2014.03.184

[4] F. Neves et al., Mechanically activated reactive forging synthesis (MARFOS) of NiTi, Intermetallics, 16 (**2008**), 889–895, doi:10.1016/j.intermet.2008.04.002

[5] P. Novak et al., Effect of SHS conditions on microstructure of NiTi shape memory alloy, Intermetallics, 42 (**2013**), 85–91, doi:10.1016/j.intermet.2013.05.015

[6] T. Yener et al., Synthesis and characterization of metallic-intermetallic Ti-$TiAl_3$, Nb-Ti-$TiAl_3$ composite produced by electric current activated sintering (ECAS), Mater. Tehnol., 48 (**2014**) 6, 847–850

[7] G. Chan et al., In-situ observation and neutron diffraction of NiTi powder sintering, Acta Materialia, 67 (**2014**), 32–44, doi:10.1016/j.actamat.2013.12.013

[8] Z. Huan et al., Porous NiTi surfaces for biomedical applications, Applied Surface Science, 258 (**2012**), 5244–5249, doi:10.1016/j.apsusc.2012.02.002

[9] M. Krasnowski et al., Al_3Ni_2-Al composites with nanocrystalline intermetallic matrix produced by consolidation of milled powders, Advanced Powder Technology, 25 (**2014**), 1362–1368, doi:10.1016/j.apt.2014.03.018

[10] A. Molladavoudi et al., The production of nanocrystalline cobalt titanide intermetallic compound via mechanical alloying, Intermetallics, 29 (**2012**), 104–109, doi:10.1016/j.intermet.2012.05.012

[11] R. Orrù et al., Consolidation/synthesis of materials by electric current activated/assisted sintering, Materials Science and Engineering R: Reports, 63 (**2009**), 127–287, doi:10.1016/j.mser.2008.09.003

[12] F. Gao et al., Abrasive wear property of laser melting/deposited Ti_2Ni/TiNi intermetallic alloy, Transactions of Nonferrous Metals Society of China, 17 (**2007**), 1358–1362, doi:10.1016/S1003-6326(07)60277-5

[13] X. Deng et al., Deformation behavior of (Cu, Ag)-Sn intermetallics by nanoindentation, Acta Materialia, 52 (**2004**), 4291–4303, doi:10.1016/j.actamat.2004.05.046

[14] Y. Liu et al., Apparent modulus of elasticity of near-equiatomic NiTi, Journal of Alloys and Compounds, 270 (**1998**), 154–159, doi:10.1016/S0925-8388(98)00500-3