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PROCESSING OF POROUS NiTi PREFORMS FOR NiTi/Mg COMPOSITES

NiTi alloys are successfully used in engineering and medical applications because of their properties, such as shape memory effect, superelasticity or mechanical strength. A composite with Mg matrix, due to its vibration damping properties, can be characterized by low weight and good vibration damping properties. In this study, a combination of two techniques was used for successful fabrication of Mg composite reinforced by NiTi alloy preform. The porous preforms synthesized by Self-propagating High-temperature Synthesis (SHS) from elemental powders were subsequently infiltrated with Mg by squeeze casting. The effects were examined with scanning electron microscope with EDS detector, X-ray diffraction and microindentation. The inspection has shown well-connected matrix and reinforcement; no reaction at the interface and open porosities fully infiltrated by liquid Mg. Moreover, analysis of samples' fracture has exhibited that crack propagates inside the Mg matrix and there is no detachment of reinforcement.

Keywords: metal matrix composite, magnesium, nitinol, SHS, squeeze casting

1. Introduction

Shape memory alloys (SMAs) based on nickel and titanium composition are one of the most popular group of smart materials nowadays which are used in engineering as well as medical applications (stents, archwires, occluders, parts of valves [1], spinal rods [2]) because of their properties, such as shape memory effect, superelasticity or mechanical strength. The reversible shape memory effect is connected with the phase transformation from austenite to martensite via a decrease in temperature.

The porous NiTi SMAs inherit the excellent properties of dense NiTi SMAs while becoming lightweight and having adjustable mechanical properties. However, change of the material structure results in lowering damping capacity, mechanical properties and inferior corrosion resistance in comparison with NiTi dense form. These disadvantages can limit the potential applications of porous NiTi alloys. To overcome the mentioned difficulties, magnesium (one of the lightest structural materials used) possessing high damping capacity was integrated with the NiTi alloys in order to develop a new composite with a combination of lightweight, improved vibration damping capacity and increased mechanical properties whilst retaining the superelasticity of NiTi SMAs [3,4]. Moreover, the developed composite can be used in biomedical applications due to biocompatibility of magnesium and NiTi alloy.

Several ways of manufacturing NiTi/Mg composite have been reported in the literature so far. Pulsed current hot pressing (PCHP) was used to fabricate a NiTi/Mg alloy AZ31 composite by Mizuuchi et al. [5]. Mg alloy plates with 20 vol% of NiTi fibers were readily hot pressed into a composite at 500°C. It seemed that interface reaction occurred close to the boundary between Mg and NiTi and as a result, there are two phases observed in the interfacial zone. In the vicinity of the matrix, about 2 μm thick layer containing Al and Ni elements was formed and about 10 μm thick layer containing Mg, Al, Ni, and O elements was formed next to the fiber.

Another approach to NiTi/Mg composite preparation is a combination of a ball-milling and the hot-pressing process [4]. Mg alloy ball-milled into powders with the content of NiTi fibers in the range 0-10% were put into a monoaxial pressing die, in which the fibers in a row were sandwiched between two layers of the Mg alloy powder. The powder and fibers were hot pressed at temperatures in the range of 250-320°C with an applied pressure increasing up to 375 MPa under which the fibers were not damaged or deformed. Microstructure analysis shows no remarkable reaction product or layer formed in the matrix-fibers interface. Moreover, the adequate bonding between Mg alloy and NiTi fibers was indicated by higher microhardness of the interfacial zone than it is in the matrix. In their next study [6], the authors used an additional process of hot-forging followed by hot treatment for successful improvement of the mechanical properties of NiTi/Mg alloy composite as a result of grain refinement after recrystallisation.

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Recently, Li et al. [3] merged space-holder technique, powder sintering and pressureless infiltration of liquid Mg alloy to fabricate NiTi/Mg alloy composite. In that study, NH_4HCO_3 and urea particles were used as spacers, which were blended, cold compacted and subsequently sintered with elemental powders of Ni and Ti. The obtained porous NiTi samples were infiltrated by liquid Mg alloy at 700°C. The results showed that the matrix and reinforcement were well-bonded. Generally, two expected phases were observed in the majority: NiTi and Mg. Nevertheless, there were also other, like $NiTi_2$ and Ni_3Ti in the NiTi as well as Mg_2Ni and MgO mainly in the infiltrating material owing to the reaction between Mg, NiTi and residual oxygen. That study indicates that if a NiTi/Mg composite were produced by a liquid infiltration process, there could be some unwanted reactions in the interface.

The pressureless infiltration was also used by Guo et al. [7] to fabricate NiTi/Mg composite. The main difference was the NiTi preform preparation. The preform was fabricated by arc melting of Ni, Ti, Gd and Nb elements and subsequent etching in nitric acid solution resulting in submicron-porous structure. The successfully fabricated composite consisted of two main phases: quite homogeneous Mg and NiTi. Additionally, no reaction products were observed at the well-developed interface between fibers and matrix.

Esen [8,9] fabricated NiTi/Mg composites by rotary hot swaging. First, mixed Mg and 5-15% NiTi powders were loaded into copper tubes. Subsequently, the tubes were vacuum and argon treated to remove air and moisture and tightly closed after the last evacuation. Vessels were deformed using a rotary swaging technique, in which both heat and deformation by 45% were applied simultaneously, and an annealing heat treatment at 450-600°C was carried out to homogenize the heavily deformed structures. There was no product of the reaction between matrix and reinforcement in the interface observed, but the Mg matrix contained elongated grains comprised of equiaxed recrystallized grains, and the NiTi preserved their starting spherical shape during processing due to their superelastic behaviour.

The quite different technique was proposed by Aydogmus [10] for fabrication of NiTi/Mg composite. In that study, elemental Mg and up to 30% of prealloyed NiTi powders were mixed and subsequently sintered in spark plasma sintering process carried out at 600°C. The results showed that almost full density NiTi/Mg composites can be obtained, but 10% NiTi addition is not sufficient to generate a fully connected network. Only the addition of 20% or more of NiTi gave this possibility. Short 5-minutes time sintering did not affect the interface with undesired porosity or phases, however, the time elongation resulted in Ni_4Ti_3 precipitation.

In this paper, Mg alloy matrix composite reinforced with NiTi porous preform was fabricated by another combination of techniques – SHS followed by squeeze casting process. Quality of connection between matrix and reinforcement as well as mechanical properties were investigated.

2. Experimental methods

A porous NiTi preform was prepared by microwave assisted SHS. For this research, commercial powders of Ti (99.5% Ti, − 325) and Ni (99.8%, – 325 mesh provided by Alfa Aesar) as starting materials were used with the molar ratio 1:1 to prepare a stoichiometric reactant mixture and fabricate NiTi alloy by SHS. Subsequently, the powders were mixed in a ball mill for 10 minutes. Afterwards, the powders were uniaxially cold-pressed in a hydraulic press into cylindrical samples under a pressure of 250 MPa for 30 s. The SHS process took place in a microwave reactor in a protective argon atmosphere. The temperature during synthesis was detected by a Raytek Marathon MM pyrometer with the measuring spot dia. 0.6 mm. Preform fabrication was followed by liquid metal infiltration in squeeze casting process. Firstly, the NiTi preform samples were preheated for 30 minutes to 600-700°C. In the second place, liquid Mg at the temperature of 750°C infiltrated preforms under the pressure of 90 MPa. Prior to the structure observation, samples were mechanically ground and polished. The phases and structures of the preform as well as NiTi/Mg composite were examined by a scanning electron microscope, Hitachi TM3000 supported with EDS detector, SwiftED3000 and X-ray diffraction (Rigaku Ultima IV Diffractometer) with Cu Kα irradiation ($\lambda = 1.5406$ Å). Identification of the phases in XRD pattern was based on the Inorganic Crystal Structure Database (ICDS) and Crystallography Open Database (COD). Additionally, the samples were fractured along the boundary between reinforcement and matrix to test the quality of the connection between them. Micromechanical properties of the composite were determined by a Vickers tester with an indenting load of 200 gf for a dwell time of 15 s measured by MicroCombi Tester. The series of 5 indents were made in approximately 100 µm from the interfacial zone (IZ) of composite and on the zone itself. The hardness and Young modulus were calculated based on the Oliver-Pharr method.

3. Results and discussion

The temperature detection allowed to follow the course of the SHS reaction. An exemplary temperature-time dependence is shown in Figure 1. It is additionally supported by the thermal-derivative analysis that points out the phase-changing points with peaks to facilitate interpretation of the curve. The ignition temperature was reached and the synthesis started at ~870°C (area A) as was reported in previous studies [11]. The combustion temperature exceeded 1100°C and the reaction front went through the whole specimen (descending slope till point B). Peak pointed as B probably corresponds to the formation of Ni_3Ti phase (Fig. 2), which was also detected in EDS analysis of the preforms.

The possible mechanism of the detected phases (Fig. 2) formation during SHS reaction was proposed by Novak et al. [12] (Eq. 1-3):

$$Ni + 2Ti \rightarrow Ti_2Ni \tag{1}$$

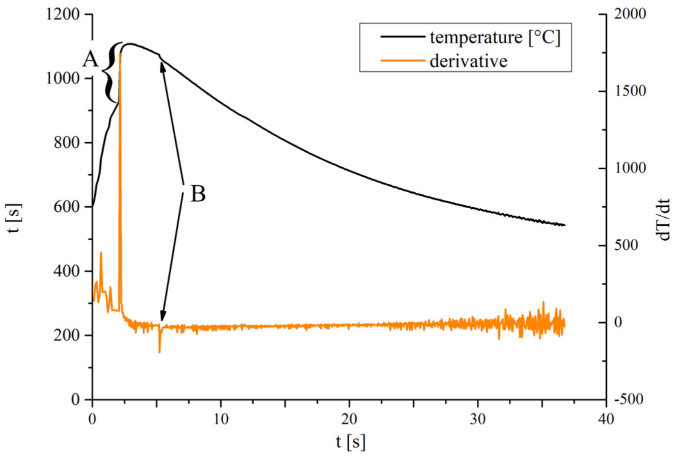

Fig. 1. SHS temperature-time dependence

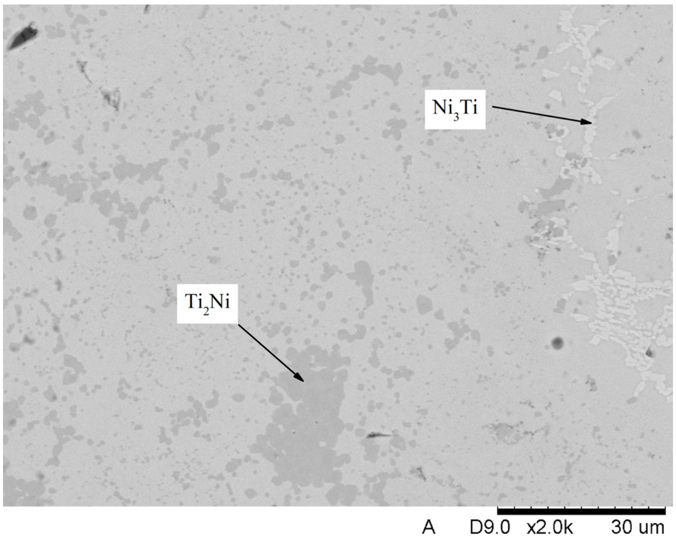

Fig. 2. Phases in the preform detected by EDS analysis. The major phase is NiTi

$$Ti_2Ni + Ni \rightarrow TiNi \tag{2}$$

$$NiTi + 2Ni \rightarrow Ni_3Ti \tag{3}$$

Those authors also supposed that there could be one additional reaction influencing the amounts of formed phases (Eq. 4):

$$5NiTi \rightarrow 2Ti_2Ni + Ni_3Ti \tag{4}$$

The cross-section of as-prepared highly porous NiTi alloy preform fabricated by SHS reaction is shown in Fig. 3a. All of the dark points and areas seen in the Fig. 3b are pores, which are mostly connected forming open porosity. The rest of them are micropores formed as a result of some of the probable phenomena: thermal migration, volume change due to crystal reordering, Kirkendall effect, gas porosity or residual porosity after pressing [13].

To investigate the microstructure and chemical composition of prepared materials, SEM studies followed by EDS analysis were carried out. The well-connected NiTi reinforcement and magnesium matrix phases in the investigated composites are shown in Fig. 4. It means that the most catastrophic failure for metal matrix composites, fractures on the matrix-reinforcement boundary [15], is not observed for proposed NiTi/Mg composite made by combination of SHS and squeeze casting. The vast majority of pores are interconnected, which allowed them to be completely infiltrated with liquid magnesium in the squeeze casting process.

The chemical analysis (Fig. 5) of the interfacial zone showed a clear boundary between the reinforcement and the matrix with an additional layer consisting mostly of Ti. The layer presumably was formed during preform preheating before infiltration by squeeze casting, when titanium atoms diffuse from NiTi towards the sample surface and connect with oxygen. Another possibility of the layer formation was proposed by Školáková et al. [16]. They modified the SHS synthesis starting material by adding various quantities of magnesium to mixture of nickel and titanium powders. They observed decrease in contribution of $NiTi_2$ phase, which probably originates from the

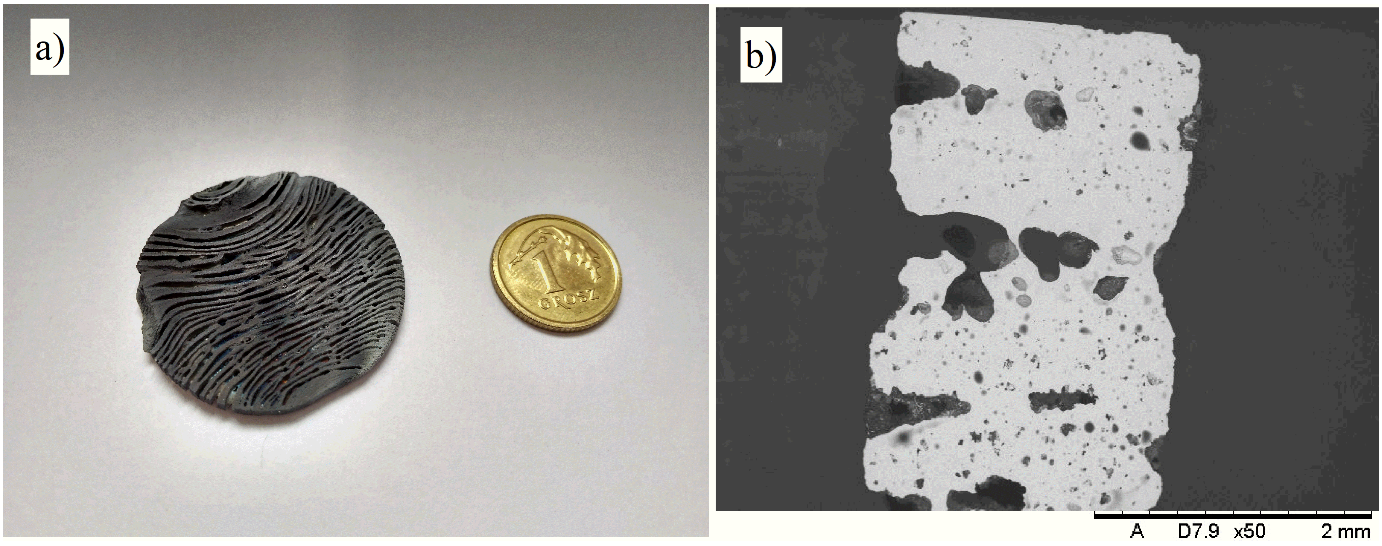

Fig. 3. a) the porous NiTi preform; b) SEM image of the preform cross-section

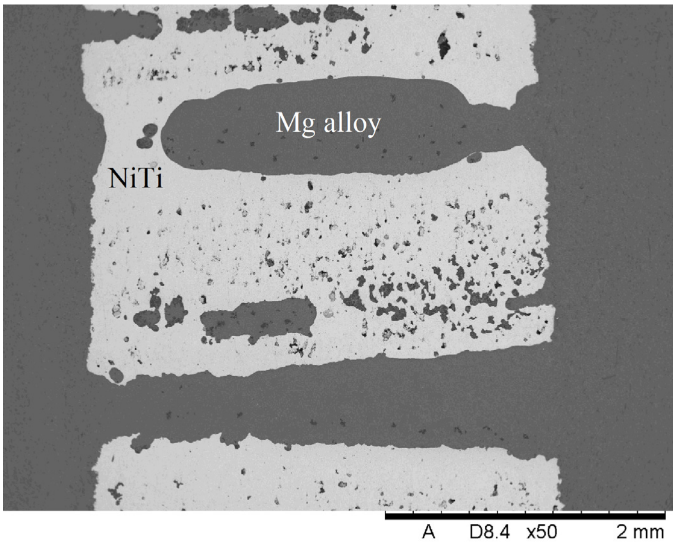

Fig. 4. Microstructure of NiTi/Mg composite

destabilization of that phase by magnesium. It is possible because of magnesium high affinity to oxygen which stabilize the $NiTi_2$ phase. Thus, basing on chemical analysis data, there is no clear evidence that an interface degrading reaction between liquid magnesium and NiTi preform has occurred as it was reported by Li et al. [3]. On the one hand, the layer formation might be omitted if there was a protecting argon atmosphere. On the other hand, such layer could be a barrier for nickel releasing form NiTi reinforcement, which is one of the problems in biomedical applications of nitinol.

In order to confirm the phases identified by EDS measurements, X-ray diffraction analysis was used. XRD measurements were performed on NiTi/Mg composite and the diffraction pattern is shown in Fig. 6. The analysis of the diffraction patterns of composite indicated typical reflections for Mg, NiTi and $NiTi_2$ phases. Additionally, the Ti phase was detected, which was also noticed during chemical analysis of the matrix-reinforcement interface (Fig. 5). Fig. 2 also shows Ni_3Ti phase from the fabrication of the porous NiTi preform. However, due to its very low volume fraction., it was not detected by the XRD.

Additionally, the NiTi/Mg composite was fractured to observe possible detachment of reinforcement from the matrix. There were no such phenomena present, as it is shown in Fig. 7. Fragments of Mg matrix are still attached to the reinforcement material. It indicates a good connection between composite elements.

The results of the microindentation measurements (Table 1) indicate that the interfacial zone has the highest indentation Young's modulus E_{IT} and hardness HV in comparison to the Mg and NiTi alloy and stay in agreement with other studies [6,14]. The increase of the values can result from the formation of ad-

TABLE 1

The average values and standard deviation of mechanical properties calculated from the microindentation tests. IZ – interfacial zone, E_{IT} – indentation Young's modulus, HV – Vickers hardness, H_{IT} – indentation hardness

	E_{IT} [GPa]		HV [-]		H_{IT} [GPa]	
	av.	**± SD**	**av.**	**± SD**	**av.**	**± SD**
Mg	42,82	0,60	85,03	2,35	0,90	0,02
IZ	59,15	2,87	383,58	18,31	1,81	0,15
NiTi	53,49	1,26	144,90	6,92	3,72	0,47

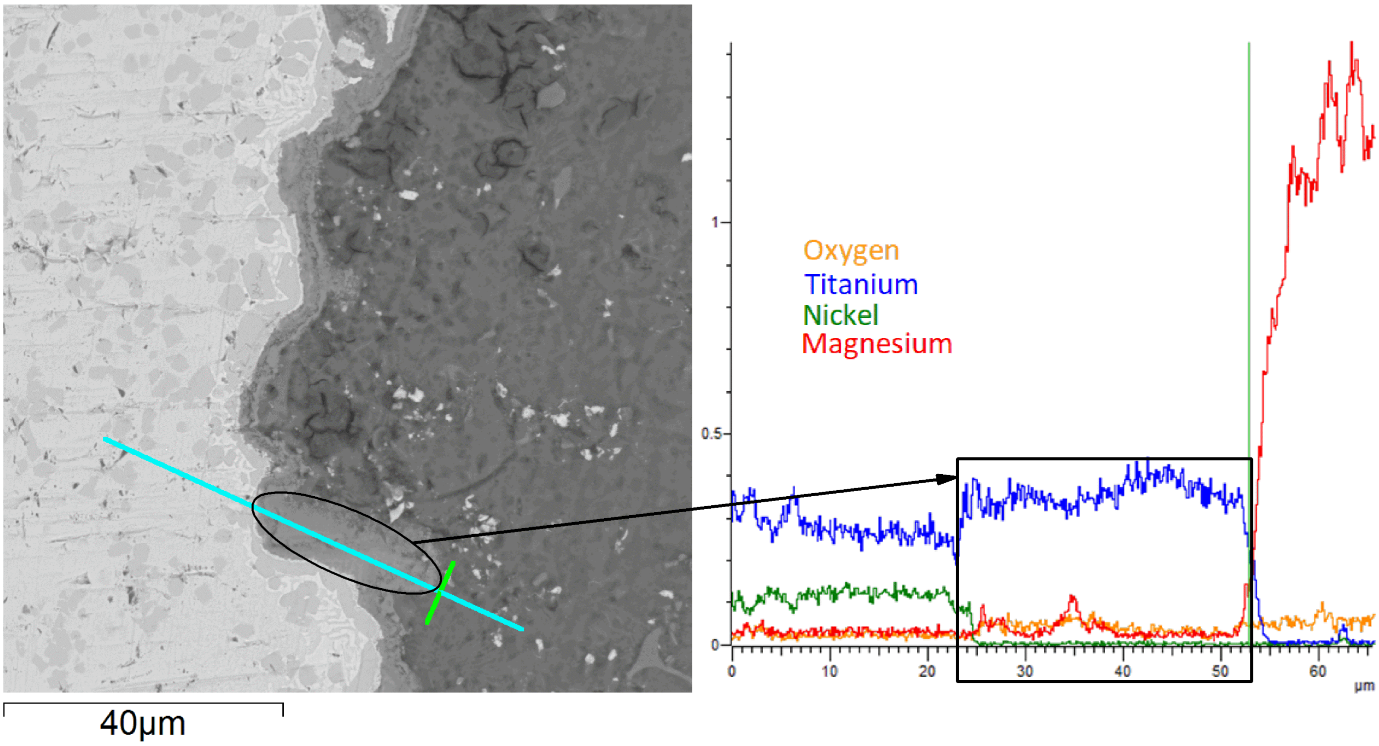

Fig. 5. Chemical analysis at the matrix-reinforcement interface

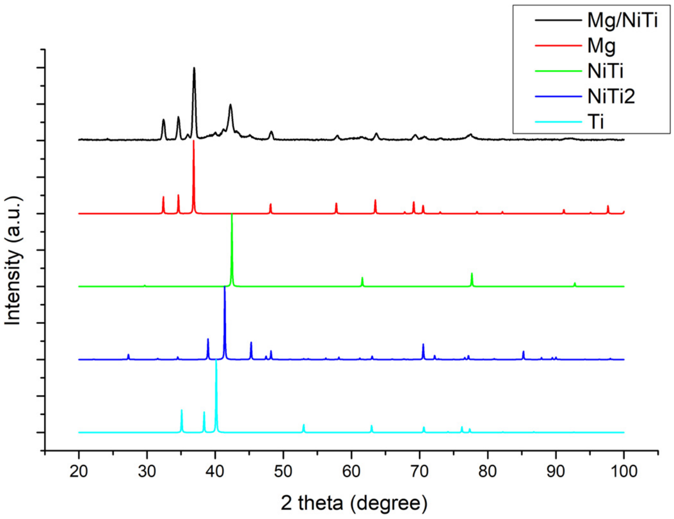

Fig. 6. X-ray diffraction patterns for NiTi/Mg composite

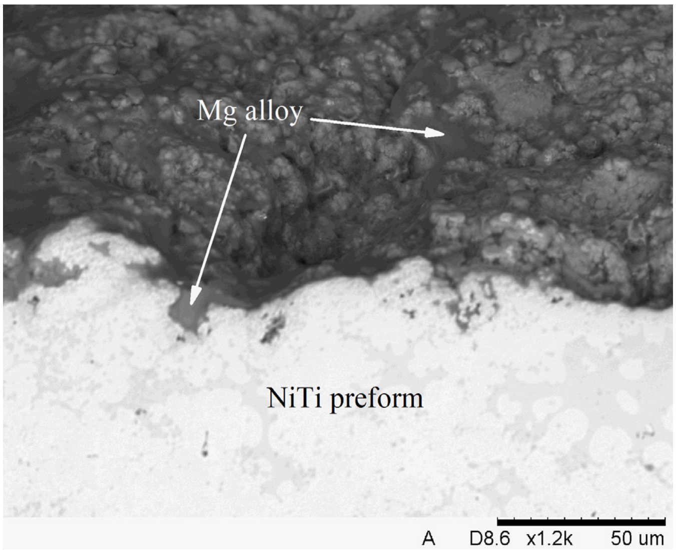

Fig. 7. Fracture surface of NiTi/Mg composite

ditional Ti layer between NiTi and magnesium during preform preheating. However, the indentation hardness H_{IT} has presented different trend, the analysis showed that the interfacial zone has lower parameters then pure NiTi and greater than Mg properties indicating the interpenetration of phases and may present the properties of the composite. Moreover, the micro indenter leaning on the NiTi on one side and on the magnesium on the other side, could influence on the results for the interfacial zone. With this assumption, the results obtained for interfacial zone can be considered as the parameters value for the NiTi/Mg composite.

4. Conclusions

The NiTi/Mg composite was successfully manufactured by a combination of SHS and squeeze casting processes, which has not been proposed earlier. The structures were investigated, what led to the following conclusions:

- in the porous preform made by SHS two types of porosity are present: open (allowing infiltration) in the majority and close in minority,
- there are 3 different phases in the preform material: main – NiTi, $NiTi_2$ and a low volume of Ni_3Ti,
- the Mg matrix and NiTi reinforcement are well-connected and there is no detachment of the matrix from the reinforcement,
- the squeeze casting process allows to fully infiltrate open porosities of the NiTi preform by magnesium,
- probably there is no reaction between matrix and reinforcement at the interface, however, there is an additional Ti layer between the preform and Mg alloy, which can act as diffusion barrier in case of allergenic nickel release in biomedical applications.
- the indentation Young's modulus and Vickers microhardness for the composite NiTi/Mg (measured in the interfacial zone) are higher than for every composite part alone.

REFERENCES

[1] S.H. Alavi, M. Soriano Baliarda, N. Bonessio, L. Valdevit, A. Kheradvar, Ann. Biomed. Eng. **45** (2), 413-426 (2017), DOI: 10.1007/s10439-016-1778-0.
[2] E. Lukina, M. Kollerov, J. Meswania, A. Khon, P. Panin, G.W. Blunn, Mater. Sci. Eng. C. **72**, 601-610 (2017), DOI: 10.1016/j.msec.2016.11.120.
[3] D.S. Li, X.P. Zhang, Z.P. Xiong, Y.W. Mai, J. Alloy Compd. **490** (1-2), 15-19 (2010), DOI: 10.1016/j.jallcom.2009.10.025.
[4] B. Yan, G. Li, Compos. Part A-Appl. S. **36** (11), 1590-1594 (2005), DOI: 10.1016/j.compositesa.2005.03.010.
[5] K. Mizuuchi, K. Inoue, K. Hamada, M. Sugioka, M. Itami, M. Fukusumi, M. Kawahara, Mat. Sci. Eng. A-Struct. **367** (1-2), 343-349 (2004), DOI: 10.1016/j.msea.2003.10.286.
[6] Q. Guo, G. Li, R. Tang, B. Yan, Mater. Sci. Forum **536**, 873-876 (2007), DOI: 10.4028/www.scientific.net/MSF.534-536.873.
[7] W. Guo, H. Kato, Mater. Lett. **158**, 1-4 (2015), DOI: 10.1016/j.matlet.2015.05.143.
[8] Z. Esen, TiNi Reinforced Magnesium Composites by Powder Metallurgy, in: W.H. Sillekens, S.R. Agnew, N.R. Neelameggham, S.N. Mathaudhu (Eds.), Cham Springer International Publishing (2011).
[9] Z. Esen, Mat. Sci. Eng. A-Struct. **558**, 632-640 (2012), DOI: 10.1016/j.msea.2012.08.065.
[10] T. Aydogmus, Mat. Sci. Eng. A-Struct. **624**, 261-270 (2015), DOI: 10.1016/j.msea.2014.11.092.
[11] C. Zanotti, P. Giuliani, A. Terrosu, S. Gennari, F. Maglia, Intermetallics **15** (3), 404-412 (2007), DOI: 10.1016/j.intermet.2006.08.002.
[12] P. Novák, P. Pokorný, V. Vojtěch, A. Knaislová, A. Školáková, J. Čapek, M. Karlík, J. Kopeček, Mater. Chem. Phys. **155**, 113-121 (2015), DOI: 10.1016/j.matchemphys.2015.02.007.

[13] P. Novák, L. Mejzlíková, A. Michalcová, J. Čapek, P. Beran, D. Vojtěch, Intermetallics **42**, 85-91 (2013), DOI: 10.1016/j.intermet.2013.05.015.

[14] M. Farvizi, T. Ebadzadeh, M.R. Vaezi, E.Y. Yoon, Y.-J. Kim, J.Y. Kang, H.S. Kim, A. Simchi, Wear **334-335**, 35-43 (2015), DOI: 10.1016/j.wear.2015.04.011.

[15] K. Gawdzińska, L. Chybowski, W. Przetakiewicz, R. Laskowski, Arch. Metall. Mater. **62** (4), 2171-2182 (2017), DOI: 10.1515/amm-2017-0320

[16] A. Školáková, P. Novák, P. Salvetr, H. Moravec, V. Šefl, D. Deduytsche, C.E. Detavernier, Metall. and Mat. Trans. A **48** (7), 3559-3569 (2017), DOI: 10.1007/s11661-017-4105-y.