# Microstructural Aspects of Some Magnesium Matrix Composites Reinforced with Amorphous/Nanocrystalline Ni-Ti Particulates

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Two magnesium matrix composites reinforced with 3 and 10% Ni-Ti particulates, respectively, were obtained by plasma sintering. The reinforcement material was obtained by grinding a mixture of powders of 68% Ni and 32% Ti atomic percent in a high energy mill for 40 hours. Particulates resulting from mechanical alloying have a partially amorphous and partially nanocrystalline structure, consisting of the following phases: Ni solid solution, Ti<sub>2</sub>Ni and NiTi (B2) phase. After sintering, both the matrix and the reinforcement material are nanocrystalline and the particulates have a polyphase structure, consisting of Ni(Ti), NiTi (R phase) and Ni<sub>4</sub>Ti<sub>3</sub>. The hardness of these composites is superior to the hardness of magnesium matrix composites reinforced with Ni-Ti particulates having 50% Ni / 50% Ti and 32% Ni / 68% Ti chemical compositions obtained under the same conditions and corresponding proportions of reinforcement material.

Key words: Mg matrix composites, amorphous/nanocrystalline reinforcement, mechanical alloying, spark plasma sintering

Matrix composites of magnesium and magnesium alloys are characterized by low density, high specific mechanical strength, rigidity, wear and creep resistance as well as good damping capacity.

The features that impose these materials as excellent choices for structural applications are largely due to the reinforcement effect and the type of the reinforcement material used.

The reinforcement currently associated with Mg matrices are ceramics, either in the form of fibers or particulates: SiC, Al<sub>2</sub>O<sub>4</sub>, TiC, but also carbon nanotubes [1].

Although reinforcement with ceramic materials improves the matrix mechanical strength, hardness and stiffness, the improvement of these properties is accompanied by a decrease in plasticity mainly due to the differences between the elastic moduli of the matrix and of the reinforcement material. Also, this decrease in plasticity occurs as a result of the different thermal expansion coefficients of the matrix, respectively reinforcement [2].

Another drawback of reinforcement with ceramic materials is the matrix/reinforcement material interface poor strength.

In order to reduce these disadvantages, various reinforcement variants have been proposed: hybrid reinforcement material, made of ceramic + ceramic or ceramic + metallic nanomaterials [3], hybrid reinforcement material made of metal + metal [4], amorphous/nanocrystalline metallic reinforcement material [5].

The choice of the latter type of reinforcement material is optimal in terms of obtaining a powerful interface - both matrix and the reinforcement element are metallic materials – and it is also leading to an improvement of the mechanical strength characteristics as well as the ductility. Alloy systems in which for certain concentration ranges of the components amorphous phases can be formed by mechanical alloying are relatively numerous, among which can be mentioned Ti-Al, Zr-Co, Ni-Ti, Nb-Fe, Fe-Zr-B, Ti-Ni-Al, etc. [6]

In the present paper, the Ni-Ti system with 68% Ni and 32% Ti (atomic percentages) was chosen as a reinforcement material for the magnesium matrix, and the reinforcement Ni-Ti particulates were obtained by mechanical alloying of the elemental powders in the specified proportions.

## **Experimental part**

Two Mg-matrix composites reinforced with 3% and 10% (wt %) Ni-Ti particulates were obtained from the solid state by powder metallurgy specific procedures.

The complementary material was made of elemental powders of Ni - 68 at.% - and Ti - 32 at.% - (Alfa Aesar), having sizes of 44  $\mu$ m and 100  $\mu$ m, respectively.

The powder mixture was encapsulated under argon atmosphere and ground for 40 h in a Retsch PM 400 highenergy planetary mill at a rotational speed of 250 rpm. The grinding balls had 15 mm in diameter and the ball / powder mass ratio was 7 to 1.

From the powder resulting from grinding and from the Mg powder with a particulate size of  $74\mu$ m (Alfa Aesar), two mixtures were made as follows: a mixture containing 3% Ni-Ti + 97% Mg, and the second containing 10% Ni-Ti + 90% Mg.

The two powder blends: Mg-3% milled Ni-Ti and Mg-10% milled Ni-Ti were sintered under argon atmosphere using the SPS technique in a FCT Systeme D50 sintering furnace.

The sintering cycle implied a maximum temperature of 590°C, holding time 8 min and a force of 5 kN. The heating

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was carried out in two steps, the first one up to 460°C at a rate of 140°C/min and the second one up to 590°C at a rate of 40°C/min. The cooling rate was 190°C/min.

Structural characterization of magnesium matrix composites was performed by X-ray diffraction using a copper anticathode PANalytical X'PERT Pro diffractometer and by scanning electron microscopy with a SEM QUANTA FEG 450 microscope.

The Vickers hardness of the magnesium matrix composites was determined using a Shimadzu HMV-2 Series microhardness tester, using a 2 N force for 15 seconds. Five measurements per sample were made, with a distance of 0.5 mm between indentations.

#### **Results and discussions**

#### Nickel titanium powder used as reinforcement

The 68 at.% Ni-32 at.% Ti powder used as reinforcement obtained after grinding for 40 hours in the planetary ball mill was analyzed by X-ray diffraction (Fig. 1 and Fig. 2), scanning electron microscopy (Fig.3) and energy dispersive X-ray spectrometry - EDS (Fig. 4). In order to achieve a better X-ray signal, EDS analysis was performed according to a new method that use perpendicularly incidence of accelerated electron beam at variable voltage [7].

The qualitative (fig. 1- upper side) and quantitative Xray diffraction analysis of the powder mixture after grinding reveals the existence of the following phases: 81% solid solution of titanium in nickel Ni(Ti), 16%Ti<sub>2</sub>Ni compound and 3%NiTi cubic structure compound (austenite).



Fig. 1. Diffractograms of the Ni68Ti32 powder mixture before grinding (below) and after grinding for 40 hours (above)



Fig. 2. Diffractogram detail obtained on the Ni68Ti32 powder milled for 40 hours.



Fig. 3. Scanning electron microscopy (BSE) image of Ni68Ti32 powder mixture

The existence of a solid solution and not of pure nickel in powder mixture after grinding is certified by shifting to the left, at smaller angles, the diffraction lines associated with the solid solution phase as against those of Ni, shown in Figure 1 - below, with the corresponding modification of interplanar distances.

Also, the enlargement of the diffraction peaks associated with this phase is attributed to a reduction in dimensions of the coherent dispersion blocks, a common phenomenon in the case of mechanical alloying by grinding in high energy mills [8-10].

Thus, the average size of Ni crystallite before grinding is 42.31 nm, while after grinding, Ni(Ti) has an average size of coherent dispersion blocks of 8.74 nm, a value indicating a high density of dislocations caused by a very strong deformation during grinding [11].

Regarding the crystallites average sizes in the other phases of the powder mixture, that of Ti<sub>2</sub>Ni is 12.36 nm and NiTi, respectively, of 40.46 nm. Taking into account these results, it can be stated that the Ni-Ti powder mixture



Fig. 4. EDS analysis of Ni68Ti32 powder mixture

after grinding is characterized by a nanocrystalline structure. The crystallites sizes for the phases forming the powder blends before and after grinding were calculated using the Scherrer formula [12].

Due to the large difference between nickel and titanium proportions in the initial mixture (68% at. Ni vs. 32% at. Tiratio very close to these in the Ni, Ti compound), a *mechanical segregation* (aggregation) of the powder during grinding occurred, favored by the different plastic deformation behavior of the two metals (nickel has a FCC lattice characterized by a high deformability, while titanium has a lower plasticity due to the HCP lattice).

Consequently, on the one hand, a majority phase with a high nickel content - the Ni(Ti) solid solution -was obtained and, on the other hand, a minority phase, rich in titanium-Ti<sub>2</sub>Ni - is also present. The free energy of formation  $\Delta G_{298}^{0}$  of the Ti<sub>2</sub>Ni compound is -78 kJ/mol and it remains negative down to 1223K (-67 kJ/mol) [13] so that the thermodynamic forming condition of the Ti<sub>2</sub>Niphase is met.

The NiTi compound formation is thermodynamically possible from elemental powders,  $\Delta G_{298}^0 = -65.5$  kJ/mol and also as a result of the Ni + Ti<sub>2</sub>Ni  $\rightarrow$ 2NiTi reaction,  $\Delta G_{1000} = -23.3$  kJ/mol [14].

 $\Delta G_{1023K} = -23.3 \text{ kJ/mol [14]}.$ Since the Ti,Ni Gibbs free energy is lower than that of the NiTi compound, the most likely sequence of phase formation during mechanical alloying is the following: Ni, Ti $\rightarrow$ Ni(Ti), Ti,Ni up to the titanium powder consumption, phenomenon favoured by a higher nickel in titanium diffusion coefficient than that of titanium in nickel [15]  $\rightarrow$ Ni(Ti), Ti,Ni, NiTi.

The absence of the Ni<sub>3</sub>Ti compound and of the nickel in titanium solid solution, phases found in bulk Ni-Ti alloys [16], can be explained by the mechanical grinding/alloying processes (plastic deformation, fragmentation, strong impact, cold welding etc.) which impedes the existence of continuous and stable interfaces between Ni, Ti, Ti<sub>2</sub>Ni, NiTi, as well as by lack of subsequent pressing and sintering.

The diffractogram aspect of the Ni68Ti32 powder mixture ground for 40 hours also indicates a mixed structure, both nanocrystalline and amorphous (enlarged peaks of small intensities and, respectively, sharp peaks characteristic for crystalline phases superimposed over the amorphous phase peak, much wider, exhibiting Gaussian shape as seen in Fig. 2).

Scanning electron micrographs (Fig.3) reveal nickel rich-white zones which occupy large areas surrounded by other light gray areas with higher titanium content. The association of differently nuanced regions is found in different proportions in each particulate/powder conglomerate, suggesting a medium uniformity degree of the mechanical alloying process. The X-ray dispersion spectrum (Fig. 4) rescinds the formation of oxides or phases other than those of the Ni-Ti system. The elements percentages are shown in Table 1.

QUANTITATIVE ANALYSIS OF MECHANICAL ALLOYING POWDER

Element	Weight, %	Atomic, %
NiK	27.35	31.57
TiK	72.65	68.43
Total	100	100

Magnesium composites reinforced with mechanical alloyed nickel titanium powder

The two SPS composites reinforced with 3% and 10% Ni-Ti particulates, respectively, were analyzed by X-ray diffraction (Figs. 5-8), scanning electron microscopy (Figures 9 and 10) and EDS analysis (Figs, 11 and 12).



Fig. 5. X-ray diffraction pattern of the Mg matrix composite reinforced with 3% Ni-Ti particulates



Fig. 6. Detail of the composite containing 3% reinforcing element diffractogram



Fig. 7. X-ray diffraction pattern of the Mg matrix composite reinforced with 10% Ni-Ti particulates



Fig. 8. Detail of the composite containing 10% reinforcing element diffractogram

The phases identified by X-ray diffraction in both composites are: Mg, Ni, NiTi - R phase and Ni, Ti, (Figs. 5 to 8) having the following crystallite dimensions (X - ray coherent dispersion blocks): 50.15 nm, 21.02 nm, 94.35 nm and, respectively, 68.82 nm.

One may see that both matrix and reinforcement particulates have a nanocrystalline structure. Regarding the phases of the complementary material, sintering resulted in an increase in Ni crystallites (21.02 nm vs. 8.74 nm) and NiTi compound (94.35 nm vs. 40.46 nm).

The qualitative X-ray diffraction analysis did not identify any Ti, Ni diffraction line. The Ni diffusion in Ti, Ni (obtained by mechanical alloying) resulting in NiTi phase formation a process initiated during grinding - continues to occur during sintering until the Ti<sub>2</sub>Ni phase is consumed.

In plasma sintering diffusion is favored, besides the temperature, by the pulsating current by increasing the density of point defects, by lowering the activation energies needed to displace these defects, as well as by electromigration [17]. Thus, taking into account the higher Ni diffusion coefficient than that of Ti in NiTi [18], as well as the reinforcement particulates high Ni content, it is possible to obtain a Ni - rich NiTi phase.

This causes the precipitation of the Ni<sub>4</sub>Ti<sub>3</sub> compound which contributes to the stabilization of the NiTi phase with trigonal lattice (R phase) [19]. Precipitation of the Ni, Ti, phase, coherent with the NiTi matrix, is responsible for the higher hardness of the Mg composite reinforced with Ni rich Ni-Ti particulates when compared to the hardness of Mg composites reinforced with equiatomic Ni-Ti particulates or Ti - rich Ni-Ti particulates [20].



Fig. 9. Scanning electron microscopy (BSE) image of the Mg matrix composite reinforced with 3% Ni-Ti particulates

Fig. 10. Scanning electron microscopy (BSE) image of the Mg matrix composite reinforced with 10% Ni-Ti particulates

Fig. 11. EDS analysis of the reinforcement particulate selected in figure 9

Fig. 12. EDS analysis of the reinforcement particulate selected in figure 10

3.98

30.55

65.47

Mg matrix composite reinforced with 10% Ni-Ti	Chemical composition of the particulates used as complementary material, [% at.]		
particulates	Ni32Ti68	Ni50Ťi50	Ni68Ti32
HV0.2	41.4 [20]	37.9 [20]	46.7

VICKERS MICROHARDNESS HV0.2 OF Mg MATRIX COMPOSITES REINFORCED WITH 10% Ni-Ti PARTICULATES WITH DIFFERENT Ni/Ti RATIOS

Table 3MICROHARDNESS OF Mg MATRIX COMPOSITESREINFORCED WITH 3% AND 10% Ni/Ti PARTICULATES,<br/>RESPECTIVELY (68% at. Ni, 32% AT Ti)

Composite Mg/Ni-Ti	Microhardness, HV0.2	
3% particulates	39.5	
10% particulates	46.7	

Table 2 shows the hardness values of Mg matrix composites reinforced with 10% Ni-Ti particulates with different chemical compositions.

The hardness values of the two composites is given in Table 3. They are in accordance with the particulates percentages.

The composite electron microscopy images (Figs. 9 and 10) reveal a strong particulate/matrix interface, without pores or microcracks.

Also, a relatively uniform distribution of the complementary (white) material particulates with a slight agglomeration tendency in the 10% reinforced composite is observed as a result of higher particulates quantity and insufficient homogenization of the powder mixture prior to sintering.

Spectrometric analysis of the reinforcement particulates of the Mg matrix is consistent with the chemical composition of the powder mixture subjected to grinding/ mechanical alloying, with small differences due to the Mg diffusion from the matrix to the particulates and the Ni diffusion from the particulates towards the matrix (Figs. 11 and 12).

## Conclusions

Milling for 40 h in a high energy mill of a 68% Ni - 32% Ti (at %) powder mixture resulted in particulates having partially amorphous, partially nanocrystalline structure. Also, the powder particulates obtained by mechanical alloying have a heterogeneous structure, consisting of Ni (as a majority) solid solution, the Ti<sub>2</sub>Ni compound and the NiTi compound with a cubic structure (austenite).

Subsequent to SPS sintering of Mg + 3% ground Ni-Ti powder and Mg + 10% ground Ni-Ti powder mixtures, the X-ray diffraction and electron microscopy analysis revealed the following:

-the resulted composites have a strong matrix/ particulate interface, free from pores or cracks;

-the reinforcement element is quite uniformly distributed in the matrix, with slight agglomeration tendencies for the reinforced composite with a larger proportion of particulates (10% Ni-Ti particulates);

-Ni-Ti particulates have a nanocrystalline structure, but with larger crystallite sizes than these found prior to sintering; it is possible to have a certain amount of amorphous phase still present after sintering but in order to confirm this assumption future rigorous quantitative assessments are required;

-Ti, Ni phase is no longer found in the Ni-Ti particulates structure, probably consumed in the formation of trigonal NiTi compound (R phase); -precipitation of the Ni<sub>4</sub>Ti<sub>3</sub> phase led to R phase stabilization, preventing martensitic transformation of NiTi austenite when rapidly cooling from the sintering temperature; this Ni-rich compound is responsible for the higher hardness of the Mg composite - 68% Ni + 32% Ti particulates as against other similar composites (Mg - 50% Ni + 50% Ti particulates, Mg - 68% Ti + 32% Ni particulates);

-the composite hardness increases as the reinforcement element proportion increases.

## References

1. DEY, A., PANDEY, K. M., REV ADV MATER SCI, 42, 2015, p. 58;

2. ESEN, Z., Magnesium Technology 2011, edited by Wim H. Sillekens, Sean R. Agnew, Neale R. Neelameggham and Suveen N. Mathaudhu, a John Wiley & Sons, Inc., Publication, Hoboken, New Jersey, 2011, p. 457;

3. GUPTA, M., WONG, W.L.E., Magnesium Technology 2014, edited by Martyn Alderman, Michele V. Manuel, Norbert Hort, Neale R. Neelameggham, Springer International Publishers, Switzerland, 2016, p. 426;

4. RASHAD, M., PAN, F., ASIF, M., SHE, J., ULLAH, A., J. MAGNESIUM ALLOYS, 3, Issue 1, 2015, p. 1;

5. JAYALAKSHMI, S., SINGH, R.A., GUPTA, M., TECHNOLOGIES, **6**, no. 40, 2018, p. 1;

6. MURTY, B.S., RANGANATHAN, S., INT.MATER.REV, **43**, no. 9, 1998, p. 101;

7. MICULESCU, F., JEPU, I., LUNGU, C.P., MICULESCU, M., BANE, M., DIG J NANOMATER BIOS **6**, No 2, 2011, p. 769;

8. WAJE, S.B., HASHIM, M., WAN YUSOFF, WAN.M.D., ABBAS, Z., APPL SURF SCI, **256**, Issue 10, 2010, p. 3122;

9. SUSNIAK, M., PALKA, P., KARWAN-BACZEWSKA, J., ARCH METALL MATER, **61**, no 2B, 2016, p. 977;

10. STANCIULESCU, M., ABRUDEANU, M., DUCU, C., PLAIASU, A.G., Rev. Chim. (Bucharest), **69**, no. 2, 2018, p. 449;

11. GUBICZA, J., Defect Structure and Properties of Nanomaterials, 2nd and Extended Edition, publisher Matthew Deans, Woodhead Publishing, 2017, p. 71;

12. SCHERRER, P., NACHR GES WISS GOTTINGEN, MATH-PHYS KL, 2, 1918, p. 98;

13. LÁENG, J., XIU, Z., XU, X., SUN, X., RU, H., LIU, Y., YANG, H., PHYS.SCR., **T129**, 2007, p. 250;

14. ABDULLAH, J., ZAKI, H.H.M., Developments in Sustainable Chemical and Bioprocess Techology, edited by Pogaku, R., Bono, A., Chu, C., Springer Science+Business Media, New York, 2013, p. 389; 15. BASTIN, G.F., RIECK, G.D., MT, **5**, no. 8, 1974, p. 1817;

16. LAENG, J., XIU, Z., ABDULLAH, J., ZAKI, H.H.M., SHAO, X., GUO,

X., HAN, Y., LIN, Z., QIN, J., LU, W., ZHANG, D., J MATER RES, **29**, no. 22, 2014, p. 2707;

17. CHAIM, R., CHEVALLIER, G., WEIBEL, A., ESTOURNES, C., J MATER SCI, **53** (5), 2018, p. 3087;

18. DIVINSKI, S.V., STLOUKAL, I., KRAL, L., HERZIG, CHR., DEFECT DIFFUS FORUM, **289**, 2009, p. 377;

19. CHANG, P.C., KO, M.L., RAMACHANDRAN, B., KUO, Y.K., CHIEN, C., WU, S.K., INTERMETALLICS, **84**, 2017, p. 130;

20.CIURDAS, M., NECSULESCU, D.A., PANTILIMON, C.M., ION, V., GALATANU, M., RUIU, G., DUMITRESCU, R.E., Rev. Chim. (Bucharest), **69**, no. 12, 2018, p. 3503

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