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NANOCRYSTALLINE AND AMORPHOUS NiTi COMPOUND OBTAINED BY MECHANICAL ALLOYING FOR METALLIC MATRIX REINFORCEMENT

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Abstract: Metal matrix composites reinforced with metallic amorphous particulate can be an alternative to conventional composites, reinforced with ceramic particles. This is due by the plasticity and toughness properties which are not attenuated by the low strength of the metal / ceramics system interface. The main purpose of this work was to obtain Ni-Ti amorphous alloys having the following compositions: Ni50Ti50, Ni68Ti32 (at.%), by powder metallurgy tehnique (mechanical alloying). Elemental powder mixtures in the specified proportions are subjected to milling for 10 and 40 hours in a planetary mill. Subsequently to milling, the samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy. The mechanical alloying occurs in both compositions after 40 hours. The blended powder mixtures with equiatomic composition present a mixed structure crystalline and amorphous.

Key words: metal matrix composites, amorphous Ni-Ti compounds, mechanical alloying, metallic amorphous reinforcement, XRD, SEM

1. INTRODUCTION

Metal matrix composites reinforced with ceramics have a number of advantages, such as high electrical conductivity, good wear resistance, high hardness, etc. These characteristics are accompanied by a significant decrease in ductility as well as toughness, due to the fragility of the complementary material, but also to the weak resistance of the matrix / particle interface. An alternative to this category of composites, which minimize the disadvantages mentioned, is the metal matrix composites reinforced with amorphous metallic particles, [2]. The first researchs in the field of lightweight metal matrix composites - aluminum alloys – reinforced with amorphous metal /fibers dates from 2004 (Lee et al., 2004), followed in 2006 by Yu's team. Promising results were also obtained with magnesium matrix [2, 3, 6]. Various techniques have been proposed, both in liquid and solid state, [10].

The paper aim is the obtaining in solid state by mechanical alloying of the Ni-Ti amorphous alloys used as a reinforcing element in magnesium matrix composites. Preparation of Ni-Ti system amorphous intermetallic compounds by mechanical alloying process dates back to the 1980's: Schwartz, RB et al, 1985, Hellstern and L. E. Schultz, 1987 Battezzati L. et al, 1988, J. Eckert et al, 1991 BS Murty et al, 1992, etc. They have obtained Ni-Ti particulate alloy, from elemental powder mixtures by mechanical alloying. In some works, the amorphous structure is reported only in equiatomic mixture; while for other compositions with varying proportions were reported amorphous and crystalline phases. On the other hand, a wide range of composition (0.28 to 0.72 atomic fraction of Ni) of amorphous alloy has been reported. It can be concluded, therefore, that the modification of the milling parameters (milling speed, time, process control agent, the type and size of the balls, the ball -to - powder mass ratio), and the characteristics of grinded powder mixture (variable proportions of Ni or Ti powder, size, morphology) conduct to the preparation of a powdered Ni-Ti system alloy, with variable amounts of the amorphous component in the structure. Thus, due to the complex influence of all grinding parameters, grinding conditions and the characteristics of the powder mixture, the mechanical alloying technique still requires a very careful evaluation.

2. EXPERIMENTAL PART

In order to obtain amorphous alloys by powder metallurgy route, were used comercially elemental Ni powder (mean size: 44 μm, purity: 99.8% Supplier: Alfa Aesar, USA) and Ti powder (mean size: 100 μm purity: 99.9% Supplier: Alfa Aesar, USA).
The chemical composition of two weighed mixtures, expressed as a weighted percentage, was the following: Mixture 1. 55 wt.% Ni and 45 wt.% Ti;

Mixture 2. 72 wt.% Ni and 28 wt.% Ti. Mixtures 1 and 2 were grinded in a Retsch PM 400 high energy planetary mill for 10 and 40 hours, respectively. Grinding was conducted in a stainless steel vial (250 ml) containing 15 mm diameter of grinding balls and the powdered sample. The ball to powder weight ratio was 7: 1 and the rotation speed was 250 rpm. About 5 wt.% stearic acids was added as a lubricating agent - PCA (process control agent).

Both powder mixtures, before and after grinding, were investigated by X-ray diffraction techniques and scanning electron microscopy using a PANALYTICAL X'PERT Pro diffractometer with horizontal Bragg-Brentano geometry and copper anticathode as well an SEM QUANTA FEG 450 electronic microscope. The notation of samples analyzed by X-ray diffraction and electron microscopy is shown in Table 1.

Table 1. Samples notation of Ni-Ti powder mixtures according to chemical composition and milling parameters

Sample	Chemical composition		Milling conditions		Milling hours
	at. %	wt.%	Air	Ar	
1.1.	$Ni_{50}Ti_{50}$	$Ti_{45}Ni_{55}$	-	-	As-mixed
1.2.			x	-	10
1.3			-	x	40
2.1.	$Ni_{68}Ti_{32}$	$Ni_{72}Ni_{28}$	-	-	As-mixed
2.2.			x	-	10
2.3.			-	x	40

3. RESULTS AND DISCUSSIONS

3.1. X-ray diffraction

Figure 1 and 2 shows the X-ray diffraction patterns of samples 1.1, 1.2 and 1.3 and samples 2.1, 2.2 and 2.3 respectively.

Samples milled for 10 hours (sample 1.2 and 2.2)

As can be seen from the x-ray diffraction pattern, both powder mixtures contain oxides: nickel titanate - $TiNiO_3$, present only in sample 2.2 and mixed nickel and titanium oxide - Ni_2Ti_4O and TiO_2 (anatase) present in sample 1.2. Oxides are formed in the presence of air from the grinding chamber. Nickel titanate was most likely formed according to the reaction: $NiO + TiO_2 \rightarrow NiTiO_3$ (1) at high temperatures arround 1000°C, [5]. In the mechanical milling process, the heat required to produce the reaction (1) is assured, on the one hand, by the impact energy transmitted from the ball to the powder, [7], and, on the other hand, the formation of NiO and TiO_2 oxides is accompanied by releasing a significant amount of energy, [8].

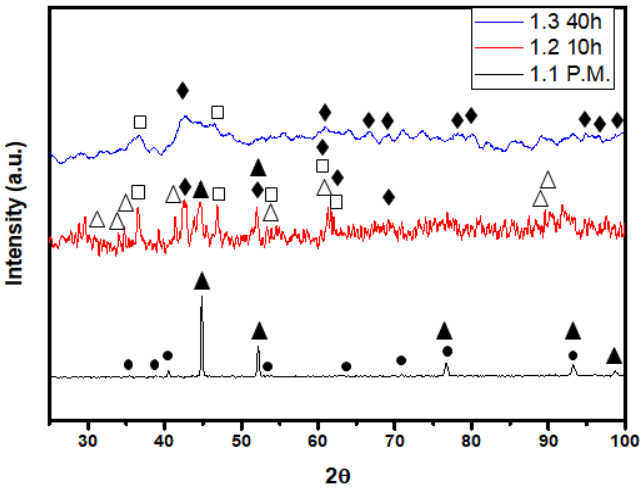


Fig. 1. X-ray diffraction patetern of samples 1.1, 1.2 and 1.3; ▲Ni,●Ti, ♦NiTi, □TiO_2, △Ni_2Ti_4O

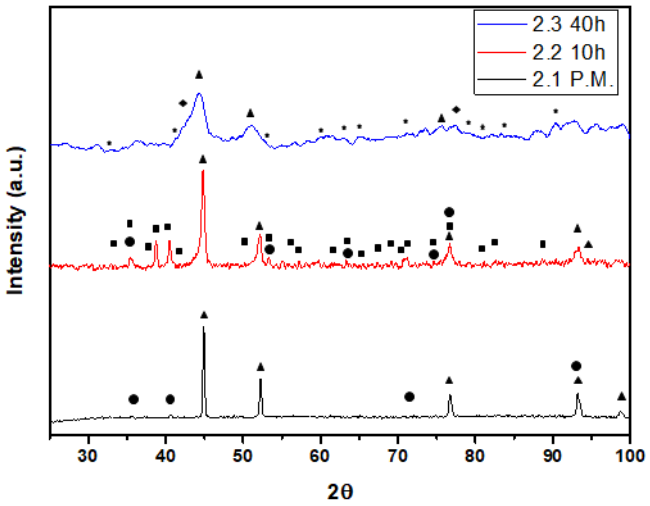


Fig. 2. X-ray diffraction patetern of samples 2.1, 2.2 and 2.3; ▲Ni,●Ti,♦NiTi,■ $NiTiO_3$,★$NiTi_2$

As mentioned above, the presence of oxygen in the grinding chamber contributes to the increasing of energy and temperature, respectively. A higher temperature than that usually developed in the vial - in the absence of exothermic reactions or oxygen - favors mechanical alloying, so in sample 1.2 the NiTi compound is formed, together with titanium oxide and mixed nickel and titanium oxide: TiO_2 and Ni_2Ti_4O. In XRD pattern of sample 1.2, nickel lines are also observed. Their presence certifies the partial production of mechanical alloying. On the other hand, in the sample 2.2.pattern only nickel and nickel titanate-specific diffraction lines are found. Due to the large differences in the Ni and Ti ratios (72% vs. 28%) which were increase the mechanical segregation of the powders, in the mixture 2.2. Ni-Ti compounds are not formed, but only the elemental powders are oxidized. It can be argued that in this case, grinding in the presence of air has a negligible influence on the formation of intermetallic compounds.

Identification in sample 1.2 of mixed nickel and titanium oxide, Ni_2Ti_4O, exhibit from the oxidation of the NiTi compound, [9], formed as a result of mechanical alloying, and the presence of the anatase phase indicates the oxidation of the titanium particles. The diffraction pattern of sample 1.2 highlights NiTi compound lines absent in sample 2.2, meaning that in the first case the mechanical alloy occurred - even partially, while in the second case only milling was performed. Thus, in the diffraction pattern of sample 2.2 was observed the nickel and titanium lines, no displacement positions of them from homologous lines shown in the sample 2.1 pattern. This demonstrates the absence of solid solutions Ti (Ni) or Ni (Ti). Broadening of diffraction lines, as well as their lower intensity, provides qualitative information on the reduction of crystallite size (mosaic blocks) after milling for 10 hours.

Samples milled for 40 h (sample 1.3 and 2.3)

The diffraction pattern of sample 1.3 reveals the presence of majority NiTi compound with nanocrystalline structure and an obvious amorphization tendency (broadening of peaks, with low intensity). There are also traces of TiO_2 (anatase) due to the absence of a perfect seal of the vials were the powders were milled. Mechanical alloying was totally occurred. In sample 2.3, the mechanical alloying take place with the formation of $NiTi_2$ and NiTi compounds as well as a solid nickel-based solution whose peaks are marked on the diffraction pattern with the ▲ symbol. The left movement of these diffraction lines related to the pure nickel in the XRD pattern of sample 2.1, confirm the formation of a solid (Ni) solution, most likely due to segregation of the powder mixture, segregation favored by the high proportion of nickel and its ductility.It can be seen a tendency to decrease the mean crystallite size that can be qualitatively estimated on diffractograms through broadening of peaks simultaneous with mouvement of their height, which also determines the "disappearance" of some of them. Analyzing the x-ray pattern shown in Figure 1, a slight decrease in intensity, accompanied by broadening of the diffraction lines of sample 1.2 versus sample 1.1 was observed. This trend is perfectly highlighted in sample 1.3. It can be conclude that in the case of the $Ti_{45}Ni_{55}$ (wt.%) mixture, the decreasing of the crystallite size occurs almost simultaneously with the mechanical alloying. From the point of view of the intensity and broadening of the diffraction lines, the diffraction pattern of sample spectrum 2.2 is similar with sample 2.1. For sample 2.3, it can been observed a significant broadening diffraction lines are observed compared to the unmilled sample, 2.1, we can not claim the presence of a mixed amorphous - crystalline structure as found in sample 1.3. The mean crystallite size was calculated using the Debye-Scherrer formula, [1]:

$$d = 0.9 \lambda / L \cos \theta \quad (1)$$

where d is crystallite size, λ is the radiation wavelength X (in this case, copper), L is the broadening at half the maximun intensity, θ is the Bragg angle of diffraction.

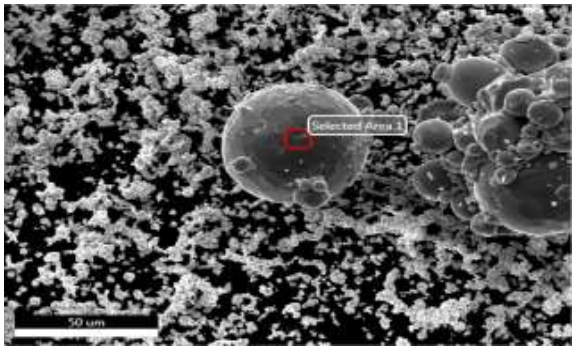
The evolution of the crystallite size by milling time for samples "1" and "2" is shown in the table below.

Table 2. Mean crystallite size of the Ni-Ti powder mixture

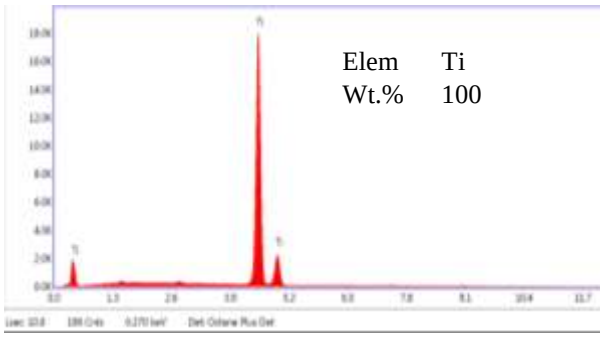
Sample	Mean crystallite size, d (nm)
1.1	44.46
1.2	38.94
1.3	20.28
2.1	51.69
2.2	48.42
2.3	32.36

3.2. Scannig electron microscopy

The scanning electron microscopy images, as well as the energy dispersive X-ray spectroscopy analysis (EDS) of samples 1.1 and 2.1 for a selected area are shown in Figures 3-5.

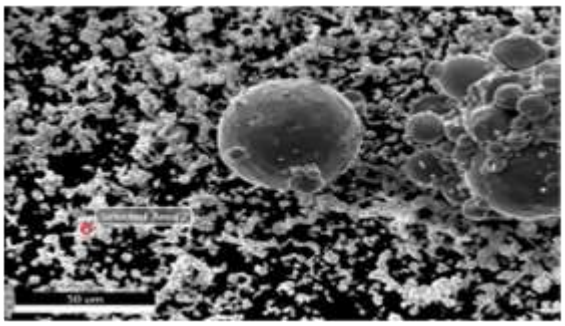


a.

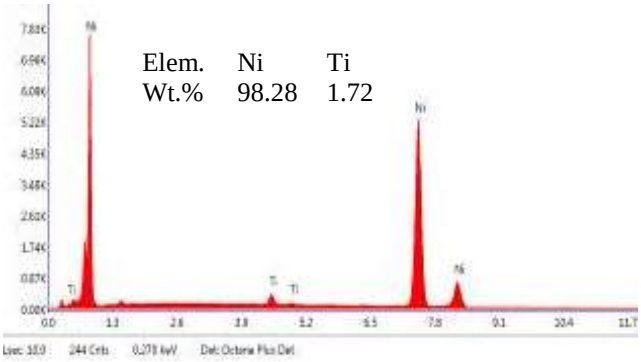


b.

Fig. 3. a. SEM –SEI image of sample 1.1; b. EDS analysis of selected area from figure 3a

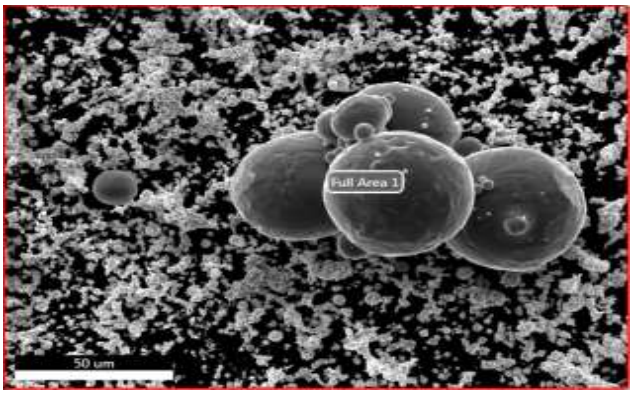


a.

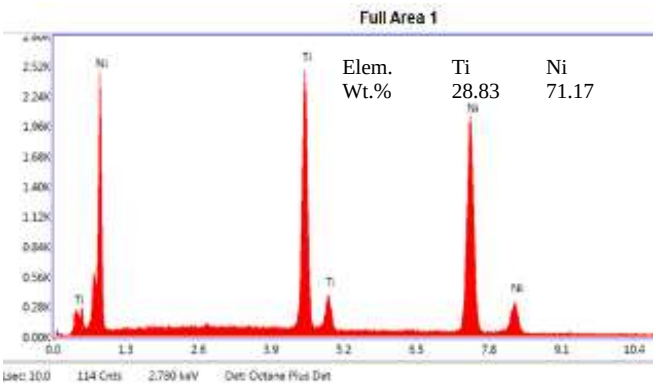


b.

Fig. 4. a. Selected area from sample 1.1 for EDS analysis; b. EDS analysis for selected area from figure 4a



a.



b.

Fig. 5. a. SEM- SEI image of sample 2.1; b.EDS analysis of full area from figure 5a

The above micrographs highlight the morphologies and dimensions of elemental powders: the large size, spherical are titanium paticules, and small, agglomerated, irregularly shaped (flakes) are nickel particles. EDS analysis confirms that the spherical particles are titanium and that irregular shape, with agglomeration tendency are nickel paticles (Figures 3 and 4). The chemical composition calculated according to the energy dispersive x–ray spectroscopy analysis (Figure 5b) is in agreement with the proportions of powders set for the mixture "2", which confirms a good homogenization.

The electron microscopy images of samples 2.1 and 2.2, as well as the energy dispersion X-ray spectra for the selected areas are shown in Figures 6-9. Micrographs shown in Figures 6 and 7 highlight the Ni clusters agglomeration, more visible in sample 2.2 (central area of micrograph), due to the fact that Ni is soft and ductile with high susceptibility to cold welding.

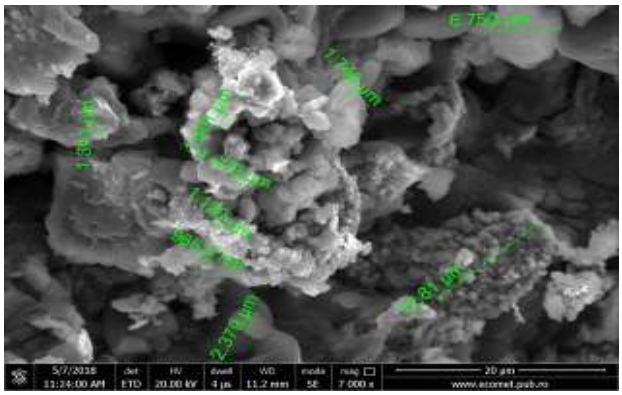


Fig. 6. SEM- SEI image of sample 1.2

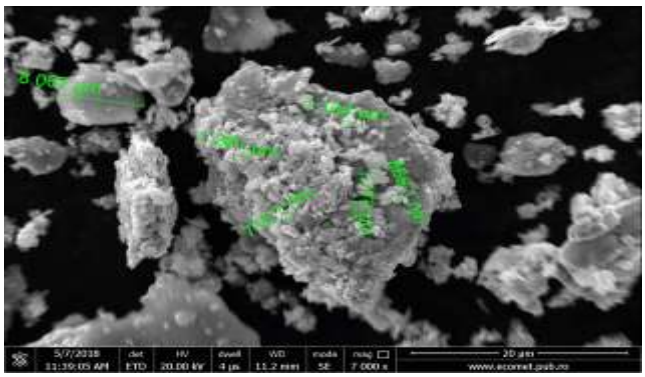
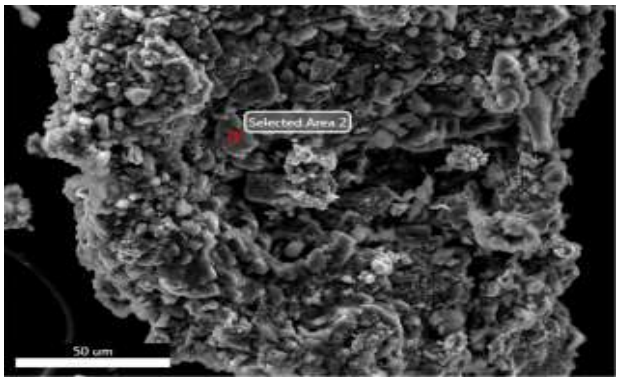


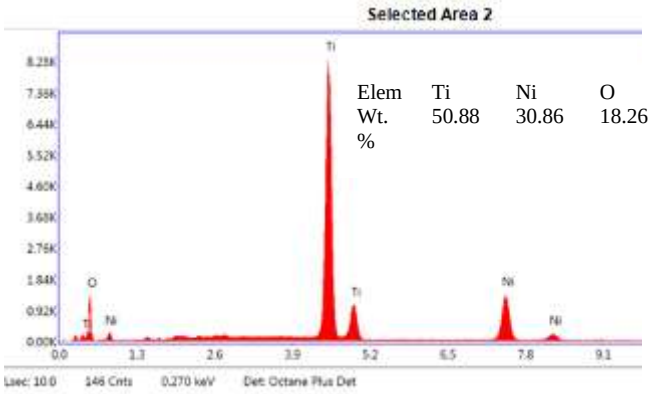
Fig. 7. SEM - SEI image of sample 2.2

The electron microscopy images are in concordance with the diffraction patterns, which conform the presence of Ni in both sample 1.2 and sample 2.2.

It can been seen the particle size varying from 1 to 30 μm (Figure 5) and 0.7 to 31 μm, respectively (Figure 6). It is noted that no major differentiation occurs from one sample to the next.



a.



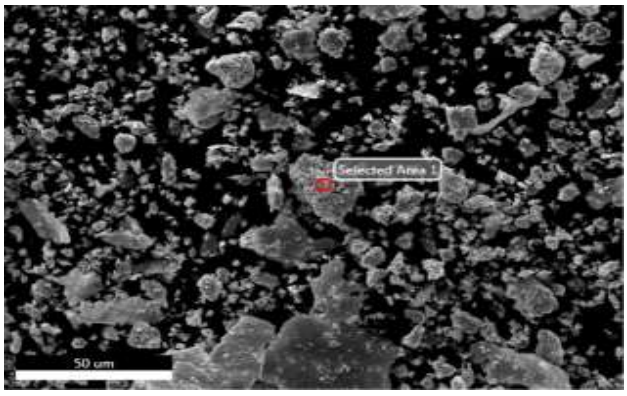
b.

Fig. 8. a. Selected area from sample 1.2 for EDS analysis; b. EDS patern of selected area from figure 8a

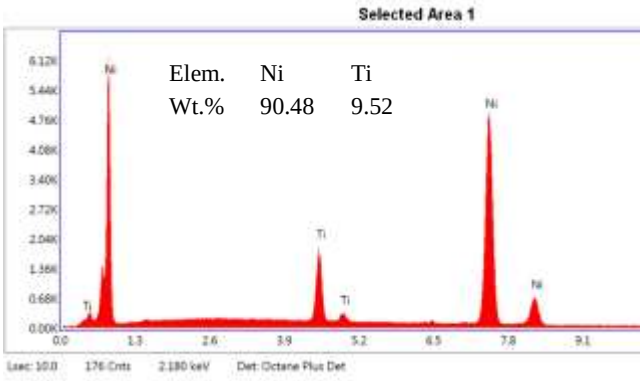
The EDS analysis confirms the presence of Ni, Ti and O, according to the phases present in the difraction patern of sample 1.2. Concidering the lower Ni, it is possible that the TiO_2 and NiTi phases to be found in the selected area.

The selected area reveals a Ni-rich area, possibly having the following phase composition: Ni and a small Ti amount. The EDS results are in agreement with the X-ray diffraction patterns.

The electron microscopy images of samples 1.3 and 2.3, as well as the X-ray energy dispersion spectroscopy for the selected areas are shown in Figure 10-13.



a.



b.

Fig. 9. a. Selected area from sample 2.2 for EDS analysis; b. EDS analysis of selected area from figure 9a

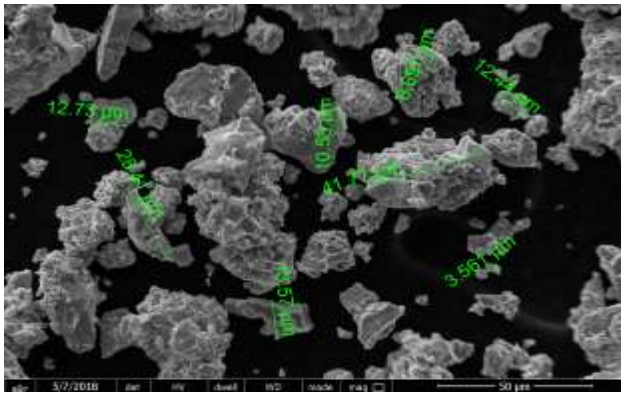


Fig. 10. SEM- SEI image of sample 1.3

The microscopic examination of 40 hours ball milled sample reveal a large size conglomerates more than in milled 10 hours sample, due to the increasing of milling time.

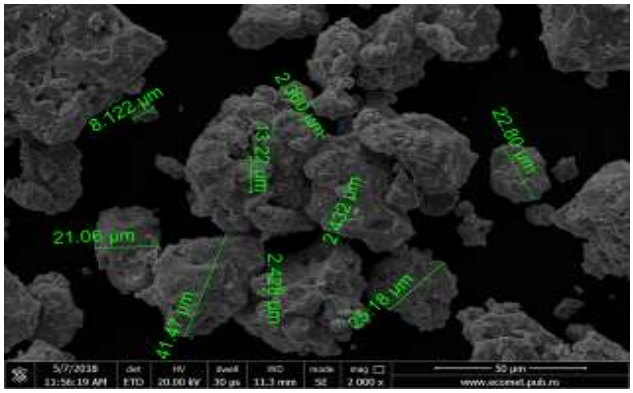
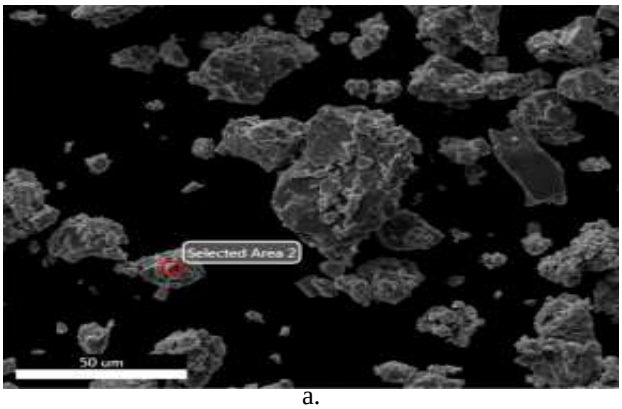


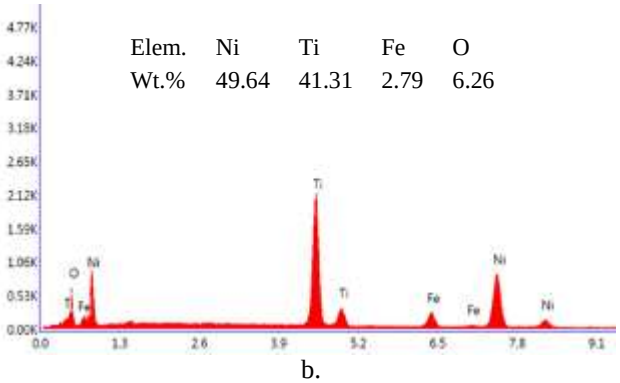
Fig. 11. SEM- SEI image of sample 2.3

In the milled samples after 40 hour, the existence of larger cthe particles size variate from 2 to 55 µm. Similar with sample 1.2 and 2.2, neither in this case there are no differences between particle size in sample 1.3 and 2.3.

The EDS analysis results confirm the qualitative phase analysis from XRD diffraction pattern and the Ni and Ti proportion of both mixtures "1" and "2":

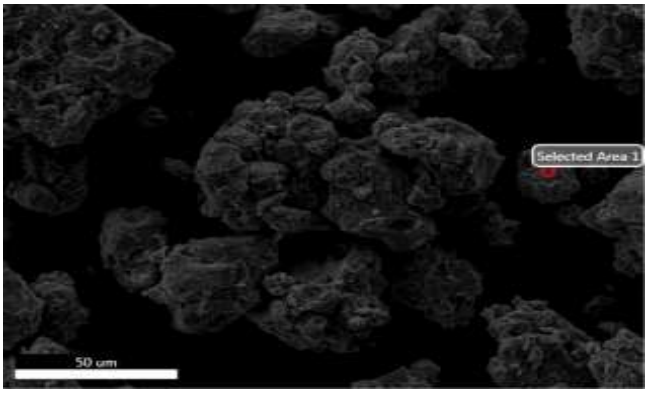


a.

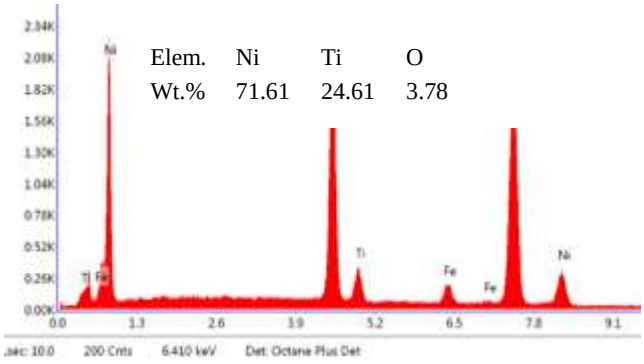


b.

Fig. 12. a. Selected area from sample 1.3 for EDS analysis; b. EDS patern of selected area from figure 12a



a.



b.

Fig. 13.a. Selected area from sample 2.3 for EDS analysis; b. EDS patern of selected area from figure 13a

- the presence of Ni and Ti percentage in both samples is in concordance with initial chemical composition of the as mixed powders;
- diffractogram of sample 1.3 reveal the presence of a small quantity of titanium oxide confirmed by the presence of oxygen determined by EDS analysis;
- the presence of iron determined by EDS analysis is due to an impurification of the samples from stainless steel milling ballsand the possible phases which are containing iron (iron oxides, iron-based solid solution) are in small quantity in the sample volume at which the X-ray diffraction has been made, so that it is below the detection limit of the diffractometer.

4. CONCLUSIONS

Ni and Ti powders mixtures having the following compositions: 45 wt.% Ni,55 wt.% Ti and 72 wt.% Ni, 28 wt.% Ti were prepared by ball milling in a high energy planetary mill for 10 hours, respectively, 40 hours.

For the sample with 45 wt.% Ni and 55 wt.% Ti after 10 hours of milling, a partial alloying was noticed accompanied with a decrease of crystallite mean size. After 40 hours of milling the mechanical alloying was totally achieved simultaneous with a significant decreasing of the crystallite size. The structure obtained is mixed (amorphous and crystalline) indicating the presence of NiTi compound and a small quantity of oxide.

In the sample with 72 wt.% Ni and 28 wt.% Ti after 10 hours of milling there was observe a decrease of crystallite size; the mechanical alloying did not occur. After 40 hours of milling the mechanical alloying was totally achieved simultaneous with decreasing of the crystallite size. The trend towards amorphization is much lower and the amorphous component in the structure is insignificant. The future researches will be focused in developing of Mg matrix composites reinforced with $Ni_{50}Ti_{50}$ (at.%) and $Ni_{68}Ti_{32}$ (at.%) amorphous alloys by powder metallurgy route.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. Birks, L. S., Friedman, H., (1946). *Particle Size Determination from X-Ray Line Broadening.* Journal of Applied Physics, 17, 687.

2. Jayalakshmi, S., Gupta, M., (2015). *Metallic Amorphous Alloy Reinforcements in Light Metal Matrices*, edited by Springer Brief Series (Materials), Springer, New York, USA, 10.1007/978-3-319-15016-1.
3. Jayalakshmi, S., Seetharaman, S., Gupta, M., (2015). *Processing and Properties of Aluminum and Magnesium Based Composites Containing Amorphous Reinforcement: A Review*, Metals, 5, 743-762.
4. Jayalakshmi, S. et al.,(2018*). Metallic Glasses as Potential Reinforcements in Al and Mg Matrices: A Review*, Technologies 2018, 6(2), 40.
5. Ruiz-Preciado M.A., Kassiba A., Gibaud A., Morales-Acevedo A., (2015). *Comparison of nickel titanate (NiTiO3) powders synthesized by sol–gel and solid state reaction*, Materials Science in Semiconductor Processing 37, 171–178.
6. Sankaranarayanan S., Agrawal N., Jayalakshmi S., Nguyen Q.B., Gupta M., (2015). *Synthesis and Characterization of Novel Magnesium Materials Containing Copper-Titanium Based ($Cu_{50}Ti_{50}$) Amorphous Alloy Particles*, in Magnesium Technology, edited by Manuel M.V., Singh A., Alderman M., Neelameggham N.R, Springer, Cham, 387-390.
7. Suryanarayana C., (2001). *Mechanical alloying and milling*, Progress in Materials Science, 46, 1-184.
8. Wang, K. Y., Wang, J. T., Shen, T. D., Quan, M. X., (1992). *Effect of atmosphere on further milling mechanically alloyed Ni60Ti40 amorphous powders*, Journal of Materials Science Letters, 11 , 1170-1172.
9. Wu, Z., Mahmud, A., Zhang, J., Liu, Y., Yang, H., (2018). *Surface oxidation of NiTi during thermal exposure in flowing argon environment*, Materials & Design, 140, 123-133.
10. Zhang, X., Wang J., Sun, Y., Liu. J., (2009). *Metallic Glass Particle Reinforced Al-Based and (Al–Ni)-Based Metal Matrix Composites*, Combustion, Explosion and Shock Waves, 45(2), 230–235.

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