The Effect of Ultrasonic activation on the Microstructure and Phase Transformation of Porous Ni-Ti Shape Memory Alloys

Dovchinvanchig Maashaa[a], Baasanjargal Narmandakh[b]

[a]*School of Applied Sciences, Mongolian University of Life Sciences, Ulaanbaatar, 17024, Mongolia*

[b]*Medical University of Ikh Zasag International University, Ulaanbaatar, Mongolia*

Porous Ni-Ti shape memory alloys (SMAs) have been widely studied in Biomaterial for biomedical applications because they have a porous structure similar to human bone and corrosion resistance. A porous Ni-Ti SMAs was obtained by self-propagating high-temperature synthesis (SHS) and investigated its microstructure and phase transformation. This article presents the results of a study of changes in the microstructure and phase transformation of porous Ni-Ti SMAs when Ni and Ti metal powders were preliminarily subjected to ultrasonic activation at different amplitude (5-25μm). The results show that the microstructure of porous Ni-Ti SMAs consists of Ni-Ti matrix and Ni-Ti_2 precipitates. Two-step phase transformation was observed in porous Ni-Ti alloys.

Keywords: Microstructure, Phase transformation, Ultrasonic, Ni-Ti alloy.

INTRODUCTION

NiTi SMAs are smart structural alloy with extensive applications due to their excellent and unique mechanical properties such as shape (SME), super elasticity (SE) [1], and corrosion resistance [2]. The recent development of NiTi SMAs as a porous, low-density, high-porosity material has attracted considerable interest from researchers due to its unusual mechanical properties similar to some natural biomaterials [3].

Porous NiTi alloy has a porous structure similar to the structure of human bones and has many advantages, such as supporting the metabolism and growth of living organisms, and improving the connection between joints, so it can be used as a hard implant for teeth, bones, muscle tissue, artificial organs, filling gaps in heart valves, and vasodilators [4-5].

Compared to the common methods of extracting NiTi alloys, the self-propagating high-temperature synthesis method is an important and efficient method to save energy and time [6]. Many researchers have identified that alloy properties are affected by (like green density, heating temperature, heating rate and preheating temperature) factors[7-9].

Alloys produced by the self-propagating high-temperature synthesis method have more additional phases. Although the presence of different phases such as $NiTi_2$ and Ni_2Ti in porous NiTi shape memory alloys make the material brittle and increases the risk of corrosion, these porous NiTi alloys show very little corrosion compared to other biomaterials [10].

The heat-treatment research by changing the strength and phase temperature of the material (final austenitic temperature) is the most proper solution to this issue. M. Kaya et al. developed a heat treatment method to obtain porous pure NiTi [10].

Research works have been carried out to change the microstructure and improve the mechanical properties of Ti-Al and Al-Mg3 alloys by ultrasonic treatment [11-12].

Previous studies have shown that the thermal conductivity of Ni-Ti powder can be changed by ultrasonic vibration. Ultrasonic activation provided the formation of a more isotropic porous structure, which was formed during SHS, due to a change in the mode of the propagation of the combustion wave from pulsed to stationary. The Ultrasonic vibrations treatment reduces the size and volume fraction of precipitates and makes the chemical composition of the Ni-Ti phase more uniform which affects the phase transformation and alloy characteristics [13].

In the previous work, we to studied the effect of preliminary activation of metal powders by ultrasound at different periods depending on the activation time on microstructure, porosity, phase transformation, and mechanical properties of Ni-Ti SMAs by SHS [14].

The purpose of this study was to investigate and compare the changes of microstructure, porosity, and phase transformation depending on the amplitude of ultrasonic application prior synthesizing the porous Ni-Ti alloy, which were activated the metals in powder form for different amplitude (5-25 μm) synthesized by SHS.

EXPERIMENTAL

The powders of high –purity Ti (catalogue type PTOM-2) and Ni (catalogue type PNK-1L5) powders with an average grain size of 40 μm were mixed in the composition of Ti-50at. % Ni-50at.%. The samples were activated by the ultrasonic disperser UZDN-1M with frequency of 22 kHz and different an amplitude of 0, 5, 15, 25 μm for 60 minutes. The mixture was put into a quartz tube with a diameter of 30 mm (mixture green density was 2.4 g/cm3), inside the thermal chamber. The mixture was heated to 350°C in an argon atmosphere (p = 1 atm) and held for 1 hour. Then, the SHS reaction was initiated by heated tungsten wire by electrical current. The SHS reaction took place for 5 seconds, and then the samples were cooled inside the thermal chamber. SEM observations were conducted using a Jeol-6000Plus s instrument (Jeol, Akishima, Japan) by method SEM equipped with EDS analysis systems made by Oxford. Heat flux measurements were carried out during cooling and heating using a DSC 214 Polyma differential scanning calorimeter NETZSCH-Gerätebau GmbH. The rate of cooling and heating was 10°C/min, the temperature range of studies was from -60ºC to 140ºC. Proteus software was used to process the results. The porosity of the porous Ni-Ti alloy sample is determined by equation 1 [15, 16] .

$$P = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\% \qquad (1)$$

Where, ρ is the density calculated from the mass and volume values of the porous Ni-Ti alloy, ρ_0 is the theoretical density of the material (6.21 $г/см^3$). The porosity of the obtained Ni-Ti SMAs was 63 – 68 vol% . If the amount of porosity (50-70%) is high open porosity NiTi SMAs and exhibit shape memory behaviour as observed in bulk NiTi shape memory alloys.

RESULTS AND DISCUSSION

The surface microstructure of the extracted samples was measured on scanning electron microscope SEM is shown in Fig. 1. As can be seen from the image of the microstructure of the side surface of the sample (Fig. 1a), the shape of the pores of the non-ultrasonic sample is uniform channel with an average width of about 250 μm and a length of about 1000 μm. This narrow channel structure is similar to the research work of Mehmet Kaya[17] and Musa Kilic [18]. The size of the pores of the samples treated with ultrasonic is larger, 500-1000 μm, and the shape is generally circular.

According to the results of measurements of the surface morphology image on a scale of 20 μm, in general, a gray phase main matrix and black phases formed on the surface of the alloy.

The composition of the phases was measured by EDS. Table 1 shows the elemental composition of Ni-Ti alloy with porous structure. In all Ni-Ti alloys with a porous structure, the gray matrix phase Ti:Ni composition volume ratio is approximately 1:1, so the matrix phase is a Ni-Ti phase. Different phases, such as additional Ti2Ni, Ni3Ti, Ni4Ti3, etc., are formed in the samples obtained by self-propagating high-temperature synthesis [15, 19].

On the surface of the Ni-Ti alloy with non-ultrasonic-treated porous, the black phase is formed by the Ti2-Ni phase phase alone. On the surface of the sample subjected to ultrasonic for oscillation amplitude of 5 μm, 15 μm, 25 μm a black phase with a Ti:Ni ratio of approximately 2:1 and a Ti2-Ni phase was formed (Figure 2 and 3).

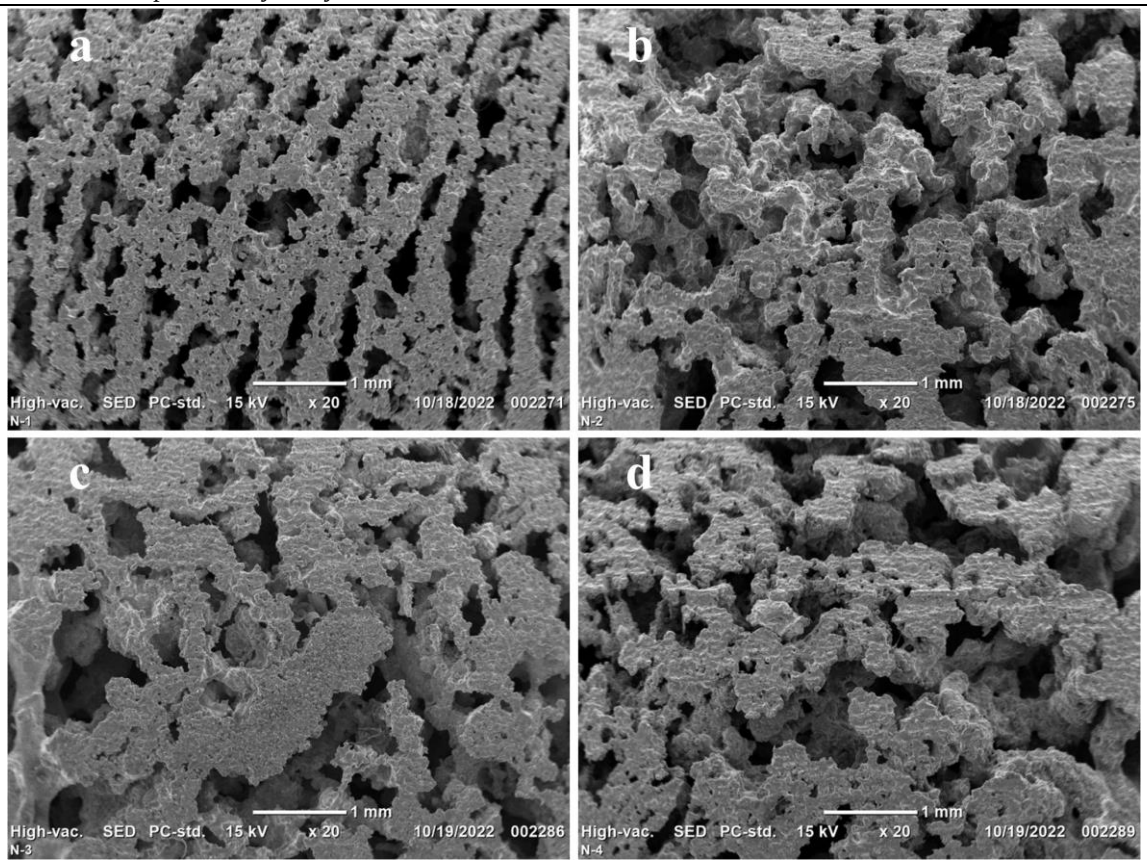

Fig. 1, Microstructure of porous Ni-Ti alloys ultrasonic activation for amplitude: (a) Not treated by ultrasonic, (b) 5 µm, (c) 15 µm, (d) 25 µm

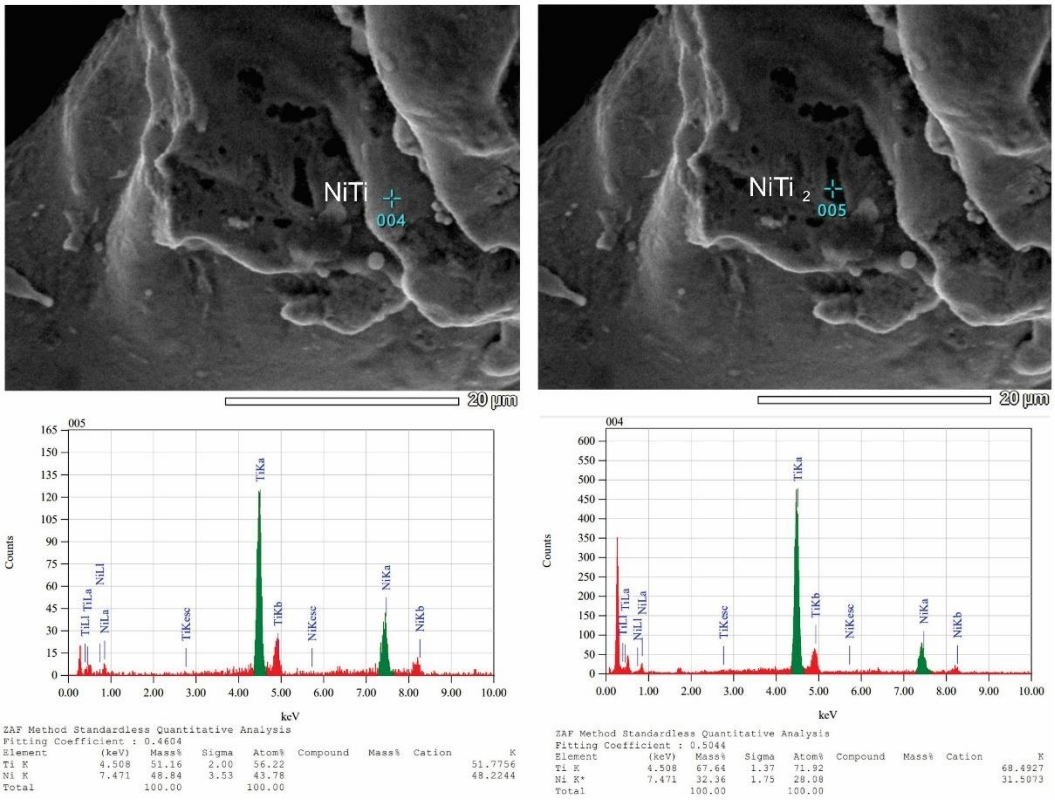

Fig. 2. Microstructure and EDS results of sample ultrasound treated for amplitude of 5 µm

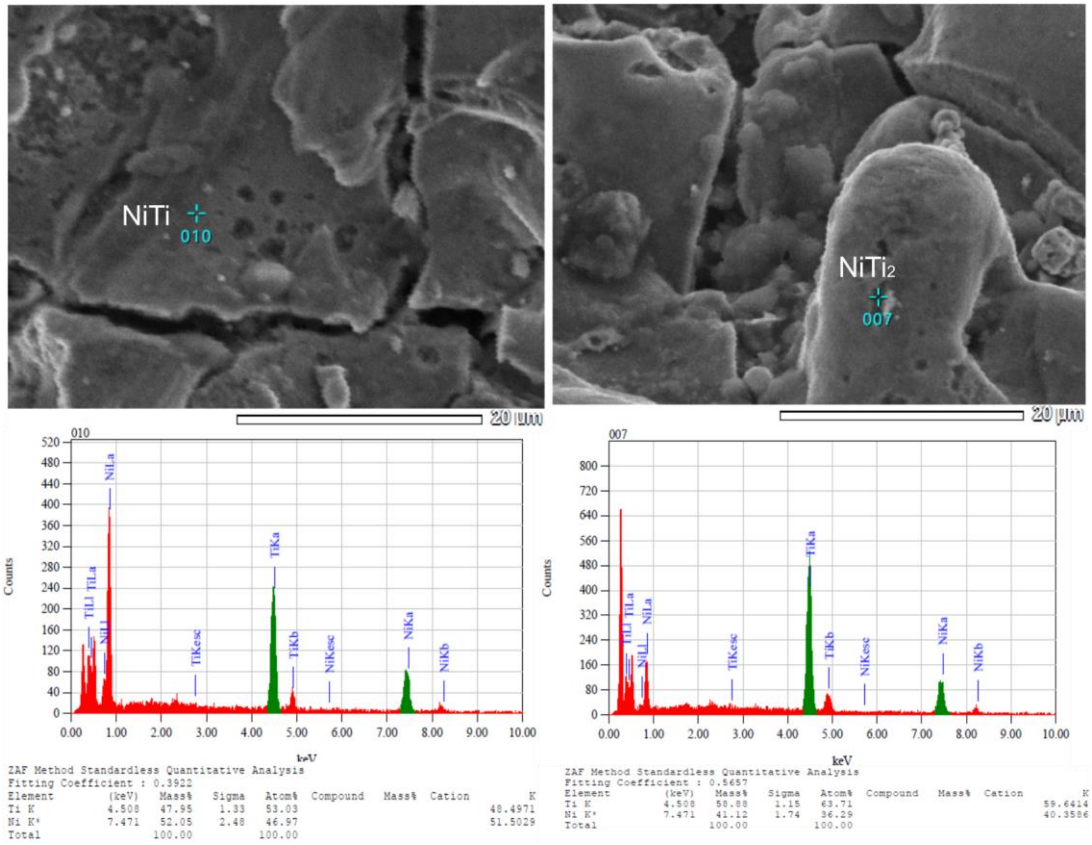

Fig. 3. Microstructure and EDS results of sample ultrasound treated for amplitude of 15 µm

Table 1. Composition of porous Ni-Ti SMAs

№	Sample	Ultrasonic activation for an oscillation amplitude µm	Phase	Ti (at. %)	Ni (at. %)	Formed phase
1	Sample A	0	Matrix	57.13	42.87	Ni- Ti
			Black phase	66.99	33.01	Ni- Ti_2
2	Sample B	5	Matrix	56.22	43.78	Ni-Ti
			Black phase	71.92	28.08	Ni- Ti_2
3	Sample C	15	Matrix	53.03	46.97	Ni-Ti
			Black phase	63.71	36.39	Ni- Ti_2
4	Sample D	25	Matrix	52.37	47.73	Ni- Ti
			Black phase	68.45	31.55	Ni- Ti_2

Typical calorimetric curves for a sample obtained by the SHS method are shown in Figure 4 Ti-Ni alloy obtained by the SHS method at a temperature of 350ºC after preliminary ultrasonic activation of Ni/Ti powder mixtures for 60 minutes with an amplitude of 0, 5, 15, 25 µm and a frequency of 22 kHz.

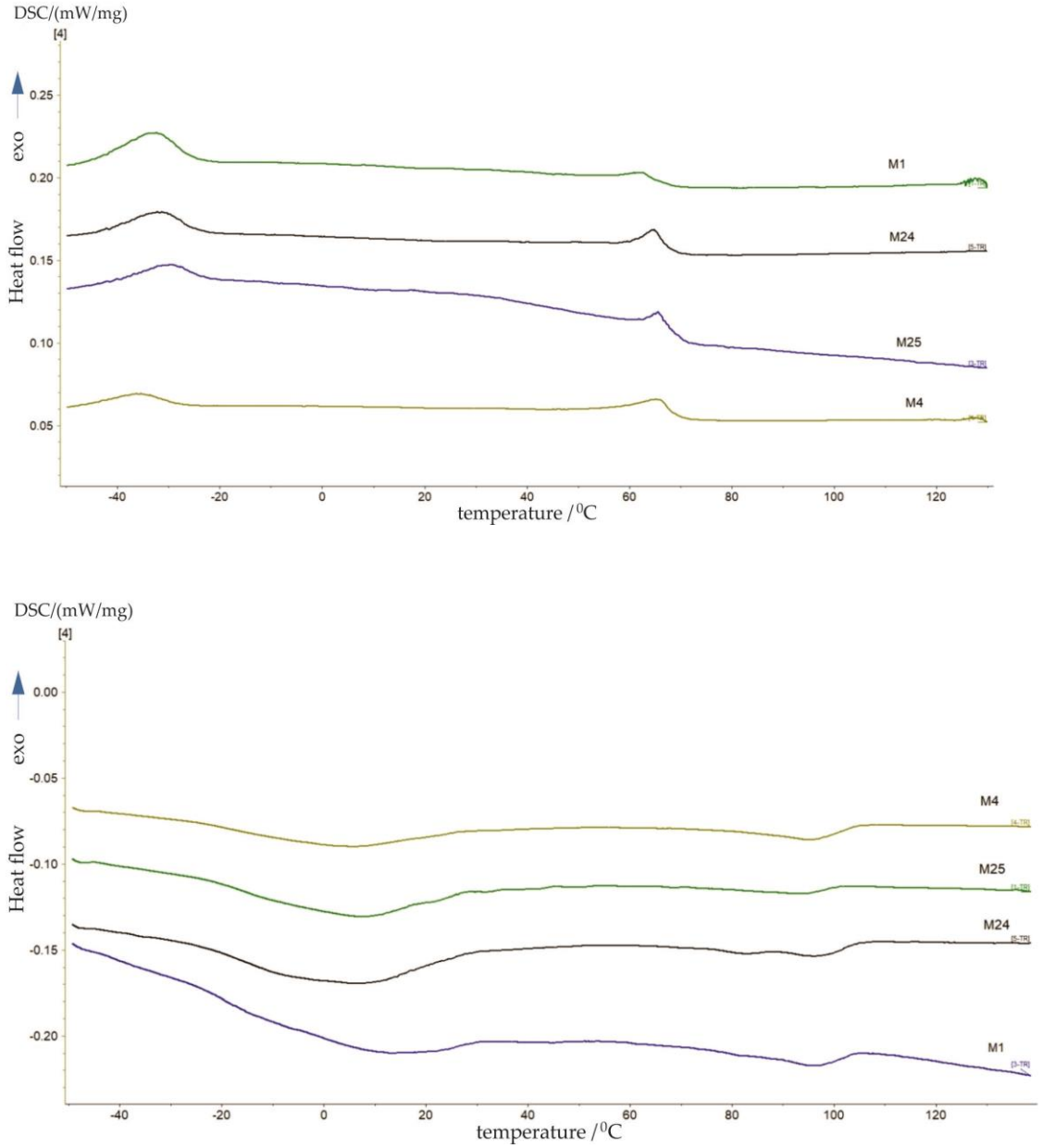

Fig. 4. Calorimetric curves obtained during cooling (a) and heating (b) of porous Ni-Ti samples obtained by SHS without ultrasonic activation (M1) and 5 μm (M24), 15 μm (M25) and 25 μm (M4)

Fig. 4 show two calorimetric peaks for all porous samples obtained by SHS upon cooling and two peaks upon heating. The high temperature peaks are due to the B2→B19' transformation in titanium rich NiTi and the low temperature peaks are due to the transformation in nickel rich NiTi. The low intensity of the high-temperature peaks of the sample M1 indicates that the volume fraction of Ti-rich NiTi regions is smaller than the fraction of Ni-rich NiTi regions [13, 20].

Preliminary ultrasonic treatment increases the intensity of high-temperature peaks. The longer the amplitude of ultrasonic testing, the greater the intensity of the peaks is observed. It is explained by an increase in the volume fraction of the Ti-rich NiTi phase. This indicates that the volume fraction of the Ti-rich NiTi phase increases when the contact of the Ti and Ni powders with each other is activated due to ultrasound. The characteristic temperatures of the low-temperature and high-temperature peaks practically do not change (Table 2), which indicates a constant Ti concentration in the NiTi regions subjected to such transformations. This may be due to the uniform distribution of Ti_2Ni precipitates.

Table 2. Phase transformation temperature of porous Ni-Ti SMAs

Sample number	M_{s1}, ºC	M_{f1}, ºC	A_{s1}, ºC	A_{f1}, ºC	M_{s2}, ºC	M_{f2}, ºC	A_{s2}, ºC	A_{f2}, ºC
M1	68	57	87	105	-25	-45	-22	27
M4	69	56	86	105	-27	-54	-24	26
M24	71	54	88	104	-24	-44	-23	27
M25	71	61	84	104	-24	-42	-22	30

CONCLUSIONS

In summary, the influence of ultrasonic a ctivation amplitude on the microstructure and ph ase Transformation of porous Ni-Ti shape memo ry alloys behavior was investigated experimentally. The microstructure of porous Ni-Ti SMAs consists Ni-Ti matrix and Ni-Ti_2 precip itates. The phase transformation temperature of p orous Ni-Ti SMAs is almost unchanged under th e influence of ultrasonic treatment amplitude.

Funding: *This project was supported by the joint Fundamental research project ShuKhtB-2021/02 of the Mongolian Foundation for Science and Technology and Belarusian Republican Foundation for Fundamental Research.*

Acknowledgments: *The researchers would like to thank Mongolian Foundation for Science and Technology for their financial support*

REFERENCES

[1] K. Otsuka, and X. Ren. Intermetallics. 1999, 7, 511. doi.org/10.1016/S0966-9795(98)00070-3.

[2] Sahar A.Fadlalah, Nader El-Bagoury, Sanaa M.F.Gad El-Rab, Rasha A.Ahmed, Ghaida El-Ousamii. J Alloys and Compd. 2014, 583, 455.

[3] N. Resnina, S. Belyaev, A. Voronkov. J Mater Eng Perfor. 2018, 27, 1257. https://doi.org/10.1007/S11665-018-3231-Z.

[4] G. Tosun, G, L. Ozle. J Alloys and Compd. 2009, 487, 605. https://doi.org/10.1016/j.jallcom.2009.08.023.

[5] G. Tosun, N. Orhan, L. Ozler, L, Mater Lett, 2012, 66, 138. https://doi.org/10.1016/j.matlet.2011.08.023.

[6] Javaherian, S.S., Aghajani, H. & Mehdizadeh, P. Int. J Self-Propag. High-Temp. Synth. 2014, 23, 47. https://doi.org/10.3103/S1061386214010051

[7] B. Y. Li, L. J. Rong, Y. Y. Li, V. E. Gjunter. Acta Mater. 2000, 48, 3895. https://doi.org/10.1016/S1359-6454(00)00184-1.

[8] W. Sirikul, D. Nipon, S. Lek. Mater. Sci. Eng. A. 2009, 515, 93. DOI: 10.1016/j.msea.2009.02.055

[9] C. A. Biffi, P. Bassani, Z. Sajedi, P. Giuliani, A. Tuissi. Mater. Lett. 2017, 193, 54. https://doi.org/10.1016/j.matlet.2017.01.097.

[10] M. Kaya, N. Orhan, B. Kurt, T. Khan,. J Alloys and Compd. 2009, 475, 378. https://doi.org/10.1016/j.jallcom.2008.07.023

[11] R.R Chen, D.H Zheng, et all.. Scientific reports. 2017, 7, 41463. doi: 10.1038/srep41463.

[12] P. Snopinski, T. Donie, et all.. Materials. 2021, 14, 1010. **https://doi.org/10.3390/ma14041010**

[13] N. Resnina, V.V. Rubanik Jr.V.V. Rubanik, S. Belyaev, V. Bysha, V. Kalganov, D. Chepela,. Letter on Mater. 2022, 12, 164. https://doi.org/10.22226/2410-3535-2022-2-164-168

[14] M. Dovchinvanchig, P. Enkhtsetseg, V.V. Rubanik Jr.V.V. Rubanik. *Materials* , 2023, *16*,6134.https://doi.org/10.3390/ma16186134

[15] Saadati, H. Aghajani. J Mater Sci. 2019, 30, 92. DOI: 10.1007/s10856-019-6296-9

[16] Jian, Y.T.; Yang, Y.; Tian, T.; Stanford, C,; Zhang, X.P,; Zhao, Ke.. PLOS one. 2015, 11, 0149051. DOI: 10.1371/journal.pone.0128138

[17] Kaya, M, Çakmak, Ö. Metall Mater Trans A. 2016, 47, 1499. https://doi.org/10.1007/s11661-015-3318-1.

[18] M.Kilic, B.Yenigun, S.Bati, Batman, Z.Balalan and I. Kirik. Materi Testing 2019, 61, 1140. DOI: 10.3139/120.111439

[19] P.Bassani, S.Panseri, A.Ruffini, M.Montesi, M. Ghetti, C.Zanotti, A.Tampieri, A.Tuissi. J Mater Sci Mater Med. 2014, 25, 2277. doi: 10.1007/s10856-014-5253-x

[20] Resnina, N.; S. Belayev, S.; Voronkov, A. Intermatellics. 2013, 32, 81. https://doi.org/10.1016/j.intermet.2012.08.009