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Preparation and Characterization of NiTi/PVA Nanofibers by Electrospinning

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HIGHLIGHTS

- Preparation of ultrafine NiTi particles by immersing sintered alloy in aqua regia.
- Preparation of composite biomedical NiTi /PVA nanofibers.
- Preparation of Nitinol nanofibers with polyvinyl alcohol.

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ABSTRACT

NiTi alloys are widely used in biomedical applications for their unique properties particularly the shape memory effect, superelasticity, and biocompatibility. In this research, NiTi/PVA composite nanofibers are fabricated by electrospinning technique, using a novel method of producing NiTi ultrafine particles by immersing amorphous NiTi alloy in dilute aqua regia solution. The NiTi particles are successfully embedded in the PVA matrix. The produced NiTi particles are analyzed by X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS), and Particle size analyzer. The XRD pattern of ultrafine NiTi particles shows much better phases as compared to the XRD pattern of the amorphous NiTi alloy sample. The morphology of the produced NiTi/PVA composite nanofibers are characterized by Field emission scanning microscope (FESEM), and Energy dispersive spectrometry (EDS). The test results show regular continuous smooth bead-free nanofibers.

1. Introduction

In recent years, more attention has been focused on the fabrication of nanomaterials [1]. Nanomaterials (nanoparticles, nanofibers, etc.) have been synthesized and developed for many scientific applications. Nanoparticles refer to objects ranging from 1-100 nm in size [2]. Nanoparticles exhibit good catalytic and have shown broad applications in many fields of materials science and engineering such as biomedicine, sensor, tissue engineering, energy storage, and environmental science [1]. Nickel-Titanium alloys are mostly used in biomedical industries due to their good biocompatibility, osseointegration, and corrosion resistance in addition to the unique characteristics: superelasticity and shape memory effect. These biomedical industries include orthopedic implants, orthodontic devices, and cardio stents. Hence, these alloys are generally categorized as smart materials [3]. The reversible solid-state martensitic transformation gives these alloys this special effect. At high temperature the material exhibits the cubic crystal structure austenite; at low temperature, it is monoclinic crystal structure martensite. At the martensitic phase, the material can be deformed by 6-8% without breaking its atomic bonds, this phenomenon known as twinning [4]. These effects occur within a certain temperature range and are highly dependent on the Ni-Ti ratio within a near equiatomic range [5]. NiTi materials conserve their properties onto nanosized, while there are many materials have different properties in nanosized compared to their bulk form [6]. There are many methods for producing NiTi nanoparticles [4]. The common method is the laser ablation of the alloy in a liquid [7]. Other production methods include ultrasonic electrolysis [7], mechanically assisted synthesis (metal powders in a planetary ball mill) [8], electro-explosion of a NiTi wire with spark-plasma sintering [9], gas-flash evaporation [10], thin-film deposition in combination with nanosphere lithography [11], electric-discharge plasma in liquid [12], and biosynthesis (bio-reduction) [13].

Electrospinning is the most common technique for nanofibers fabrication since it is conventional to use and control [14]. Fibers produced by spinning are ranging from micro to less than 100 nm, these fibers have a high surface area to volume, high porosity, and other superior properties that make them required in many fields for several applications [15]. In the NiTi spinning process, polyvinyl alcohol (PVA) was chosen because of its solubility in water, biocompatibility, and non-toxicity, in addition to good chemical and thermal stability. PVA is also forming fiber easily because of its nature, which makes it widely

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used in many applications [16–21]. Bai Jie, et al. prepared PVA/Gold nanoparticle composite nanofibers by electrospinning method [19]. Anjaneyulu et al. fabricated and characterized Ag-doped hydroxyapatite/PVA composite nanofibers for bone tissue engineering applications successfully by electrospinning with different concentrations of Ag-doped hydroxyapatite and PVA. They used sol-gel as a solution preparation method [20]. Akram R. Jabur, et al. fabricated PVA/Cu doped nanofibers by electrospinning for improving conductive and mechanical properties of PVA [21].

This work aims to synthesize ultrafine NiTi particles by using a novel method of immersing amorphous NiTi alloy in aqua regia solution, to be used in fabricating NiTi/PVA composite nanofibers by electrospinning.

2. Experimental

2.1 Preparation of NiTi particles

Nickel-Titanium alloy samples were prepared by powder metallurgy method from elemental components (properties of metal powders are shown in Table 1). 55% wt. of Nickel powder was mixed with 45% wt. of Titanium powder in a ball milling machine for 2 hours. After mixing, the green samples were obtained by placing the powder mixture in a tool steel die (10 mm diameter), and pressed by a 6 Ton hydraulic pressing machine (Model: KPD-50E, company: MEGA, Spain). The green samples were then sintered in Argon atmosphere furnace at temperature 950˚ C, for 6 hours.

Table 1: Properties of metal powders

Metal (powder)	Appearance	Purity (%)	Average particle size (µm)	Molecular weight	Company (Production)
Ni	Black to gray.	99.5	6	58.69	Metco, England.
Ti	Gray.	99	200	47.87	Fluka, Germany.

The sintered NiTi alloy sample (5 grams) was immersed in diluted aqua regia ($3HCL+HNO_3$) solution. 20 ml of aqua regia was prepared in the laboratory by mixing 15 ml of HCL and 5 ml of HNO_3 in a beaker [4], then diluted with 200 ml of water. After 3-4 weeks of immersing the sample, agglomerated particles of the alloy were precipitated in the bottom of the used vessel. These agglomerated particles have been washed many times with distilled water by using filter paper to remove the undesired contaminates. A conventional drying oven was used to remove the excessive moist from the particles. The agglomeration was dispraised by using a ceramic laboratory Morter and pestle to obtain the final ultrafine NiTi particles.

2.2 Electrospinning of NiTi ultrafine particles

Polyvinyl alcohol (PVA) was used as a matrix for the ultrafine NiTi particles in the spinning process. 15%wt. of PVA (Germany, M.w. 67,000) was dissolved in distilled water by stirring it for 2 hours, at ~40˚C temperate, and 20 rpm in speed. 2% wt. of the prepared NiTi particles were then added to the PVA solution and stirred for 10 minutes. An ultrasonic homogenizer (Model: 300 VT, company: Biologics, INC) was utilized to increase the dispersion of the particles with a 20 kHz frequency. Bio Electrospinning/ Electrospray system (Stent coating) (Model: ESB-200, company: NanoNc, South Korea) was used for nanofibers fabrication. The prepared colloidal solution was supplied in a conventional plastic syringe and a capillary needle (anode) connected to the nozzle of the syringe. A plate of stainless steel was used as a fiber collector (cathode). The solution was electrospun at 16 kV, 1 ml/h. flow rate, and 15 cm distance between the tip of the needle and the collector. The obtained electrospun fibers were removed carefully from the collector after finishing the spinning process.

2.3 X-ray diffraction (XRD analysis)

The sintered NiTi alloy sample and the produced ultrafine NiTi particles were both characterized by an X-ray diffractometer (Model: LabX XRD-6000, company: Shimadzu, United states). The X-ray tube: Cu (1.54060 A), 40 kV, and 30 A was used at operating. The XRD data were collected over a scan range of 10–90˚, with a step-size of 0.2˚step and a count time of 1.20 sec.

2.4 Particle size analysis

The produced ultrafine NiTi particles were characterized in particle size analyzer (NanoBrook 90Plus, company: Brookhaven, USA). The liquid that was used during the test was water, and the elapsed time was (00:01:30).

2.5 Energy Dispersive Spectroscopy (EDS)

The EDS analysis (company: Bruker, Germany) was used to investigate the elemental composition of both: the ultrafine NiTi particles, and the NiTi/PVA nanofibers.

2.6 Field emission scanning electron microscopy (FESEM)

The morphology of the NiTi/PVA composite nanofibers was examined by using field emission scanning electron microscopy (company: TESCAN, USA).

3. Results and Discussion

3.1 X-ray diffraction and particle size results

The sintered NiTi alloy sample has been examined under an Optical microscope after grinding, polishing, and etching. The etching solution is composed of 10 ml of HF, 20 ml of HNO_3, and 150 ml of distilled water at room temperature [22]. There are plenty of pores in the sample, which are the dark areas, shown in Figure 1. The matrix represents the NiTi phase and the granulated particles represent the Ni_3Ti phase [23].

The XRD patterns of sintered NiTi alloy and the produced NiTi particles are shown in Figures 2 and 3, respectively. In Figure 2, the highest peak in the XRD pattern refers to the Ni_3Ti phase, and there are also high peaks for intermetallic phases NiTi, and TiO_2. The high amount of Titanium oxide (TiO_2) is attributed to the impure Argon atmosphere (air leaking) of the utilized furnace during the sintering process. Since Ti is more active as compared to Ni [24], when Ti is in contact with oxygen, instantly TiO_2 forms on the surface of the alloy [25, 26]. It is composed of TiO_2 as the free enthalpy of formation of TiO_2 is negative, it exceeds the enthalpy of the formation of nickel oxides [25]. TiO_2 protects the alloy from corrosion, and it creates a physical and mechanical barrier for the oxidation of nickel [25, 27]. On the other hand, the XRD pattern of NiTi nanoparticles (Figure 3) major intermetallic phases are NiTi, Ni_3Ti, and Ti_2Ni, which are the stable phases of NiTi alloy [28].

The particle size results are illustrated in Figure 4, and Table 2. In Figure 5, the logarithm diagram represents the NiTi particle size diameter ranging (50-5000) nm. Table II, clarify the particle size distribution from 244 to 264.4 nm, and the effective diameter is (250.8 nm). Chemical treatments of Ti and its alloys are mainly based on chemical reactions occurring at the interface between Ti and a solution. These Ti treatments include acid, alkali, Hydrogen peroxide H_2O_2, and passivation treatments [29]. Acid treatment is usually used to remove oxide and contamination to obtain a clean, uniform surface finish, and improve the properties of Ti and its alloys [29]. Titanium has a moderate resistivity to aqua regia solution (Chemical Resistance Chart for SITRANS F M), the longtime of immersing the NiTi alloy sample in the diluted aqua regia leads to decomposition (reduction) of TiO_2. The decomposition of TiO_2 also led to a decrease in the volume of the NiTi particles.

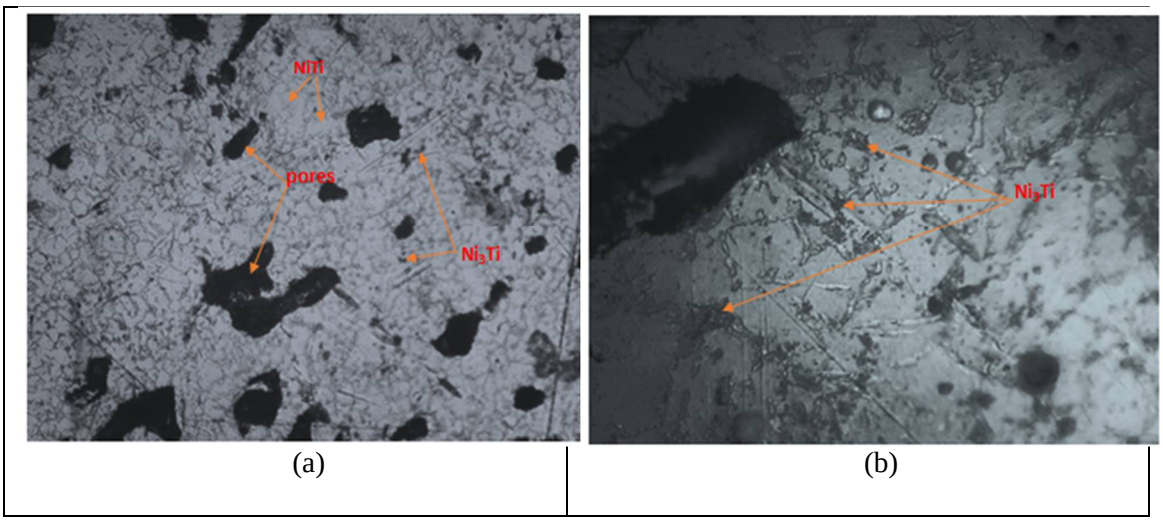

Figure 1: (a) Sintered NiTi alloy sample phases under optical microscope at magnification 20x, (b) Sintered NiTi alloy sample phases under optical microscope at magnification 80x.

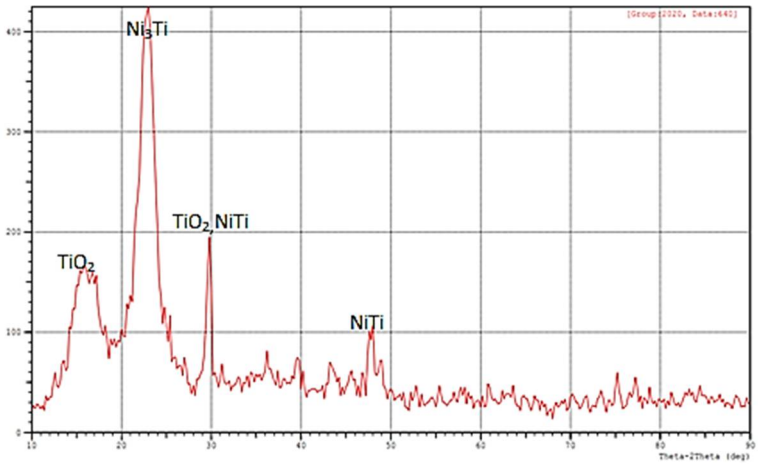

Figure 2: XRD pattern of NiTi alloy after sintering

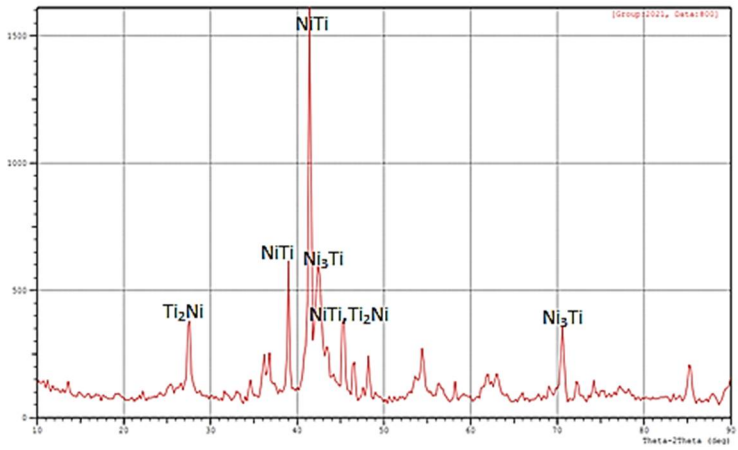

Figure 3: XRD pattern of NiTi particles

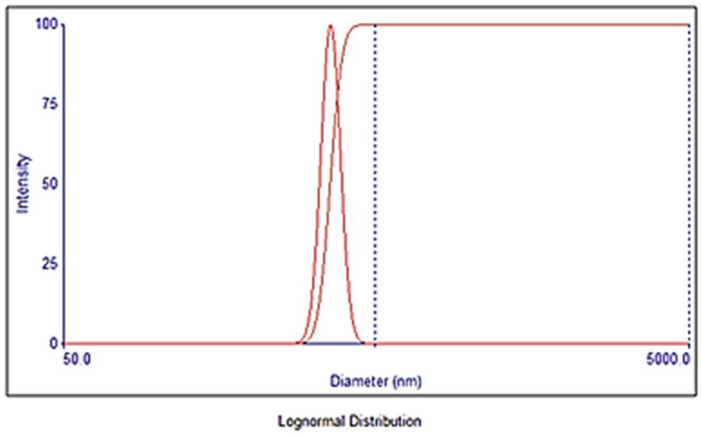

Figure 4: Particle size analysis diagram of NiTi nanoparticles

Table 2: Particle size distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
244.0	0	0	250.8	100	69	257.8	0	100
244.6	0	0	251.4	64	91	258.5	0	100
245.2	0	0	252.1	28	100	259.1	0	100
245.8	0	0	252.7	0	100	259.8	0	100
246.4	0	0	253.3	0	100	260.5	0	100
247.0	0	0	254.0	0	100	261.1	0	100
247.7	0	0	254.6	0	100	261.8	0	100
248.3	0	0	255.3	0	100	262.4	0	100
248.9	0	0	255.9	0	100	263.1	0	100
249.5	36	12	256.5	0	100	263.7	0	100
250.2	72	36	257.2	0	100	264.4	0	100

3.2 Energy Dispersive Spectroscopy (EDS) and field emission scanning electron microscopy (FESEM) results

The objective of the EDS analysis is to investigate the elemental composition. The result of ultrafine NiTi particles is illustrated in Figure 6, where the composition of Ti is 78.22% wt., and the composition of Ni is 21.78% wt. It is observed that the elemental composition ratio of the NiTi particles is different from the ratio of the prepared NiTi sintered sample. This difference in the composition of elements might be attributed to the resistivity of each one to the acids in aqua regia solution since the Ti is more resistive to acids than Ni. Moreover, the Ni particles, used in the sintered alloy, were smaller than Ti particles (Table 1). Furthermore, the EDS analysis of electrospun NiTi/PVA nanofibers (Figure 6-b) showed the presence of 3.88% wt. Titanium, and 0.15% wt. Nickel, in addition to 68.77% wt carbon, and 27.20% wt. Oxygen, The existence of Ni and Ti elements gives evidence that this method of fabricating NiTi/PVA nanofibers by electrospinning process is successful.

Morphologies of the NiTi/PVA composite nanofibers test were performed using microscopy FESEM. In general, FESEM gives information about the presence of voids, the homogeneity of the composite nanofibers, the presence of aggregate, the distribution of the particles within the continuous polymeric matrix, and the possible orientation of nanoparticles [30]. The FESEM images of NiTi/PVA nanofibers are shown in Figures 6-(a) and (c). The obtained fibers are regular, continuous, and bead-free. The nanofibers diameter ranges from (120-210) nm, while the average diameter is 163 nm. It seems that the insertion of NiTi particles into the PVA matrix has no significant effect on the morphology of a conventional pure PVA fibers

mat. Although the NiTi particles' average diameter is 250.8 nm, which is more than the average diameter of NiTi/PVA fiber diameter (163 nm), the particles were highly embedded within the fibers as shown in Figure 6-(d). The green dotes represent the Ni element, and the red dotes represent the Ti element. Analyzing this morphology, there are two main reasons for the smoothness of the NiTi/PVA resulted fibers: First, during the electrospinning process the high voltage can fragment particles (or decrease particle agglomerations), which led to particle size reduction. Second, while preparing the colloidal electrospinning solution the ultrasonic homogenizer helped to disperse the agglomerated particles.

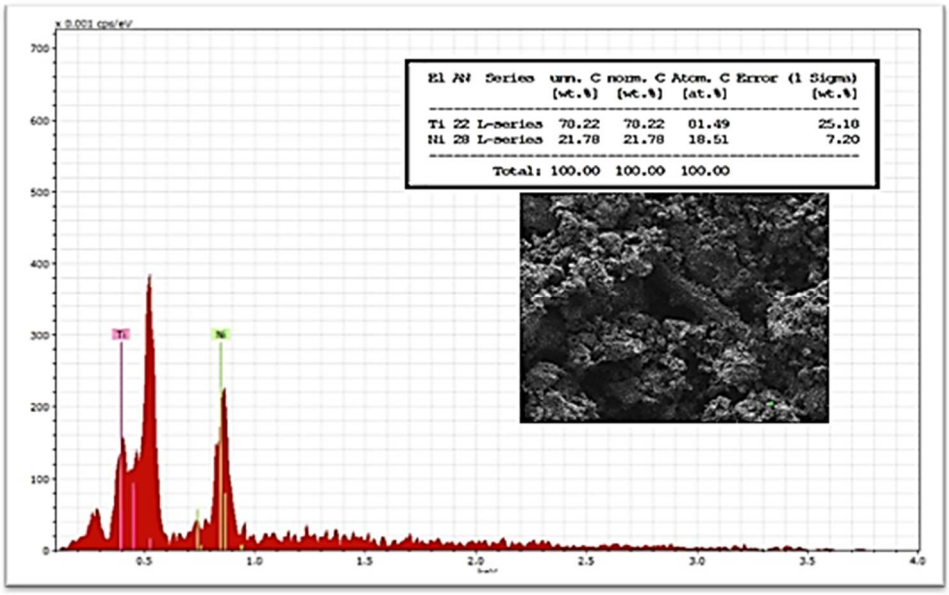

Figure 5: : EDS analysis of NiTi particles

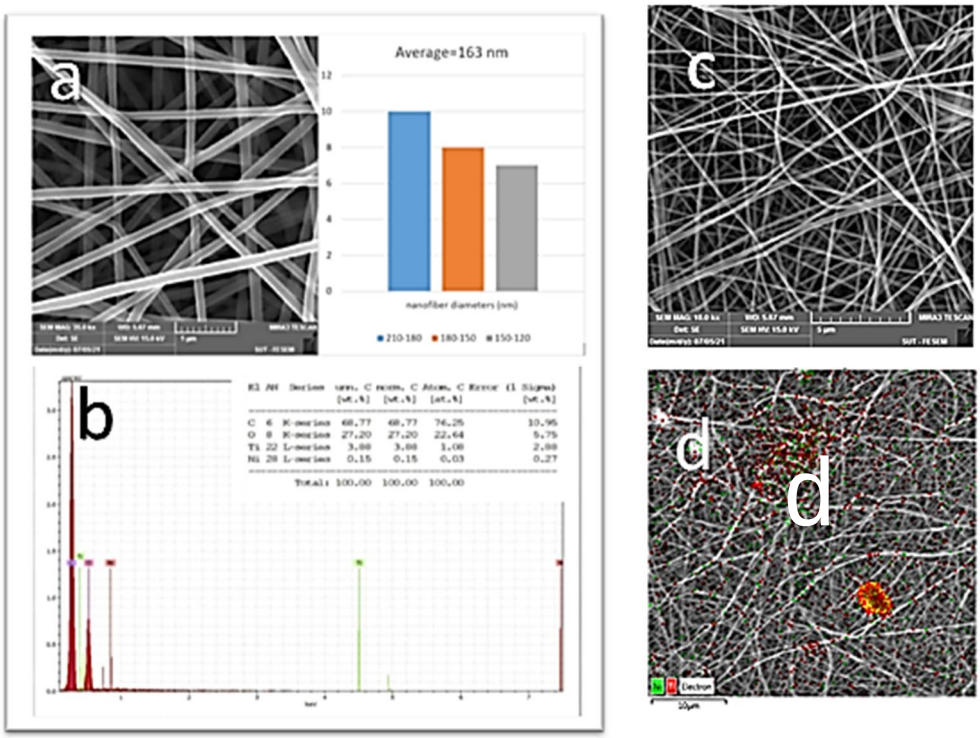

Figure 6: NiTi/PVA nanofibers, (a) Average fiber diameter. (b)EDS analysis (element composition). (c) FESEM image. (d) Mapping of elements: Ni and Ti.

4. Conclusions

The ultrafine NiTi particles and NiTi/PVA nanofibers were successfully prepared by this method. The major phases of the sintered alloy were Ni_3Ti, TiO_2, and NiTi, while after immersing in diluted aqua regia solution the presence of oxide has much decreased, and the phases of NiTi particles became: NiTi, Ni_3Ti, and Ti_2Ni. The aqua regia solution has shown excellent enhancement of NiTi phases, and the effective diameter of NiTi particles was 250.8 nm. The FESEM images and EDS analysis

of NiTi/PVA showed smooth regular fibers with a good distribution of NiTi particles. For future work, it is suggested that this preparation method can be applied to other metals and alloys.

Author contribution

All authors contributed equally to this work.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

References

[1] S. Zhang, Z. Jia, T. Liu, G. Wei, Electrospinning Nanoparticles-Based Materials Interfaces for Sensor Applications, Sensors, 19 (2019) 3977– 4001. https://doi.org/10.3390/s19183977

[2] S. Hasan, A review on nanoparticles : their synthesis and types, Res. J. Recent. Sci., 4(2014)9–11.

[3] E. O. Nasakina, M. A. Sevostyanov, A. S. Baikin, A. V. Seryogin, S. V. Konushkin, K. V. Sergienko, A. V. Leonov , A. G. Kolmakov, Applications of nanostructural NiTi alloys for medical devices, Shape Mem. Alloy. - Fundam. Appl., (2017).

http://dx.doi.org/10.5772/intechopen.69238

[4] P. Majeric, R. Rudolf, I. Anzel, B. Friedrich, J. Bogovic, S. Stopic, Nanoparticles prepared from NiTi orthodontic wire, Livar. Vestn ., 62 (2015) 142–151.

[5] M. Speirs, X. Wang, S.V. Baelen, A. Ahadi, S. Dadbakhsh, J. P. Kruth, J. V. Humbeeck, On the transformation behavior of NiTi shape-memory alloy produced by SLM, Shape. Mem. Superelasticity., 2 (2016) 310–316. http://dx.doi.org/10.1007/s40830-016-0083-y

[6] D. Mutter , P. Nielaba, Simulation of the thermally induced austenitic phase transition in NiTi nanoparticles: Simulation of phase transitions in NiTi nanoparticles, Eur. Phys. J. B, 84(2011)109–113 . http://dx.doi.org/10.1140/epjb/e2011-20661-4

[7] S. Barcikowski, M. Hustedt, B. Chichkov, Nanocomposite manufacturing using ultrashort-pulsed laser ablation in solvents and monomers.,Polimery, 53 (2008) 657–662. http://dx.doi.org/10.14314/polimery.2008.657

[8] D. D. Radev, Mechanical synthesis of nanostructured titanium–nickel alloys, Adv. Powder Technol., 21 (2010) 477–482. http://dx.doi.org/10.1016/J.APT.2010.01.010

[9] M. Kurumada, Y. Kimura, H. Suzuki, O. Kido, Y. Saito, C. Kaito, TEM study of early Ni4Ti3 precipitation and R-phase in Ni-rich NiTi nanoparticles, Scr. Mater., 50 (2004)1413–1416. http://dx.doi.org/10.1016/j.scriptamat.2004.02.029

[10] C. Shearwood, Y. Q. Fu, L. Yu, K. A. Khor, Spark plasma sintering of TiNi nano-powder, Scr. Mater., 52 (2005) 455–460. http://dx.doi.org/10.1016/J.SCRIPTAMAT.2004.11.010

[11] W. Crone, W. Drugan, A. Ellis, J. Perepezko, Final technical report: nanostructured shape memory aLloys, University of Wisconsin-Madison, (2005).

[12] S. Yatsu, H. Takahashf, H. Sasaki, N. Sakaguchi, K. Ohkubo, T. Muramoto , S. Watanabe, Fabrication of nanoparticles by electric discharge plasma in liquid, Arch. Metall. Mater., 58 (2013) 425–429. http://dx.doi.org/10.2478/amm-2013-0011

[13] H. B. Liu, G. Canizal, P. S. Schabes- Retchkiman, J. A. Ascencio, Structural selection and amorphization of small Ni Ti bimetallic clusters, J. Phys. Chem. B, 110 (2006) 12333–12339. http://dx.doi.org/10.1021/jp061856e

[14] A. R. Jabur, E. S. Al-Hassani, A. M. Al-Shammari, M. A. Najim, A. A. Hassan, A. A. Ahmed, Evaluation of stem cells' growth on electrospun polycaprolactone (PCL) scaffolds used for soft tissue applications, Energy. Procedia, 119 (2017) 61–71. http://dx.doi.org/10.1016/j.egypro.2017.07.048

[15] F. A. Chayad, A. R. Jabur, N. M .Jalal, Effect of NaCl solution addition on improving some of the physical properties of nylon 6 solutions used for electro spinning purpose, Eng. Technol. J., 34 (2016) 1265–1274. http://dx.doi.org/10.30684/etj.34.7A.1

[16] A. R. Jabur, Multiwall carbon nanotube / polyvinyl alcohol nanofibers film, electrical conductivity improvement, Eng. Technol. J., 38 (2020)431–439. http://dx.doi.org/10.30684/etj.v38i3A.530

[17] A. R. Jabur, L. K. Abbas, S. M. Muhi, Effects of Ambient Temperature and Needle to Collector Distance on PVA Nanofibers Diameter Obtained From Electrospinning Technique, Eng. Technol. J., 35 (2017) 340–347. http://dx.doi.org/10.30684/etj.35.4A.5

[18] A. R. Jabur, L.k.Abbas, S. M. Aldain, Ambient temperature affect the pore size of PVA nanofibers tissues, Eng. Tech. J., 33 (2015) 1040–1047.

[19] J. Bai, Y. Li, S. Yang, J. Du, S. Wang, J. Zheng, Y. Wang, Q. Yang, X. Chen, X. Jing, A simple and effective route for the preparation of poly(vinylalcohol) (PVA) nanofibers containing gold nanoparticles by electrospinning method, Solid. State. Commun., 141 (2007) 292–295. http://dx.doi.org/10.1016/j.ssc.2006.10.024

[20] U. Anjaneyulu, B. Priyadarshini, A. Nirmala Grace, U. Vijayalakshmi, Fabrication and characterization of Ag doped hydroxyapatite-polyvinyl alcohol composite nanofibers and its in vitro biological evaluations for bone tissue engineering applications, J. Sol-Gel .Sci. Technol., 81 (2017) 750–761. http://dx.doi.org/10.1007/s10971-016-4243-5

[21] A. R. Jabur, M. H. Abdulmajeed, S. Y. Abd, Effect of Cu nanoparticles addition on improving the electrical conductivity and mechanical properties of PVA electrospun polymeric film, AIP. Conf. Proc., 1968 (2018) 030016 http://dx.doi.org/10.1063/1.5039203

[22] S. M. Al-Saffar, E. S. Al-Hassani, R. A. Hussein, Characterization of Niti super elasticity shape memory alloys, Eng. Tech. J., 31 (2013) 3035–3051. http://dx.doi.org/10.30684/etj.31.16A.3

[23] J. Wang, Z. Pan, G. Yang, J. Han, X. Chen, H. Li, Location dependence of microstructure, phase transformation temperature and mechanical properties on Ni-rich NiTi alloy fabricated by wire arc additive manufacturing, Mater. Sci. Eng. A, 749 (2019) 218–222. http://dx.doi.org/10.1016/j.msea.2019.02.029

[24] M. Badr, A. Mohammadzadeh, J. Khalil-Allafi, M. Khoshghadam-Pireyousefan, A. Mostafaei, In-situ formation of TiN-TiO2 composite layer on NiTi shape memory alloy via fluidized bed reactor, Ceram. Int., 46 (2020) 21097–21106. http://dx.doi.org/10.1016/j.ceramint.2020.05.184

[25] N. Lepojević, I. Š´cepan, B. Gliši´, M. Jenko, M. Godec, S. Hoˇcevar , R. Rudolf, Characterisation of NiTi orthodontic archwires surface after the simulation of mechanical loading in CACO2-2 cell culture, Coatings, 9 (2019) 440. http://dx.doi.org/10.3390/coatings9070440

[26] S. M. Al-Saffar, E. S. Al-Hassani, F. J. Al-hassani, Effect of alloying elements (Mo and Al) on biomaterials Ti-Ta shape memory alloys, Eng. Tech. J., 32 (2014) 932-951. https://dx.doi.org/10.30684/etj.32.4A.10

[27] E. M. Saeed, N. M. Dawood, S. F. Hasan, Improvement corrosion resistance of Ni-Ti alloy by TiO2coating and hydroxyaptite/TiO2 composite coating using micro arc oxidation process, Mater. Today. Proc., 42 (2021) 2789–2796. https://dx.doi.org/10.1016/j.matpr.2020.12.723

[28] B. Li, L. Rong, Y. Li, Microstructure and superelasticity of porous NiTi alloy, Sci. China, Ser. E Technol. Sci., 42 (1999) 94–99. https://dx.doi.org/10.1007/BF02917064

[29] E. S. Al-hassani , F. J. Al-hassani, Effect of dual surface activation on the surface roughness of titanium dental implant, J. Nat. Sci.,7(2017) 35-44.

[30] K. Choo, Y. C. Ching, C. H. Chuah, S. Julai, , N. S. Liou, Preparation and characterization of polyvinyl alcohol-chitosan composite films reinforced with cellulose nanofiber, Mater., 9 (2016) 644. https://dx.doi.org/10.3390/ma9080644