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Synthesis of biomedical Ti-25Ni-15Si-10HA alloy by mechanical alloying and spark plasma sintering

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Abstract-

In this research approach, a β-phase titanium alloy was produced successfully employing mechanical alloying and consolidated with spark plasma sintering (SPS) process. Herein, Ni, Si and HA powders with varied weight percentage were used to fabricate the Ti alloy. The influence of HA addition on microstructure of the alloy was assessed using optical microscopy route and further amplified using field emission scanning electron microscopy (FESEM). The elemental composition and phase of Ti-alloy was investigated using x-ray diffractometer. Vicker hardness (HV) tester was employed to estimate the micro hardness of the specimen surface. During the FESEM analysis, it was observed that within the sintering process, alloy exhibits complex reactions with HA, which leads to the progress of bioactive compounds (CaO, TiO_2, $Ca_3(PO_4)_2$, Ti_2Ni, $CaTiO_3$ and $CaTiSiO_5$) enhancing the bioactivity of the Ti alloy. The fabricated Ti alloy (Ti-25Ni-15Si-10HA) exhibited superior microhardness (~458HV) at 900°C, comparative to the other alloys of the native category. Based upon the current investigation, Ti-25Ni-15Si-10HA alloy could find applications as bioimplants in dental and orthopedic areas.

1. Introduction

Since inception, fatal injuries to human have always justified the development of implants used to heal injuries or serve as replacements [1]. Bio-implants are extensively used for restoring functionality of disorder, fractured organ or body tissue. The implant material must be compatible mechanically, biologically and have properties similar to retrofittewd human body parts in terms of corrosion and wear resistance, adhesion, etc. The implanted material biologically fix with the fractured part for self-bone healing process and cell growth [2]. Categories of artificial biomaterials commonly adopted include metallic, ceramics and polymers respectively. The need and demand of biomaterials is increasing at a brisk pace due to advancements in the field of medical sciences, technology and economy [20]. The risk of hard tissue failure was explicitly discussed in [1]. According to a study, 70-80% of biomedical implants are developed using different classes of metallic materials. This is because metallic based implants are extraordinarily vital for regenerating failed hard tissues. Also, the population ratio of aged people globally is rapidly increasing [3]. Metallic implants such as Cobalt-chromium (Co-Cr) alloys, stainless steel (SUS-316L), titanium (Ti) and its alloys [4-5] are being commonly adopted. Similarly, other non-metallic polymeric based biomaterials like silicone rubber, Ultra High Molecular Weight Polyethylene (UHMWPE), PE, Polymethylmethacrylate (PMMA), acrylic resins, polyurethanes, polypropylene (PP) and Polyethylene Terephthalate are also being used [21]. Ceramic biomaterials are generally utilized as bioactive coating to metallic biomaterial. This help restrict the release of harmful ions affecting bone-implant adhesion and biological fixation. Hydroxyapatite (HA), titanium carbide (TiC), silicon carbide (SiC), zirconium oxide (ZrO_2), titanium oxide (TiO_2) or TNT and aluminum oxide (Al_2O_3) are some of the ceramic biomaterials [6]. SUS-316L and Co-Cr alloys have been found to release harmful elements such as nickel (Ni), chromium (Cr) and cobalt (Co) causing toxicity within the individually. Furthermore, stainless steel 316L and ceramics have lower fracture strength and higher modulus in comparison to bone [8]. Being biocompatible, strong, cheap and resistant to corrosion, SUS-316L is frequently used as bio-implant. But its main limitation is its higher elastic modulus (200 GPa) which is 10 times greater than that of the human bone. Co-Cr alloys are better in strength and offers better corrosion resistance comparative to stainless steel. While using Co-Cr alloys for implantation, they are generally composed of Co 30-60%, Cr 20-30%, Mo 7-10% and a range of units of Ni. Titanium (Ti) and its alloys have a lot of potential to be used as an implant owing to their superior bioactivity and better mechanical properties in term of low young's modulus (nearer to human bone), better resistance towards wear and corrosion resistance and minimum density when compared to rest of the metallic biomaterials [7]. Titanium alloys are also utilized because of their long term replacement solutions such as knee joints and total hip replacement. The recent scenario demands to develop Ti based alloy with non-toxic and non-allergic elements composition having low modulus of elasticity. Such as Ti-Ni, Ti-Zr, Ti-Nb-Zr or many more which cut down the toxicity of Ti-V based alloy [9-11]. The β phase titanium alloy is the most important group of titanium alloys due to its better formability, mechanical features and potential application. It has high fatigue and corrosion resistance. The β phase titanium alloy contains non- toxic elements such as Ni, Ta, Si, Zr. Recent research shows that β-type Ti alloy has lower elastic modulus 55 GPa, high weight-to-strength ratio, low density, good corrosive resistivity and high biocompatibility as compare to CP-Ti material and Ti–6Al–4V alloy [12]. Amid all physical and mechanical properties, biomaterial must own porosity which facilitates the healing process faster providing proper bone-implant adhesion and better cell growth. Numerous techniques such as ion beam machining, hot sintering, hot isostatic pressing (HIP), and laser beam machining, etc. were developed and utilizing widely for the fabrication of nano-porous biocompatible structure of β-phase titanium alloys [13-14]. Although these fabrication methods generate porosity or nano-porous structure, but high elevated temperature, longer sintering time, weaken the corrosion resistance and other mechanical properties of the substrate material. As a result, implant fails during the cyclic loading and long term performances conditions particularly in case of hip and knee replacement. Recently, spark plasma sintering (SPS) was utilized to fabricate nano-pores β-type titanium alloys via powder metallurgy consisting of mechanical alloying powders [15]. C. Shearwood et.al [16] produced specimens at temperature of 800°C using spark plasma sintering (SPS) of Ti50Ni50 nano-powder and observed good density and shape memory effect of the treated sample. It was observed that temperature below 800°C depicts higher porosity, but poor or apparent shape memory effect. Consequently, oxidation is observed at sintering temperature higher than 900°C accompanied by the loss of shape memory characteristic and greater increase in the density. Copious intermetallic phases for instance $NiTi_2$ and Ni_3Ti were examined at high temperatures which significantly affect the inter-diffusion of the atoms in solid state. A progressive increase in the transformation temperatures is witnessed as the sintering temperature varies from 700°C to 800°C in relation to the nano-powder. Zhu et al. [17] used amorphous $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ powders (diameter<63 μm) with hydroxyapatite (HA) particles to fabricate the titanium based alloy/HA composite employing SPS technique. They investigated the fabricated material for changed surface topography, mechanical and thermal properties to validate the influence of hydroxyapatite particles on the specimen. The specimens with the addition of hydroxyapatite 1 wt % or 2 wt%, homogeneous HA particle distribution was observed over the whole sintered sample.

However, with increase of HA concentration during process, the observed particle distribution was inhomogeneous. For the specimen with 5 wt% hydroxyapatite addition, HA agglomerates were observed and when HA addition increased to 10 wt%, most of glassy alloy powders exist in the HA. N.F. Gao et.al [18] reported that Ti_3SiC_2 was rapidly produced and then at the same time combined from the starting mixture of Ti-Si-2TiC using spark plasma sintering technique. During the SPS process, Ti_3SiC_2 was formed by an intensive reaction at temperature around 1200°C (measured). The range of temperature depends upon the rate of applied pressure and dimensional specifications of the sample used. Furthermore, the crystallographic basal plane was examined with the aid of XRD analysis. He et al. [19] studied the effect of variation of HA content (0, 5, 10, 15 and 20 wt%) on the micro-structure, corrosion and mechanical properties of the fabricated Ti-13Nb-13ZrHA based alloy. The nano-particles of Ti, Nb, Zr and HA were first obtained in a planetary ball mill and were then consolidated by spark plasma sintering process to obtain a compact bio-composite. The results showed that there is a linear relationship between relative density of bio-composites. Also it was observed that HA concentration and comparative density decrease, with the raise in HA content. Raising the initial hydroxyapatite content to 5wt%, compression as well as yield strength increased and further decreased with increase in HA content. During the in-vitro corrosion analysis in simulated body fluid (SBF), bio-composites with 10% of HA exhibit an optimal corrosion resistance.

Based on the literature survey, it was evident that no research work has been carried out yet to fabricate Ti-25Ni-15Si-10HA alloy by the powder metallurgy technique combined with SPS method. Herein, the fabrication of Titanium based porous Ti-Ni-Si-HA alloy was investigated to necessitate the next generation of implants offering better biocompatibility, and avoiding the limitations of other titanium alloys employed as biomaterial. A widespread and significant analysis of as-prepared Ti alloy was conducted to assess the effectiveness of spark plasma sintering (SPS) technique for preparing porous implant surface. Output analysis of the fabricated material in terms of morphology, compositional changes, and mechanical properties such as microhardness and elastic modulus was scrutinized for biomedical use.

2. Materials and Method

2.1 Powder selection and mechanical alloying

Element powders of Ti-Ni-Si-HA having particle size 25µm and purity 99.9% was used as alloying material. First of all, for mechanical alloying, the powders were combined in the atomic wt% (25%Ni, 15%Si, 10%HA) with the titanium.

Figure 1 illustrates the microstructure, size and shape of powder constituents prior to mechanical alloying of material. The powders were then mixed by wt% and poured in a bowl rotating at the speed of 300 rpm having tungsten-carbide balls for 3 hours.

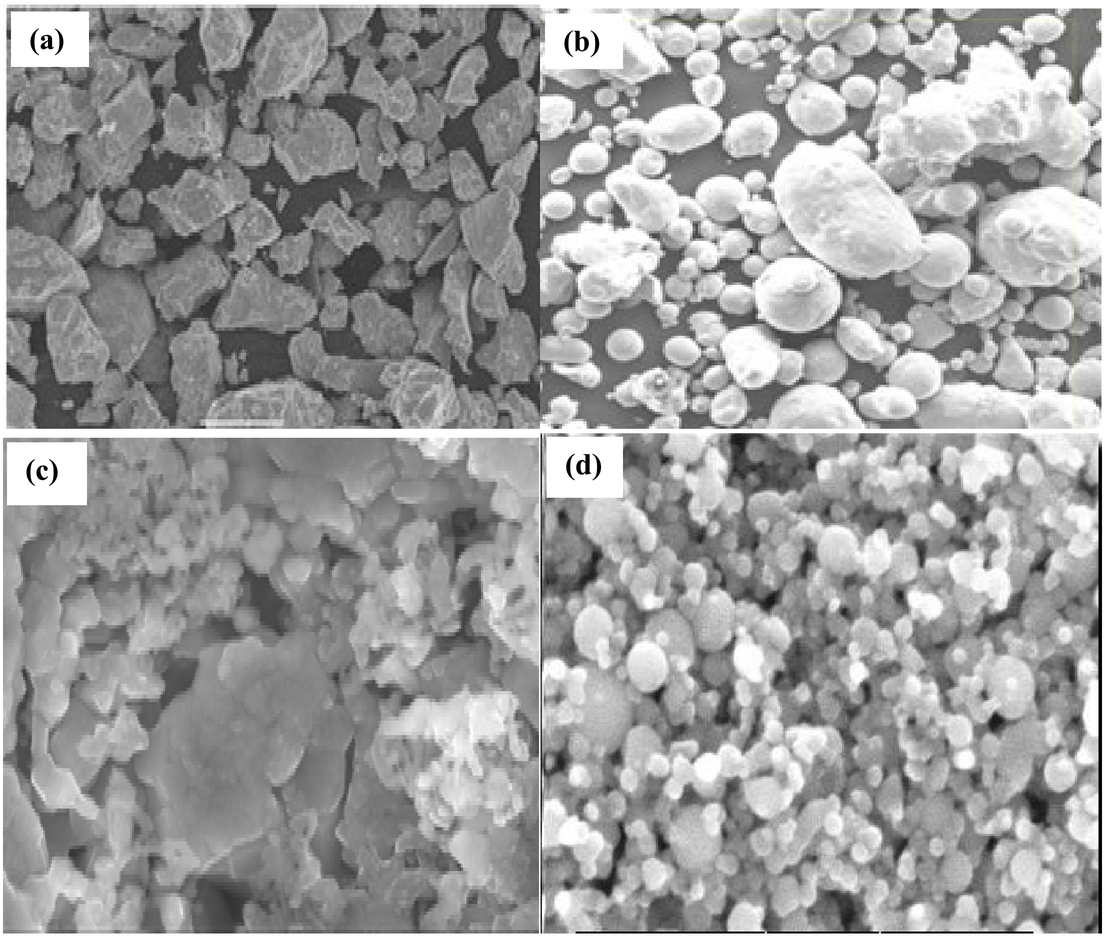


Figure 1: SEM microscopy of powder particles: (a) Titanium; (b) Nickel; (c) Silicon; (d) Hydroxyapatite

2.2 Solidification of alloying powder

After mechanical alloying the powders were consolidated by spark plasma sintering machine as shown in figure 2(a). The moisture content of the alloyed powder was evaporated by pre-heating the mixture at 500°C for 2 hours in an argon atmosphere. The alloyed powder was put in a graphite die of spark plasma sintering machine and consolidate at different sintering temperatures 900, 1100 and 1300 °C with heating rate of 100°C per minute and holding time of 10 minute under vacuum condition and 50MPa pressure used during whole process. After this process, fabricated sample was taken out from the graphite die which had circular diameter 20mm and thickness 5mm.

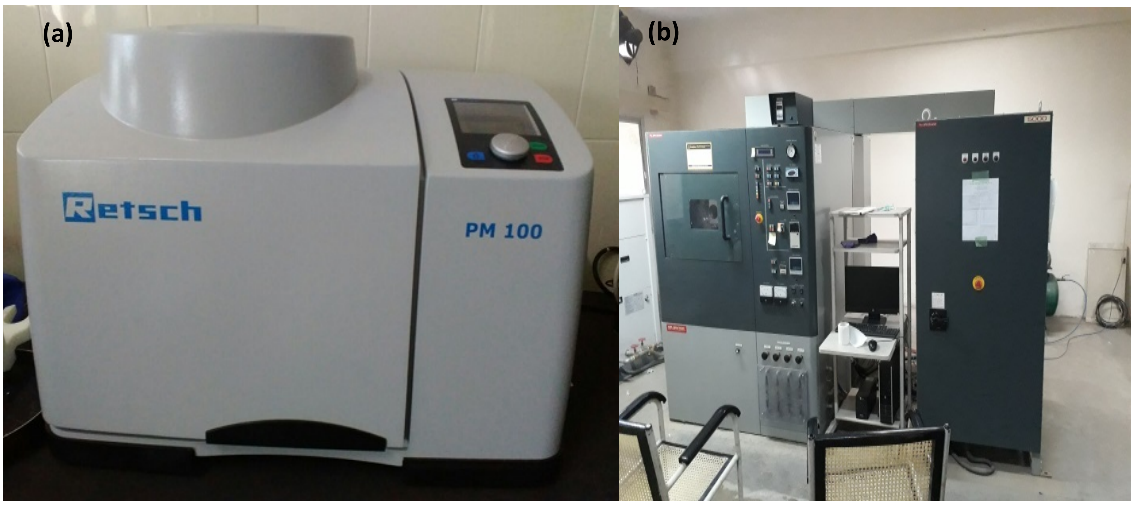
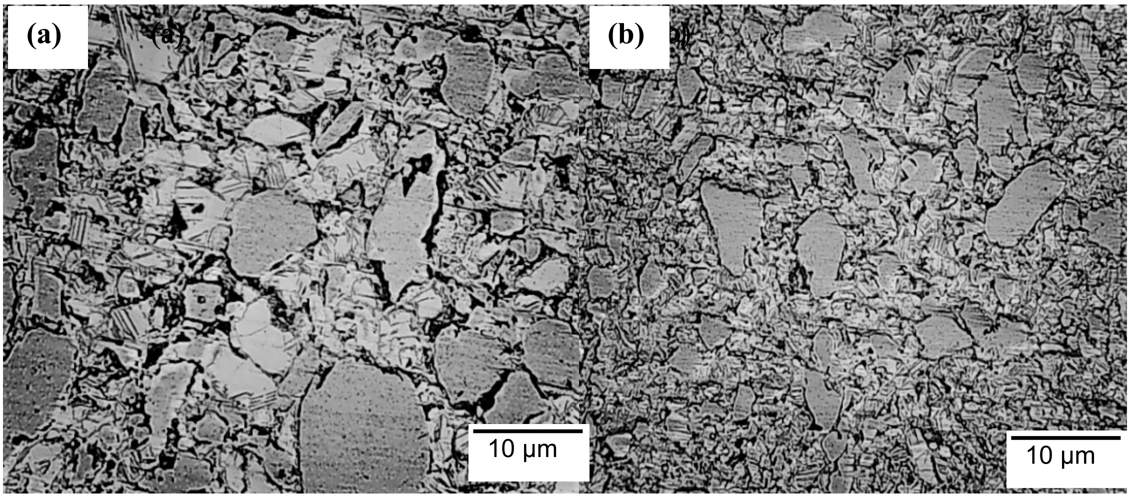


Figure 2: (a) High energy planetary ball mill, (b) Spark plasma sintering (SPS) machine

3. Results and discussions

3.1 Analysis of sintered alloy morphology (Ti-Ni-Si-HA)

Figure 3 demonstrates the microstructure of the polished Ti-Ni-Si-HA alloy surface sintered at variant temperatures. The grain boundaries of the different homogenous sintered powders can be witnessed from the microstructures. From the morphology, it has been revealed that with the rise in sintering temperature, the contact among the powders mixture increased and subsequently decrease in the gap between the powders particle. At the higher temperature, nickel change the phase of α to β. As a result intensity peak of nickel gradually augmented with increased in sintering temperature but at very high temperature intensity peak of HA gradually decreased and made the sample porous. So, it was observed that at very high sintering temperature, greater amount of gases are released as a result of chemical activities within the alloying constituents and hydroxyapatite powder, causing cracks creation on the top surface of sintered alloy.



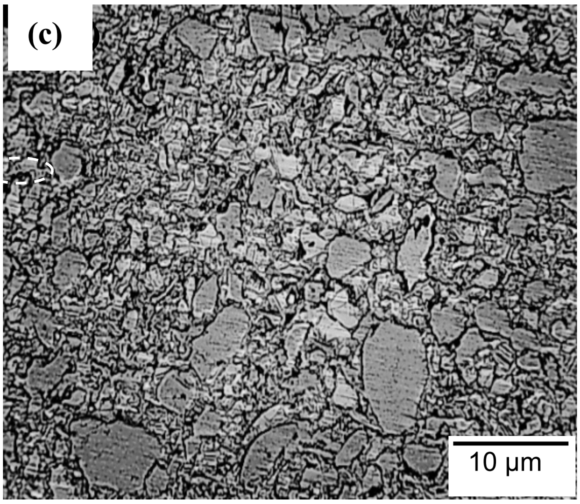


Figure 3: SEMs of the Ti-Ni-Si-HA alloy sintered at (a) 900ºC, (b) 1100ºC and (c) 1300ºC

3.2 Analysis of XRD of sintered Ti-Ni-Si-HA alloy

The XRD pattern of SPS titanium alloy shows the Ti phase with weak Ni peaks partially with Si and HA content. The figure 4 shows the XRD pattern at 900°C sintered alloy in which it can be witnessed that intensity peak of Ni is high as compare to characteristics peak of HA. The XRD pattern of sintered Ti-Ni-Si-HA alloy at 900°C showed the presences of $Ca_3(PO_4)_2$, $CaTiO_3$, CaO, $CaTiSiO_5$, Ti_2Ni, and TiO_2 which is beneficial and enhanced the bioactivity of the titanium alloy. This is due to the fact that at high elevated temperature HA reacts with the other element and leads to the formation of novel bioactive compounds and phases in sintered alloy offering better bioactivity.

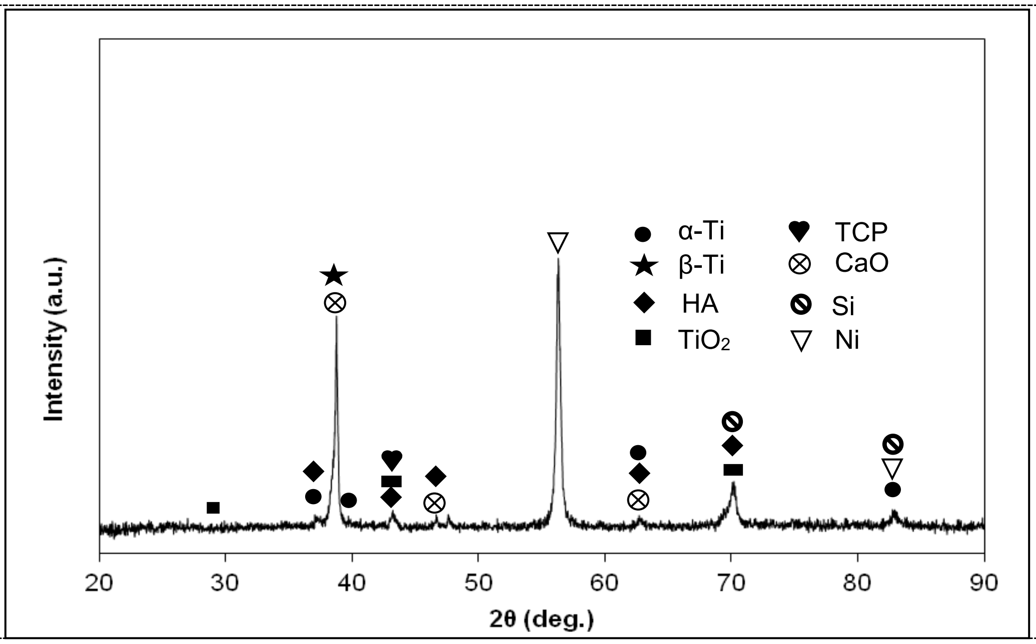


Figure 4: X-ray diffraction trends of the Ti-Ni-Si-HA sintered at 900ºC sintering

3.3 Hardness of sintered Ti-Ni-Si-HA alloy

During this study, the hardness of Ti-Ni-Si-HA alloy was measured at numerous sintering temperatures (900°C, 1100°C, 1300°C). It has been mentioned earlier that when the sintering temperature increases, the gap linking the powders particles decreased and the hardness of the alloy increased. This is because at lower temperature, alloy which has α phases with low hardness whereas when sintering temperature increased, α phase gradually transform into β phase. As the β phase has high strength as compare to α phase, so the hardness of alloy was more at high temperature as compare to low temperature.

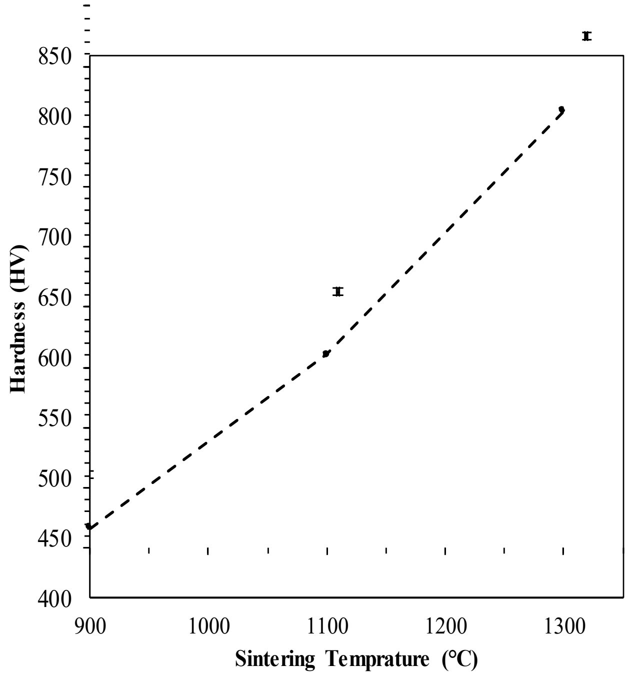


Figure 5: Micro-hardness values of Ti-25Ni-15Si-10HA alloy at different sintering temperatures

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4. Conclusion

From the current mechanical alloying and spark plasma sintering (SPS) investigation of powders (Ti, Ni, Si and HA), followed conclusions can be summarized:

1. A bio-composite titanium alloy (Ti-25Ni-15Si-10HA) was profitably fabricated using mechanical alloying of powders followed by SPS technique.
2. FESEM analysis revealed that the fabricated bio-composite distinctly exhibits the grain boundaries on the surface of sintered alloy.
3. It was observed that spark plasma sintering process depicts the formation of bioactive compounds ($Ca_3(PO_4)_2$, $CaTiO_3$, CaO, $CaTiSiO_5$, Ti_2Ni, and TiO_2) which was confirmed by XRD analysis. These compounds are suitable for apatite cell growth thus enhance bioactivity of the material.
4. The developed Ti-25Ni-15Si-10HA material showed the superior microhardness (~458 HV) at 900°C, than other alloys reported in the other studies.

References

[1] Hench, L. L. (1998). Biomaterials: a forecast for the future, vol. 19, 1419 -1423.

[2] Geetha, M., Singh, A.K., Asokamani, R. & Gogia, A.K. (2009) Ti Based Biomaterials, the Ultimate Choice for Orthopaedic Implants—A Review. *Progress in Materials Science, 54*, 397-425.

[3] Nowakowski, A. (2006). Quantitative active dynamic thermal IR-imaging and thermal tomography in medical diagnostics. 22-30.

[4] Vaccaro, A. R., Singh, K., Haid, R., Kitchel, S., Wuisman, P., Taylor, W. & Garfin, S. (2003). The use of bioabsorbable implants in the spine. *The Spine Journal*, *3*(3), 227-237.

[5] Niinomi, M., Nakai, M., & Hieda, J. (2012). Development of new metallic alloys for biomedical applications. *Acta biomaterialia*, *8*(11), 3888-3903.

[6] Amin, A. N. (Ed.). (2012). *Titanium Alloys: Towards Achieving Enhanced Properties for Diversified Applications*. BoD–Books on Demand.

[7] Bains, P. S., Mahajan, R., Sidhu, S. S., & Kaur, S. (2019). Experimental investigation of abrasive assisted hybrid EDM of Ti-6Al-4V. *Journal of Micromanufacturing*, 2516598419833498.

[8] Niinomi, M. (2008). Metallic biomaterials. *Journal of Artificial Organs*, *11*(3), 105.

[9] Elias, L. M., Schneider, S. G., Schneider, S., Silva, H. M., & Malvisi, F. (2006). Microstructural and mechanical characterization of biomedical Ti–Nb–Zr (–Ta) alloys. *Materials Science and Engineering: A*, *432*(1-2), 108-112.

[10] Okazaki, Y. (2001). A new Ti–15Zr–4Nb–4Ta alloy for medical applications. *Current Opinion in Solid State and Materials Science*, *5*(1), 45-53.

[11] Zaman, H. A., Sharif, S., Idris, M. H., & Kamarudin, A. (2015). Metallic Biomaterials for Medical Implant Applications: A Review. In *Applied Mechanics and Materials* , *735*, 19-25. Trans Tech Publications.

[12] Okazaki, Y., Rao, S., Ito, Y., & Tateishi, T. (1998). Corrosion resistance, mechanical properties, corrosion fatigue strength and cytocompatibility of new Ti alloys without Al and V.*Biomaterials*, *19*(13), 1197-1215.

[13] Arifin, A., Sulong, A. B., Muhamad, N., Syarif, J., & Ramli, M. I. (2014). Material processing of hydroxyapatite and titanium alloy (HA/Ti) composite as implant materials using powder metallurgy: a review. *Materials & Design, 55*, 165-175.

[14] Ning, C., & Zhou, Y. (2008). Correlations between the in vitro and in vivo bioactivity of the Ti/HA composites fabricated by a powder metallurgy method. *Acta Biomaterialia, 4*(6), 1944-1952.

[15] Zhan, G. D., Kuntz, J., Wan, J., Garay, J., & Mukherjee, A. K. (2002). Alumina-based nanocomposites consolidated by spark plasma sintering. *Scripta Materialia, 47*(11), 737-741.

[16] Shearwood, C., Fu, Y. Q., Yu, L., & Khor, K. A. (2005). Spark plasma sintering of TiNi nano-powder. *Scripta Materialia*, *52*(6), 455-460.

[17] Zhu, S. L., Yang, X. J., & Cui, Z. D. (2011). Effect of hydroxyapatite content on the microstructure, thermal and mechanical properties of Ti-based glassy alloy/hydroxyapatite composite prepared by spark plasma sintering. *Intermetallics*,*19*(4), 572-576.

[18] Gao, N. F., Li, J. T., Zhang, D., & Miyamoto, Y. (2002). Rapid synthesis of dense Ti3SiC2 by spark plasma sintering. *Journal of the European Ceramic Society*, *22*(13), 2365-2370.

[19] He, Y. H., Zhang, Y. Q., Jiang, Y. H., & Zhou, R. (2016). Effect of HA (Hydroxyapatite) content on the microstructure, mechanical and corrosion properties of (Ti13Nb13Zr)-xHA biocomposites synthesized by sparkle plasma sintering. *Vacuum*, *131*, 176-180.

[20] Bhui, A. S., Singh, G., Sidhu, S. S., & Bains, P. S. (2018). Experimental investigation of optimal ED machining parameters for Ti-6Al-4V biomaterial. *Facta Universitatis, Series: Mechanical Engineering*, *16*(3), 337-345.

[21] Navarro, M., Michiardi, A., Castano, O., & Planell, J. A. (2008). Biomaterials in orthopaedics. *Journal of the royal society interface*, *5*(27), 1137-1158.