

Wear characterization of nano-hydroxyapatite with addition of titanium (HA-Ti)

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Abstract. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA), is an attractive material of an inorganic compound whose chemical composition and crystallographic structures are similar to the composition of the bone. A natural source such as egg shells is composed of 94 wt. % of calcium carbonate (CaCO_3), which can be calcined as calcium oxide (CaO) by the calcinations process. The efficient temperature to produce CaO is 900 °C for 2 hours. The synthesis of nano-HA was done by the mixing the diammonium phosphate (DAP) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) and subjected into a microwave for 30 minutes at 1100 W irradiation power. Ball milling process was used for 30 minutes to mix the nano-HA with different compositions of titanium. These were pressed to form pallets by hand hydraulic pump (force= 2300 psi). The pallets then were sintered at 1200 °C with the heating rate of 3 °C/min for 2 hours. The pallets were tested by several mechanical testing including hardness, compression strength and wear. From the results, HA-25wt. %Ti composite gave the highest hardness, compression and coefficient of friction for wear test values which were 89.6 Hv, 82.5MPa and 0.76 μ respectively. It showed that by adding Ti to nano-HA, the mechanical properties of nano-HA could be enhanced. The microstructure analyses by optical micrograph showed that nano-HA-Ti particles displayed shape likes needle morphology. The particles showed the high tendency to form the agglomerations.

1. Introduction

Hydroxyapatite, HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), is an inorganic, insoluble salt [1]. It belongs to a family of calcium phosphates (CaPO_4) and is one of the most stable crystal structures of the CaPO_4 [2]. This inorganic salt has a similar chemical composition to that of human bones and teeth [3], and may consequently serve as a useful coating for human implantations and dental affixtures [4]. Unfortunately, because of poor sinterability, HA shows low strength and toughness, especially in wet environments under physiological condition [5]. The poor mechanical properties of pure HA have limited its use in any load-bearing applications [6]. Ti materials are generally regarded to have good biocompatibility and also possess favorable properties, such as relatively low modulus, low density, and high strength [7]. By producing a composite with HA as the matrix phase, Ti will exhibit the favorable mechanical properties and excellent biocompatibility and bioactivity.

Many significant synthesis methods have been explored to prepare HA with controllable properties. Especially for nano scale HA, there are a lot of special behaviors. For example, nanocrystalline HA



powder could enhance densification and improve the fracture toughness of HA ceramics. Many methods have been developed to prepare HA nano powders including sol–gel method, hydrothermal reaction, precipitation method, mechano-chemical, emulsion technique, wet-chemical method, template method [8] and also microwave synthesis [9], as being used in this research. However, most of these methods are costly and require a strict pH control, vigorous agitation and long time for hydrolysis. Use of nanograin ceramics can also improve sinterability due to the higher surface area, and resultant nano scale grains can enhance mechanical reliability by reducing the critical flaw size. The high volume fraction of grain boundaries in nano grain compacts can increase fracture toughness as well as other mechanical properties [10].

The sintering temperature of nano-HA with the addition of Ti was studied by microwaves synthesis [11]. They found the nano-HA can be obtained purely using microwave synthesis at 1100 W. The HA powder at 1100 W showed well defined broad crystalline peak with the average of crystallizing size was 39 nm. From the results, they found the optimum sintering temperature for nano-HA-Ti, were obtained at 1200°C. It caused by the highest value of mechanical properties such as in hardness and compression tests were recorded. The Scanning Electron Micrograph (SEM) showed that increased the sintering temperature may cause a crack to nano-HA-Ti pallets.

2. Methodology

Nano-HA was extracted from eggshells. The eggshells were calcined in a furnace at 900 °C for 2 hours to extract CaCO₃ from calcium oxide (CaO). The CaO produced was blend using ball milling with 200 rpm for 15 minutes to get fined powder. Then, CaO had undergone hydrolysis process where water is added to change CaO to calcium hydroxide Ca(OH)₂. Ca(OH)₂ then mixed with di-ammonium phosphate solution (DAP). The solution was synthesized by using a microwave with power 1100 W for 30 minutes to get HA solution. After that, HA solution produced was dried using freeze dryer at temperature -50 °C to get HA powder. XRD used to characterize the presence of the high purity crystalline HA. HA powder then was mixed with Ti at different percentage of Ti which was 10, 20 and 30 wt. % and made into pallet by using a hydraulic press. After that, the pallets were sintered with a heating rate of 3 °C/min and soak at 1000 °C for 2 hours. Mechanical properties of the each pallet were analyzed using hardness and compression technique. The hardness of the sintered pallets HA-Ti was tested by using Hardness Vickers Tester (SHIMADZU). Compression testing was performed strength using Instron Universal Testing (5582) machine under load 100 kN with speed of 5 mm/min. The microstructures of the surface of the samples were examined using SEM with 5000X magnification.

3. Results and discussions

Hardness values for sintered Ti-HA composite with different Ti contents were shown in Table 1. It can be clearly seen that the addition of Ti contents has resulted in increased hardness values. Ti acts as a soft phase during sintering and aids in superior densification during the sintering process. Furthermore, metallic Ti acts as a bond between ceramic HA and contributed to the rigidity of the sintered samples when Ti is added to the composite. It's clearly shown that the density of sintered sample also increased with increasing of Ti contents. Superior densification and improved bonding between the ceramic grains can effectively contribute to the improved hardness of the Ti added composites compared to pure HA.

Table 1. Hardness and density of HA-Ti composites sintered at 1200 °C

% Ti	Hardness, Hv	Density
0	69.5	2.79
5	71.5	2.80
10	80.0	2.80
15	83.3	2.85
20	83.0	2.90
25	89.6	2.91

Compressive test results are tabulated in Table 2. It can be clearly seen from the table that, an addition of Ti has resulted in improved compressive strength. As discussed earlier, the addition of Ti has

resulted in superior densification and improved bonding between the ceramic particles, which has resulted in improved compressive strength.

Table 2. Compressive strength of Ti added HA-Ti composites sintered at 900 °C

% Ti	Compressive Strength, MPa
0	60.0
5	65.5
10	65.0
15	78.0
20	77.5
25	82.5

Pure Ti was mixed with the microwave processed HA nanoparticles to prepare HA-Ti composites. The mixture of HA and Ti powders are pressed into green pellets and sintered at 1200 °C temperature for 2 hours. Sintered samples were subjected to wear by employing pin-on-disk apparatus (20N load). Hardened steel disks were metallographically polished and used as disks against the sintered HA-Ti composite during the wear tests.

Figure 1 shows the curve variation of coefficient of friction with sliding time during pin on disk wear test. This variation of coefficient of friction with the Ti content in the HA-Ti composite is shown in figure 2. It can be observed from the wear data that the coefficient of friction for sintered pure HA pellets is minimal compared to the Ti added pellets. Coefficient of friction for pure HA sample is 0.62 and increased to 0.66 for 5 wt.% Ti, 0.69 for 10 wt.% Ti, 0.72 for 15 wt.% Ti, 0.73 for 20 wt.% Ti and is maximum at 0.76 for 25 wt.%. It can be clearly seen that addition of Ti to the HA has resulted in increased friction between the sample pin and the rotating steel disk during the pin-on-disk wear testing.

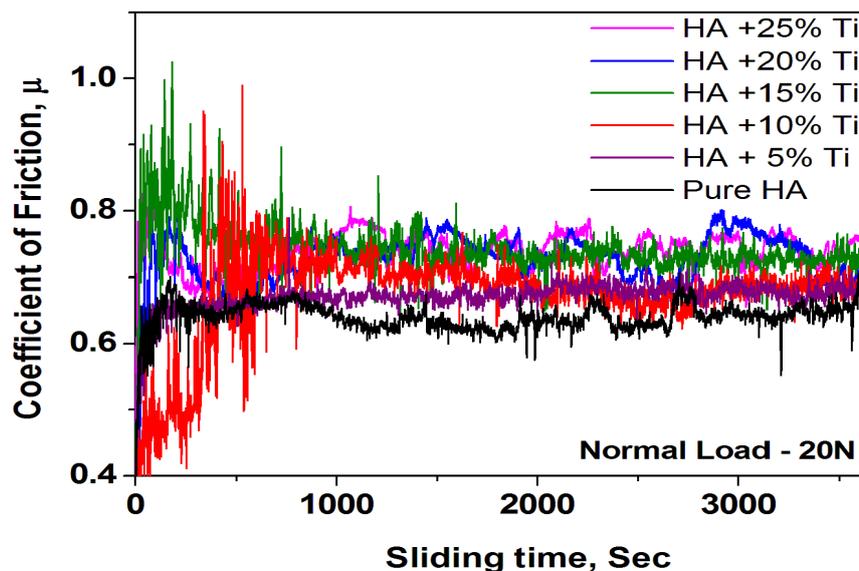


Figure 1. Variation of coefficient of friction with sliding time during pin on disk in wear test

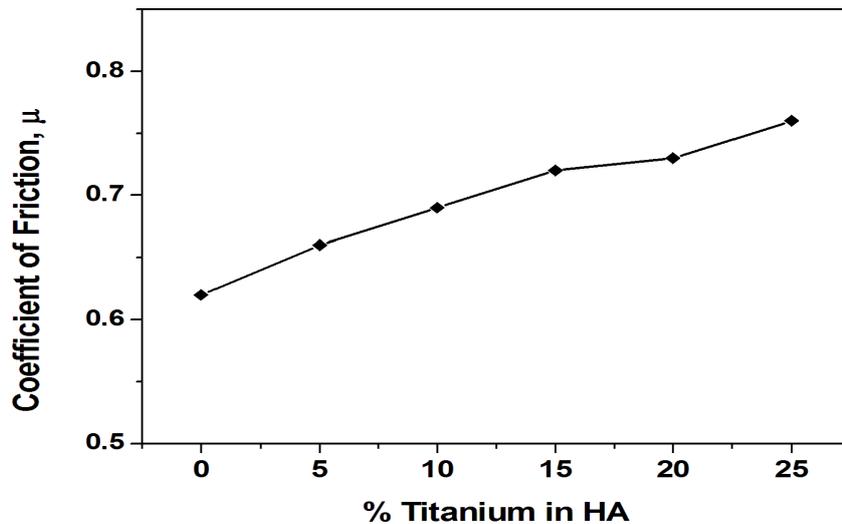


Figure 2. Graph of coefficient of friction during pin on disk wear test on the HA-Ti composites with different Ti contents.

Deep wear tracks can be observed on the surface of the wear sample. With the addition of Ti to the composite, metallic Ti being soft compared to the ceramic HA, would permit adhesion of titanium grain surface to the steel disk and follow by rupture of bonded surface. Furthermore, delaminated HA grains promote third body wear, which would typically result in deep wear track features, as observed in Figure 2 with increasing Ti content. The abrasive wear mechanism is basically the same as machining, grinding, polishing or lapping that we use for shaping materials. Two body abrasive wear occurs when one surface (usually harder than the second) cuts material away from the second, although this mechanism, very often changes to three body abrasion as the wear debris then acts as an abrasive between the two surfaces. Abrasives can act as in grinding where the abrasive is fixed relative to one surface or as in lapping where the abrasive tumbles producing a series of indentations as opposed to a scratch.

This adhesion of two surfaces under consideration and third body abrasion between surfaces during wear can result in increased frictional forces and result in a high coefficient of friction as observed to increase with increased Ti content. It can be seen from the Figure 3, that wear volume has decreased with the increased addition of Ti to HA-Ti composites. However, it is expected that increased coefficient of friction generally results in increased wear volume which is contrary to the current observation.

Earlier, it is stated that when two surfaces are brought together under load, asperities of the two surfaces adhere to each other. The conditions at the interface of these junctions are similar to those of a cold weld. A strong bond is formed, but without much interdiffusion of atoms and crystallization as would occur in a hot weld. During sliding, these junctions are sheared. Shearing may occur at the interface or within one of the two asperities. Most junctions shear at the interface, but occasionally shearing will occur in one of the two materials. This will result in a worn fragment being transferred from one surface to the other. It would seem that shearing should always occur at the interface since it should have the greatest weakness. This generated loose particle which in turn aid in scratching the surfaces involved in wear. All these factors increase the friction between the surfaces which can be directly correlated to the direct material loss during wear.

However, in the current work, the contrast, decreased wear volume with increased coefficient of friction was observed. This could be explained as follows. It is true that higher the friction, higher will be the material loss during wear. The above statement is true as long as wear mechanism involved remains constant with all the samples. However, as discussed earlier, the wear mechanism progressively changed from fatigue assisted delamination for pure HA to abrasive wear as Ti is added.

Furthermore, as discussed earlier, the hardness of samples increased with increased Ti content in the HA-Ti samples. Ti at the grain boundaries of HA acts as sinter aid and results in better densification during the sintering process resting in higher strength values. Sintered pure HA samples are relatively weakly bonded due to insufficient densification and can easily delaminate its grains during wear even at low frictional forces.

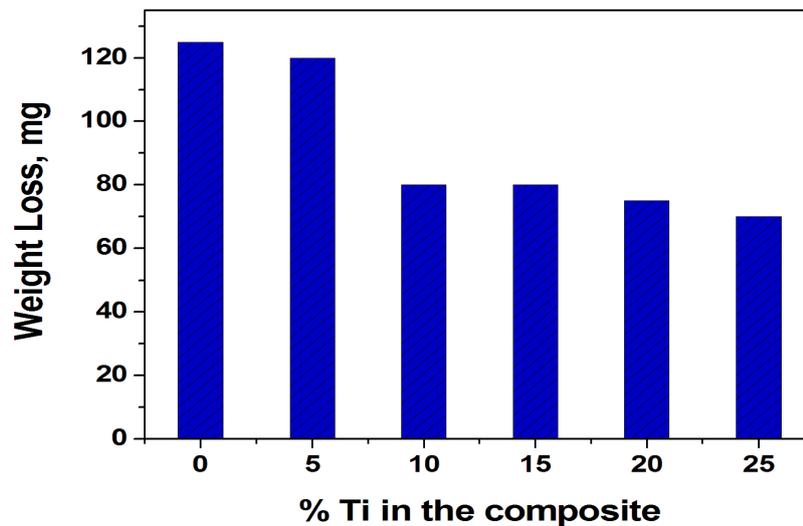


Figure 3. Effect of Ti content on the weight loss of HA-Ti composite during pin on disk wear test

Optical micrographs of worn out surfaces of composite HA samples after the pin-on-disk testing, were shown in figure 4. It can be clearly seen from the micrographs that type of wear failure has progressively changed from delamination for pure HA samples to abrasive wear as Ti content increased in the composite. Pure HA sample wear tracks have shown a surface with no considerable visual deformation and loss of material is due to delamination of small particles by the propagation of cracks. This crack propagation could be, however, inter-granular or intra-granular, assisted by fatigue of the surface during wear of the surface.

Pure HA, being a ceramic, displays a little tendency for considerable plastic deformation and as a result resists the adhesive type of wear during testing. Furthermore, no metal transfer from the steel disk to the HA sample was observed, supporting the low coefficient of friction values observed for pure HA samples. Microplastic deformation followed by subsurface crack nucleation is the preliminary stage of delamination failure during wear. These subsurface cracks propagate and lead to detachments of particles from the surface of the sample resulting in this delamination failure of surfaces underwear. No visible plastic deformation and no visible deep wear tracks are typical features of fatigue assisted delamination. With the addition of Ti to the Ti-HA composites, has resulted in the gradual transformation of delamination failure mode to combined adhesive and third body surface failure modes. Adhesive wear is produced by the formation and subsequent shearing of welded junctions between two sliding surfaces. For adhesive wear to occur it is necessary for the surfaces to be in intimate contact with each other.

Thus it can be concluded that, the addition of Ti to sintered HA-Ti composites has resulted in wear mode to change to abrasive wear from fatigue assisted delamination during wear testing. The addition of Ti has resulted in superior densification and has resulted in reduced wear volumes.

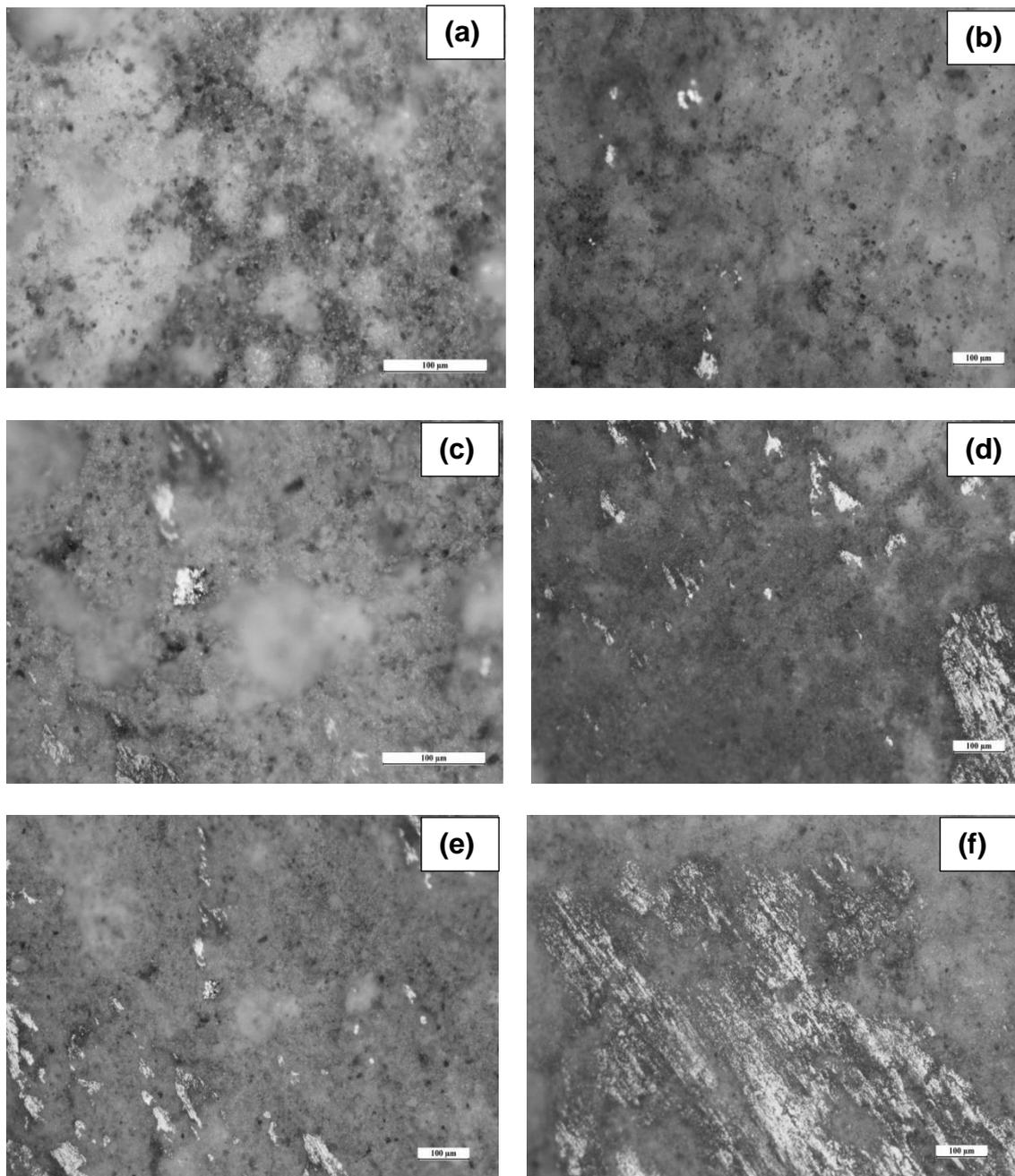


Figure 4. Optical micrographs of nano HA-Ti composite wear tracks after pin-on-disk wear tests ; a) pure HA, b) HA + 5wt.% Ti, c) HA + 10wt.% Ti ,d) HA + 15wt.% Ti ,e) HA + 20wt.% Ti and f) HA + 25wt.% Ti

4. Conclusions

In summary, it can be concluded that by sintering the sample at the temperature of 1200 °C, the highest value for hardness (290.80 Hv) and compression strength (80.04 MPa) could be obtained. Meanwhile, with the addition of 25wt. %Ti, the highest values for hardness and compression test were recorded with 89.6Hv and 82.5MPa respectively. The morphology was illustrated from optical microscope for HA-25wt. %Ti composite before sintered. It was found that the particles between nano-HA and Ti were agglomerated without any bonding. Post-sintering, the both types of particles seem to attach to each other. The size of Ti was found to be larger than nano-HA, making it more visible than nano-HA. Wear test study showed that the coefficient of HA-25 wt. % Ti composites was

recorded at 0.76, while the pure HA showed at 0.62. Therefore, it can be clearly seen that the addition of Ti onto HA has resulted in the increase of friction between the sample pin and the rotating steel disk during the pin-on-disk wear testing.

5. References

- [1] KJ Sato 2007, *J. Ceram. Soc. Jpn.* **115**, 124–130
- [2] S Raynaud, E Champion D, Bernache-Assollant, P., Thomas 2002 *Biomaterials* **23**, 1065–1072
- [3] TMG Chu, DG Orton, SJ Hollister, SE Feinberg, JW Halloran 2002 *Biomaterials* **23**, 1283–1293
- [4] L El-Hammari, H Marrouna, A Laghzizila, A Saoiabia, C Rouxb, J Livageb, T Coradinb 2008 *J. Solid State Chem* **181**, 848–854
- [5] A Banerjee, A Bandyopadhyay, S Bose 2008 *Materials Science and Engineering C* **27** 729-735
- [6] S Bose, W Xue, A Banerjee, A Bandyopadhyay 2010 “In Handbook of nanostructured oxides for life sciences,” edited by Kumar, C.S.S.R., (eds.) Weinheim: Wiley-VCH
- [7] K Niespodziana, K Jurczyk, J Jakubowicz, M Jurczyk 2010 *Materials Chemistry and Physics* **123** 160–165
- [8] J Klinkaewnarong, E Swatsitang, S Maensiri 2009 *Solid State Sciences* **11** 1023–1027
- [9] AZO Arawi 2015 “Synthesis and Mechanical Properties of Nano-Hydroxyapatite from Egg-Shells and Effects of Nano-HA-Titanium Composite Using Microwave Technique” MSc Thesis, Universiti Teknologi MARA 2015.
- [10] RW Rice, CC Wu, F Borchelt 1994 *J Am Ceram Soc* **77**, 2539–2553.
- [11] AZO Arawi, R. Rosmamuhamadani, M.K Talari 2012 *Adv. Mater. Research* **538-541**, 2392-2395.

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