

Full Length Research Paper

Fabrication of functionally graded Hydroxyapatite-Titanium by applying optimal sintering procedure and powder metallurgy

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This paper demonstrates the functionally graded metal-ceramic composite fabricated via pressure-less sintering. The pure metallic and ceramic components are Titanium (Ti) and Hydroxyapatite (HA), which were located at the ends of a cylindrical specimen. FG samples are prepared with mixing ratios of 100:0, 75:25, 50:50, 25:75, 0:100. The cylindrical samples had a thickness of 6 mm in size and 20 mm radius. Samples are created by using carbon cylindrical die. The optimum thermal load mapping is obtained experimentally. The properties of all FGM products are characterized by shrinkage, optical microscope, scanning electron microscope (SEM), energy dispersive spectrometry (EDX) and hardness test. The grade of the FGM material is proven by results from all recorded measurements, as well as linearity of shrinkage. Result from optical micrograph and SEM indicate that the HA/Ti FG cylinder can be produced successfully by cold pressing with developed thermal mapping. Vicker's hardness of HA/Ti is higher than that of pure microcrystalline Ti (metal) and reduces by decreasing the density of the layer of HA/Ti.

Key words: Hydroxyapatite-Titanium, functionally graded material (FGM), sintering, pressure-less fabrication method.

INTRODUCTION

Functionally graded materials (FGMs) are a new class of advance composites that consist of two or more than two continuous, or discontinuous, gradient in composition and microstructure. Such gradients can be customized to meet desired needs while providing the best use of composite components (Lannutti, 1994; Shukla et al., 2007). FGM technology is also a new interfacial technology for solving the problems of the sharp interface between two dissimilar materials (Somiya, 2003). Successful application of FGMs to decrease thermal and residual stresses due to smooth transition through the thickness was done by Reddy (2000). Several different physical and chemical methods depending on type of materials and facilities are used to fabricate FGMs (Schwartz, 2002). A best-fit single method to fabricate of

FGM is difficult to define, because each method has its own advantages and drawbacks. Some researchers have used the optimal combination of several methods depending on the properties of the component materials (Kieback et al., 2003; Miyamoto, 1999). This is possible due to close micro-structural control, inherent versatility, sizable, bulk and cost-efficient powder metallurgy or ceramic sintering (Hanawa, 2010). Bio-medical applications are new field for FGMs, where they are used for implants and artificial parts of the body (Watari et al., 2004). The human body is supported by 206 bones, each of which directly or indirectly affects our brain and other organs. Researchers are trying to find a new material that can work as a replacement for bones. These materials are expected to have attributes such as appropriate hardness, corrosion resistance, biological compatibility, and harmlessness. HA and Ti are two important bio-medical materials that have been investigated in some studies as FG materials (Chenglin et al., 1999; Chu et al.,

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2001). HA/Ti FG can be made a best promising material for human tissue implantation, orthopedic, and dental applications due to its excellent biocompatibility and bioactivity. Because of their biomedical, mechanical, and biocompatibility properties, some studies to produce an HA/Ti FG have been reported (Kondo et al., 2004). In some studies (Bai et al., 2009; Cannillo et al., 2008; Ding, 2003; Xiao et al., 2005) fabrication of HA/Ti coating using sol-gel, cold isostatic pressing (CIP), hot sintering, plasma spray and some new methods were considered. The effect of Ti additions through the composition, microstructure, thermal stability and the bonding strength of HA/Ti coating using hydrothermal–electrochemical technique was investigated by Xiao et al. (2005). Lim et al. (2002) studied fabrication of HA/Ti coating on Ti-6Al-4V by chemical solution deposition. A plasma spray process to fabricate functionally graded HA/Ti coatings and find the microstructure, density, porosity, micro-hardness, and Young's modulus was developed by Khor et al. (2003). Zhang and Tao (2006) prepared HA/Ti coating by electrochemical deposition technology and discussed the effect of the deposition voltage and electrolyte concentration in their research. Fabrication of HA/Ti as a FG dental implant using CIP and sintering method was experimented by Watari et al. (1997) to satisfy both mechanical and biocompatible properties. Chenglin et al. (1999) developed a FG biomaterial in a HA/Ti system by an optimized powder metallurgical method. They investigated micro-structural analysis and mechanical tests. In the continuation of their research in this field, Chu et al. (2001) examined a fabricated HA/Ti biomaterial FG by employing a hot-pressing method. They also optimized the distribution function of its components based on classical lamination theory and thermo-elastic mechanics to overcome the tendency toward micro-cracking in the samples. The gradation of the FG was proven using an electron probe microanalyzer (EPMA) and X-ray diffraction examination methods. They concluded that the titanium layer supplied considerable assistance to the mechanical properties for the whole FG biomaterial. In another major research, Chu et al. (2003) developed and fabricated an FG HA/Ti biomaterial by optimizing the best combination of their biocompatibility and mechanical properties. In their method, they first examined the thermo-elastic properties of uniform HA/Ti related to each graded layer of the FGM. In their results, the thermal expansion coefficients of the HA/Ti increased with the rise in temperature or content of HA, and the residual thermal stress was confirmed by an X-ray and theoretical method.

Other FG fabrication methods were considered by researchers. Jiang et al. (2000) and (Pei and De Hosson, 2000) studied processing modeling, structural analysis and performance evaluation of FGMs based on laser cladding (LC) fabrication method. Some porosity reduction and sintering models using pressure-less sintering method was investigated by Pines and Bruck

(2006a, b). Ogawa et al. (2006) expanded the theoretical study on fabrication of FG with density gradient by a centrifugal solid particle method. Watanabe et al. (2002) also studied the particle size distribution in FGMs fabricated by the centrifugal solid particle method. Nindhia et al. (2008) fabricated HA/Silk FG by pulse electric current sintering method and showed that silk film utilized as a bound between each layer had positive effect on its fracture toughness.

The present work focuses on fabrication of FG from HA/Ti using pressure-less method in detail. The thermal map is optimized experimentally and the effects of powder percentage, blending, sintering and cold pressing also are discussed. Microstructure and properties of FG samples are evaluated and the gradation of HA/Ti FG cylinder is proven by some examinations.

METHOD OF FABRICATION

Here, the fabrication process used to produce the HA/Ti is discussed in detail. The densification of the components and the degradation of the Ti phases from severe reactions with the HA ceramic and layer compositions are very important.

Preparation of materials

To prepare the powders, the following criteria play significant roles in the fabrication of the HA/Ti FG.

Selection criteria

The combination of HA and Ti powders as the ceramic and metal materials is considered for an FG plate. HA (produced by Sigma-Aldrich) as a biomechanical and cohesive material with a melting point close to Ti (produced by Sigma-Aldrich). Ti has high stiffness and the ability to develop a new powder composition. This property can decrease layer discontinuity and increase powder homogeneity. However, it is inevitably expensive. The combination can possibly be an excellent replacement component as a hard tissue in the human body because of the closely resembled of its crystallographic and chemical properties to bones and teeth (Nindhia et al., 2008). The characteristics and geometry of the selected powders are tabulated in Table 1. The maximum difference in the melting points for the components used in the cold pressing method should be small.

Determination of powder percentage

The particle size, purity, and shrinkage are three important parameters to determine the percentage of each layer. Meanwhile, the entire thickness of a specimen, tonnage of press, and shape of the die play important roles in computing the mixed powder for layers. A smooth change between layers can prevent the cracking, porosity, and linear shrinkage that is expected to occur.

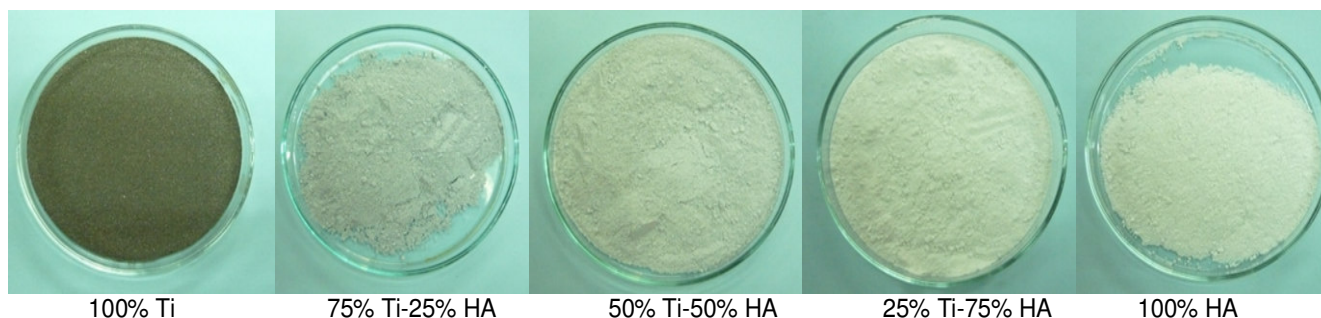
Based on the experimental work, in order to produce a good quality FG structure, at least five layers are required. The configurations of these five layers are highlighted in Table 2. In this study, after some trial-and-error approaches, the compositions (in %weight) of the layers were selected to be 100% pure Titanium, 75% Titanium+25% HA, 50% Titanium+50% HA, 25% Titanium+75% HP, and 100% pure HA. The weight of the mixed

Table 1. Physical and chemical properties of powders.

Physical and chemical properties	HA	Ti
Melting point (°C)	1760	1660
Molecular weight (g. /mol.)	502.3	47.88
Specific gravity (g. /cc.)	3.0 –3.3	4.510
Particle size (μm)	10-20	20-30
Purity (%)	99.9	99.9

Table 2. Percentage of layers.

Layer number	Percentage of layers	Total weight (g)
1	100% pure Titanium	1x47.88
2	75% Titanium + 25% HA	(0.75x47.88) + (0.25x502.3)
3	50% Titanium + 50% HA	(0.5x47.88) + (0.5x502.3)
4	25% Titanium + 75% HP	(0.25x47.88) + (0.75x502.3)
5	100% pure HA	1x502.3

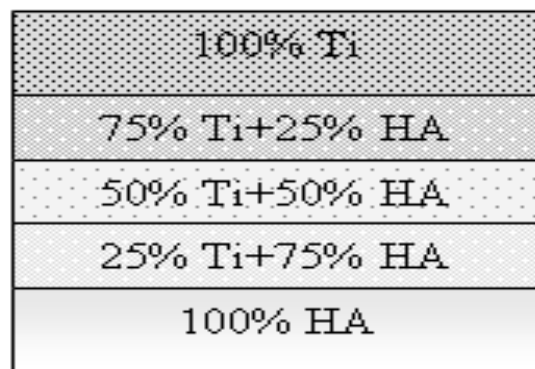
**Figure 1.** Layer powder compositions.

powders is measured using a digital weighing machine (GF-300). The details of the material can be seen in Figure 1, and the arrangement of the composition is as shown in Figure 2.

By considering the percentage of each layer and molecular weight (g/mol), as mentioned in Table 1, the total weight of each layer is calculated. The shape and size of samples are two important parameters to select the weight. The empirical work in this study revealed that the thicknesses of the first and last layers should be greater than the other layers. The manual injection process for a specimen is to avoid for any cracks during pressing that can be considered crucial. A load of 10 (Ton) is applied to produce the desired thickness, as shown in Table 3. The thickness values for each layer, that dependent on position of layers and percentage of combinations in a FG plate are found experimentally and empirically.

Blending procedure

One of the most important fabrication steps involves the method and amount of the blending for each component and layer configuration. This will enhance the quality of the FG samples and decreases the damages during their processing. In the following, some significant elements are introduced.

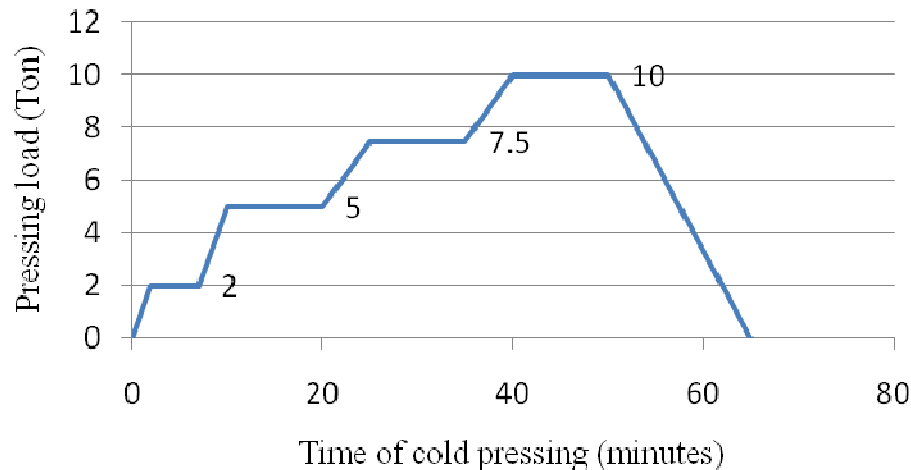
**Figure 2.** Arrangement of functionally graded HA/Ti.

Drying

It should be noted that, not only before, but also after ball milling processes (planetary ball mill, LMS, E3A05), the powders should be dried in an oven at 110°C for at least 12 h. This procedure is necessary in order to produce a dry mixture with no moisture.

Table 3. Layer thickness of HA/Ti.

Layers	1	2	3	4	5
Thickness (mm)	1.5	1	1	1	1.5

**Figure 3.** Cold pressing loads.

Ball milling

The ball milling procedure can be affected by the following factors:

- i) Type of ball mill machine.
- ii) Bowl capacity.
- iii) Material, size, and number of balls.
- iv) Velocity of machine.
- v) Duration of ball milling.
- vi) Cleanness of balls and bowl.

The powders should be blended separately for at least 1 h and together for 5 h to ensure the maximum dispersion of particles and reach the optimal physical properties. The mixed powder should be gray in color. A planetary ball mill machine is recommended to blend the powders. In this research, a planetary ball mill (LMS, E3A05) was used to rotate the bowl (contain of both mixed powders) along with its axes and the center of a circle. Based on experimental work, at a maximum, the bowl should be filled to 40%. In this research, the capacity of the bowl was 13 gm. The size and material properties of the balls were determined to decrease the particle size and increase the homogeneity of the powders. The suitable diameter of the hard steel balls for this work was 8 mm and the number of ball was 7. The ball milling process can be done in two stages. The first one is to promote homogeneity and decrease the particle size of the powders separately (1 h, 300 rpm), while the second one is for the dispersion and homogeneity of the mixed powders (5 h, 300 rpm). It should be noted that the status of the mixed powder should be checked because of the high adhesive properties of HA in comparison with Ti in the mixing powders. The cleaning of the ball mill equipment (bowl and balls) has four steps: soft soil cleaning, mineral water cleaning, soft cloths, and ethanol. In this study, the soft soil cleaning was done for 10 min at 300 rpm, which was followed by washing with mineral water and drying with soft cloths. Finally, ethanol (absolute-3241039) was used for washing.

Cold pressing

In the cold pressing step, a green compact is created using a cylindrical type of carbon die with a diameter of 20 mm. It consists of 5 layers with the same thickness for all of the layers except the top and bottom layers. In this process, the compositions are compacted at 10 (Ton) using a uni-axial hydraulic press to make a green compact. The applied force should be increased slowly for 50 min and then decreased linearly in 15 min (Figure 3). The hydraulic press is shown in Figure 4. The contacting shear stress between the outside of the sample and inside of the die can be decreased by using Al_2O_3 powder due to its lubrication property. These surfaces can be smeared by a thin layer of Al_2O_3 .

Sintering step

Traditionally, ceramic objects are fabricated using a sintering method, and this method has potential uses in the manufacture of FG structures. A flowchart of the fabrication steps for functionally graded Ti-HA by a pressure-less sintering method are shown in Figure 5. In the last step of the fabrication, green compacts are sintered inside a tube furnace under flowing argon to prevent oxidation, as seen in Figure 6. The heating map depends on the melting points of the two powders. The type of furnace and green compact must be selected accurately. The heating map is obtained by a trial-and-error approach to obtain an appropriate product (Figure 7). The temperature is increased from 30 to 1200°C during 8 h. In this research, the best maximum temperature was 1200°C, which was 72% of the Ti melting point. The adhering of each layer to the others is directly related to the maximum selected temperature used in sintering. Besides the thermal specification mentioned previously, two other parameters are important, the position and direction of the green compact inside the furnace. The best position for a green compact is the middle of the furnace, and it is recommended that the heavier component should be at the



Figure 4. Hydraulic press.



Figure 6. Sintering machine.

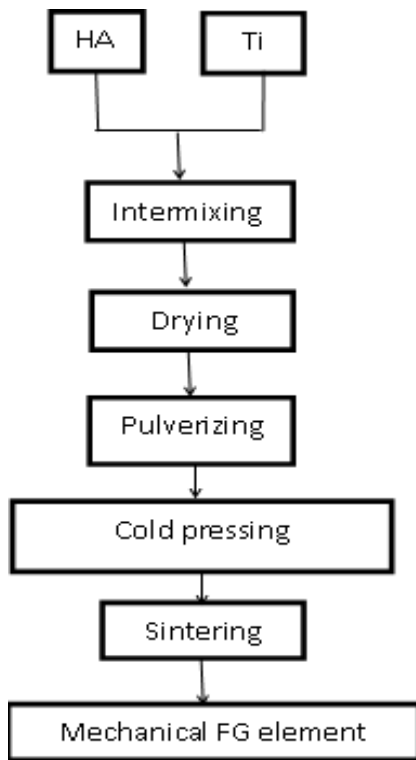


Figure 5. Fabrication steps flow chart.

upper surface.

RESULTS AND DISCUSSION

The gradation of the FG HA/Ti was proven by using shrinkage measurements, scanning electron-microscopy

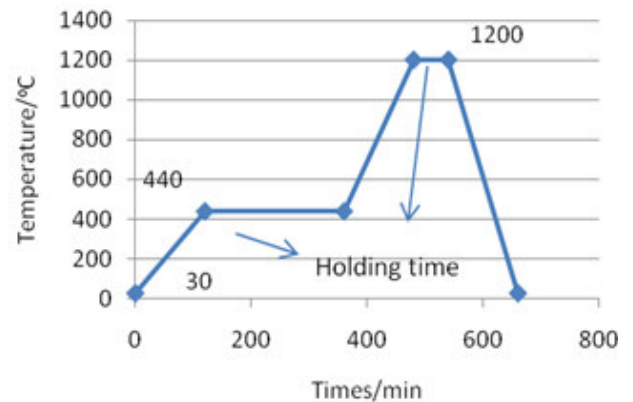


Figure 7. Heat treatment map.

(SEM), energy dispersive spectrometry (EDX), and micro-hardness tests. Grounding and polishing were required for the samples after cutting with a diamond saw to achieve accurate observations in the micro-structural examination.

Shrinkage

Linear shrinkage is one of the important parameter for evaluating the quality of component gradation in an FG structure. Shrinkage could be calculated by accurately measuring the green compact, and then comparing it with the size of the sample after sintering (Figure 8). Figure 9 illustrates the effect of increasing the Ti percentage versus the shrinkage of the diameter of an HA/Ti cylinder fabricated by a pressure-less method. The diameter of

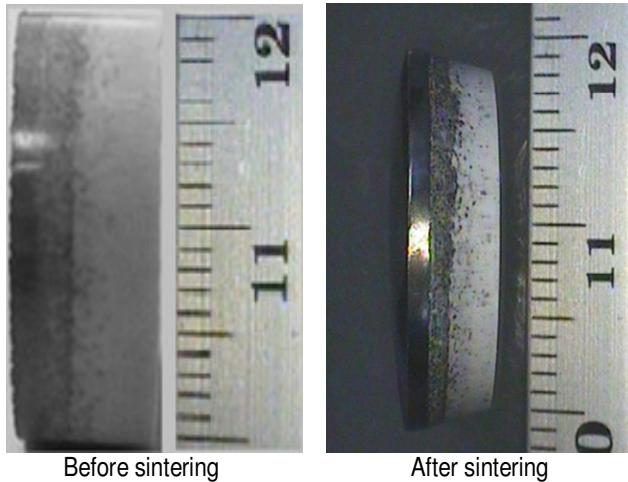


Figure 8. Before and after sintering.

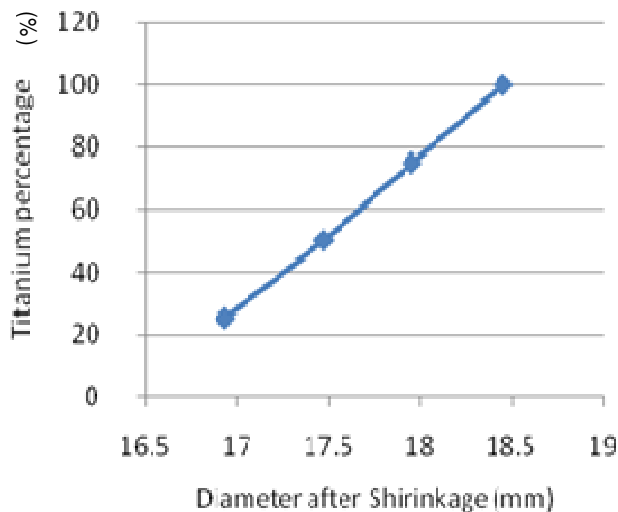


Figure 9. Titanium percentage against diameter after shrinkage.

the cylinder before sintering was 20 mm, which decreased after the sintering process according to Figure 9.

Scanning electron-microscope (SEM)

The thickness and each layer of the samples were individually examined using an optical microscope and scanning electron-microscope (SEM). Figure 10 (a) shows the gradation of HA/Ti from left to right. Figures 10 (b) and (f) represent the full metal and ceramic of a specimen, respectively. The linear variations of Ti to volumetric HA are given in Figures 10 (c) to (e). As expected, the color of each layer changed from a dark to

light color, as shown in Figure 10(b) to (e) with full Ti and HA, respectively.

Energy dispersive spectrometry (EDX)

Electrical energy was sent into an FG cross section covered by a thin film of gold (by vacuum-deposition) to examine the reflected wavelength in order to determine the chemical composition of the produced samples. Figures 11 (a) to (d) record the chemical components from full Ti into full HA. It is clear that the percentage of Calcium, which indicates the HA, is gradually decreased from Figure 11 (a) into a full percentage of Ti in Figure 11 (d).

Micro-Hardness

The Vickers' micro-hardness of the samples was measured using a micro-hardness tester on polished surfaces under a load of 200 g (Figure 12). The averages of 5 indentations in each layer were used to calculate the micro-hardness values of the layers. It should be noted that the Vicker's hardness increased with a rise in the HA percentage in HA/Ti, while, because of decrease in density in layers 3 and 4 (25 to 75% HA combination), the hardness of the layers was reduced.

Conclusion

A pressure-less powder metallurgy procedure was presented in this research as a fabrication technique for an HA/Ti functionally graded (FG) cylinder using an optimum experimental heat sintering. The gradation of the components was considered from the metallic (Ti) end to the ceramic (HA) end. All of the steps such as the selection criteria for the powders, percentages, blending, the effect of gravity in the cold pressing, and sintering were indicated in detail. An optimum sintering map was derived experimentally. Four methods, shrinkage, SEM, EDX, and Vickers' micro-hardness, were employed to validate the results of this study. The structure and composition analysis of the FG cylinder produced with different layers confirmed the functionality of the design. The linear shrinkage obtained was an appropriate indicator of validity. The Vicker's hardness of HA/Ti was higher than that of pure microcrystalline Ti metal and decreased in layers 3 and 4 of the HA/Ti FG. It is considered that these examinations could lead to an estimate of the grading index value that could be used for the theoretical formulation of FGM material properties.

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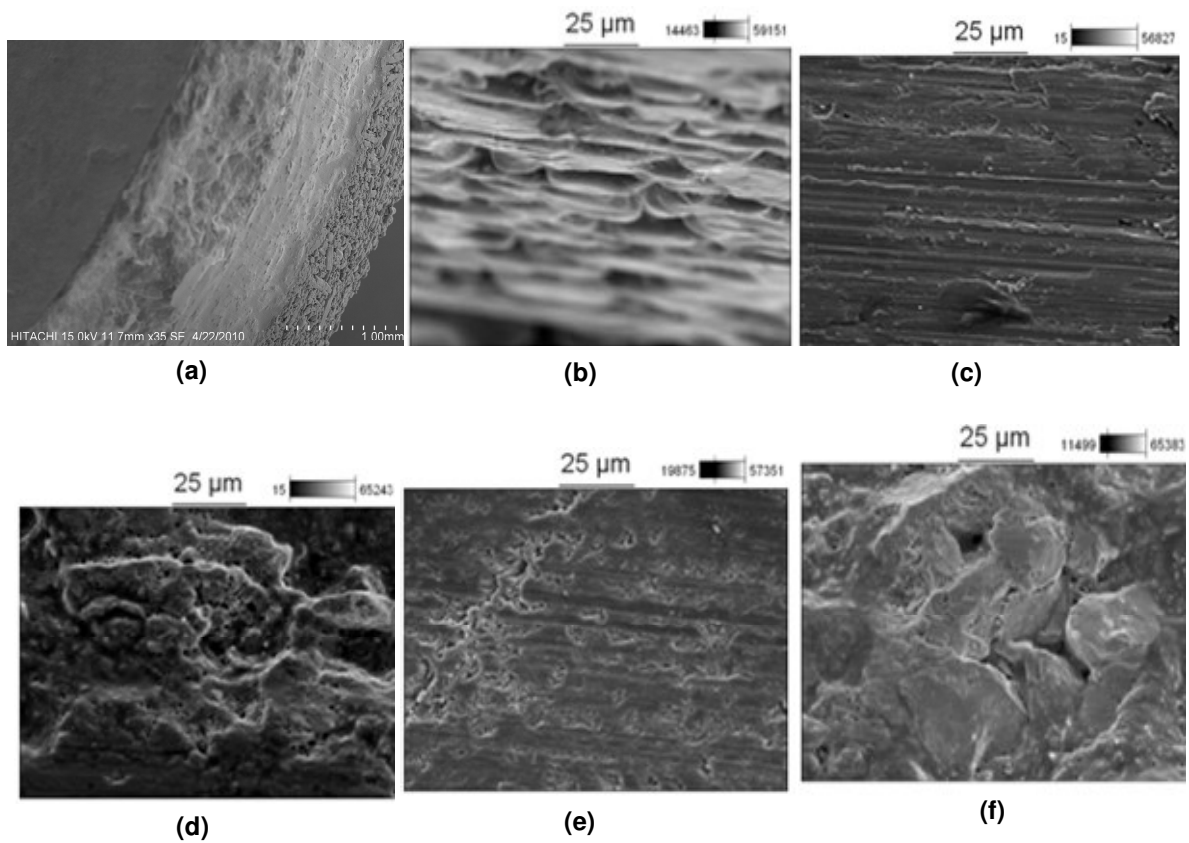
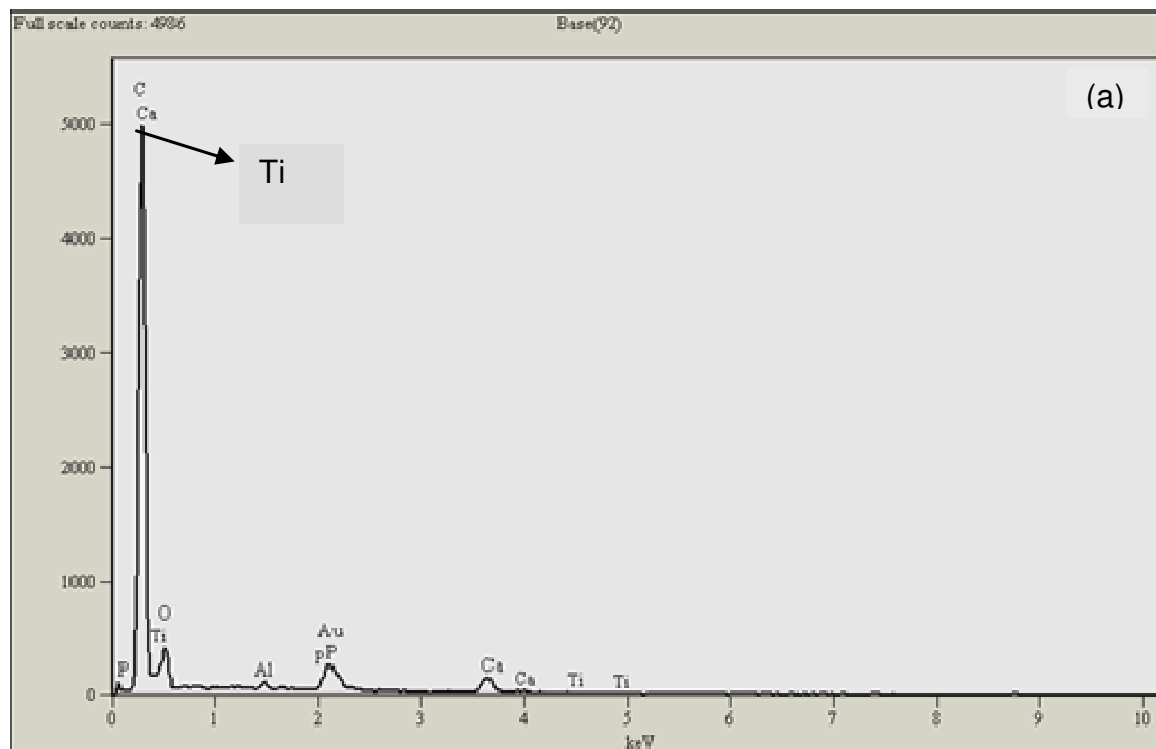
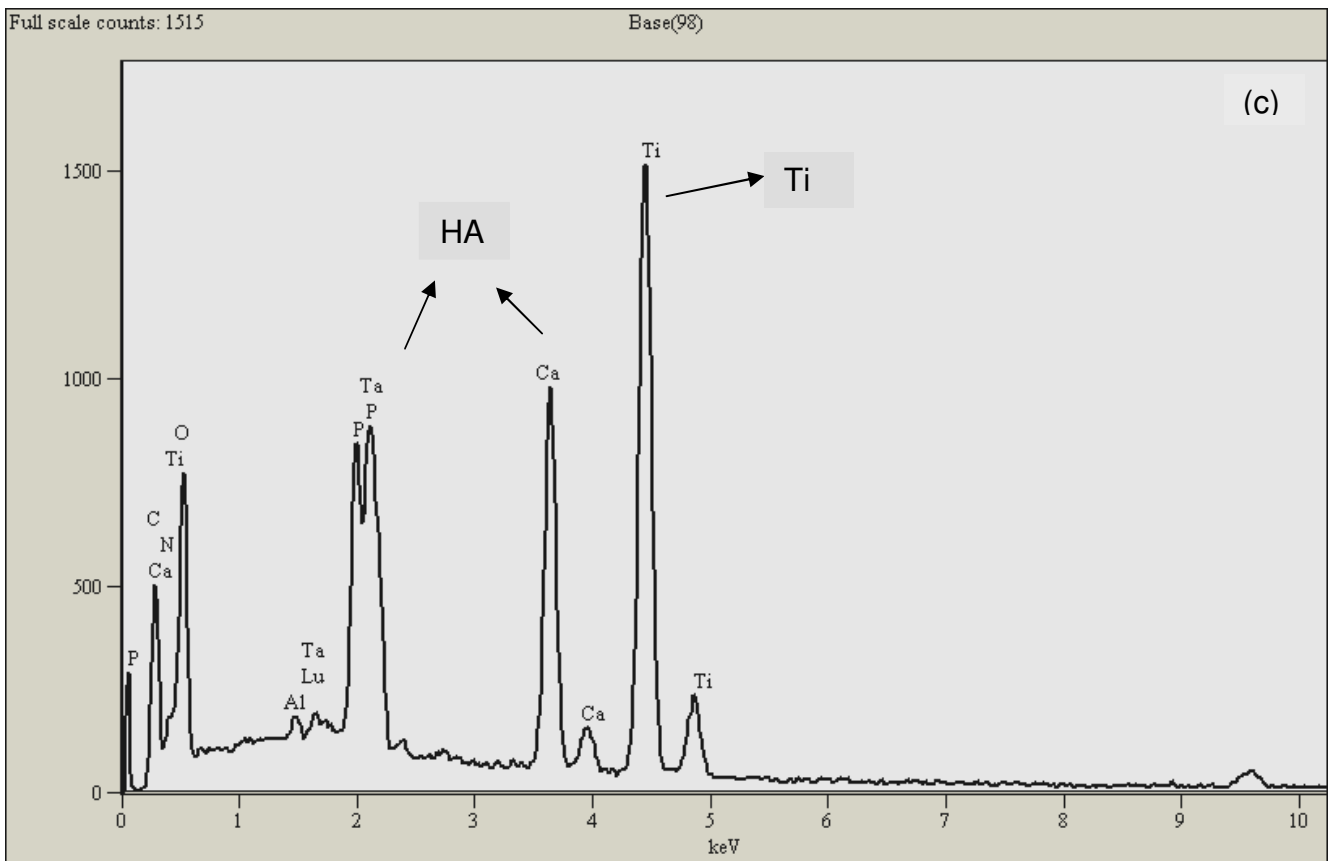
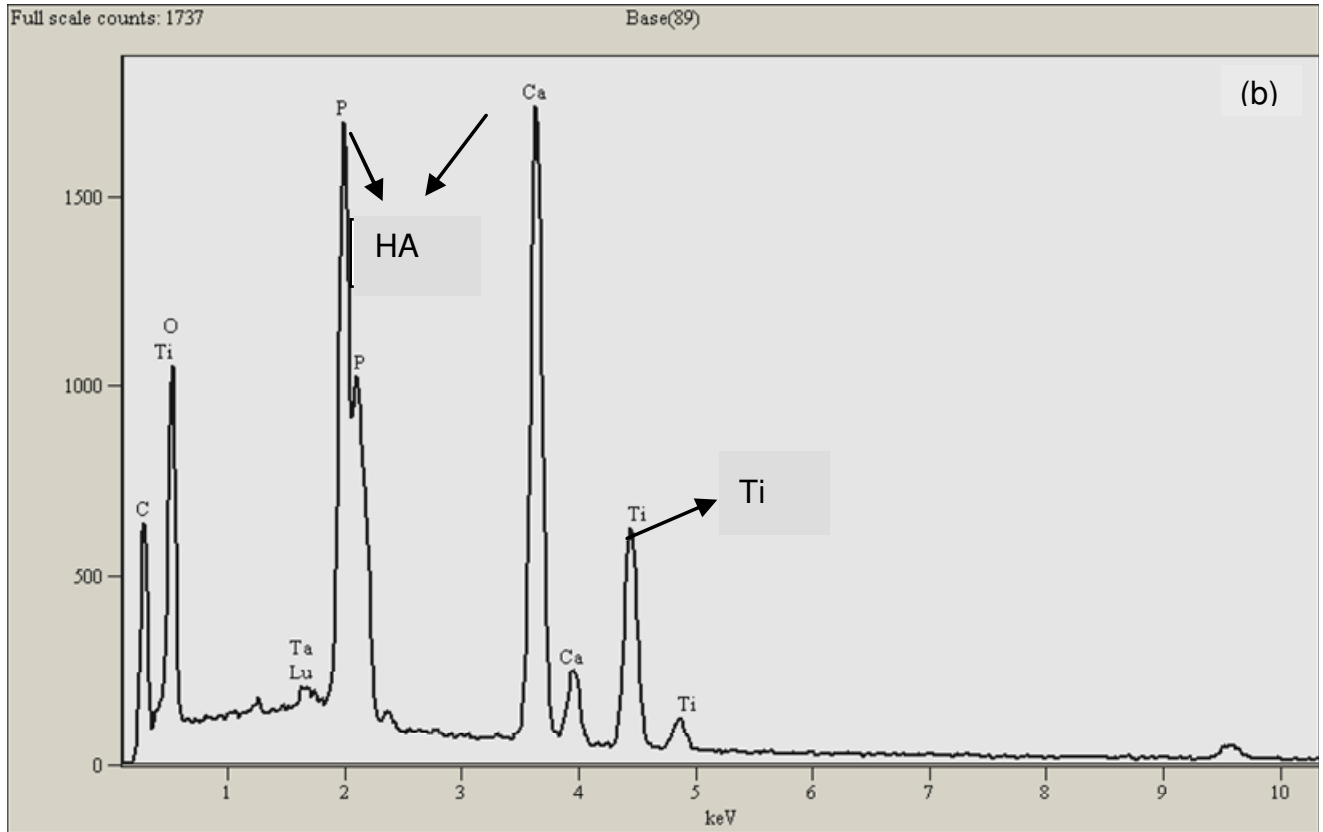


Figure 10. Digital SEM image of HA/Ti, SEM image of layers in experiments (Accelerating Voltage: 15.0 kV Magnification: 1000), (a) all layers; (b) layer 1 consist of 100% Ti; (c) layer 2 consist of 75% Ti+25% HA; (d) layer 3 consist of 50% Ti+50% HA; (e) layer 4 consist of 25% Ti+75% HA; (f) layer 5 consist of 100% HA.





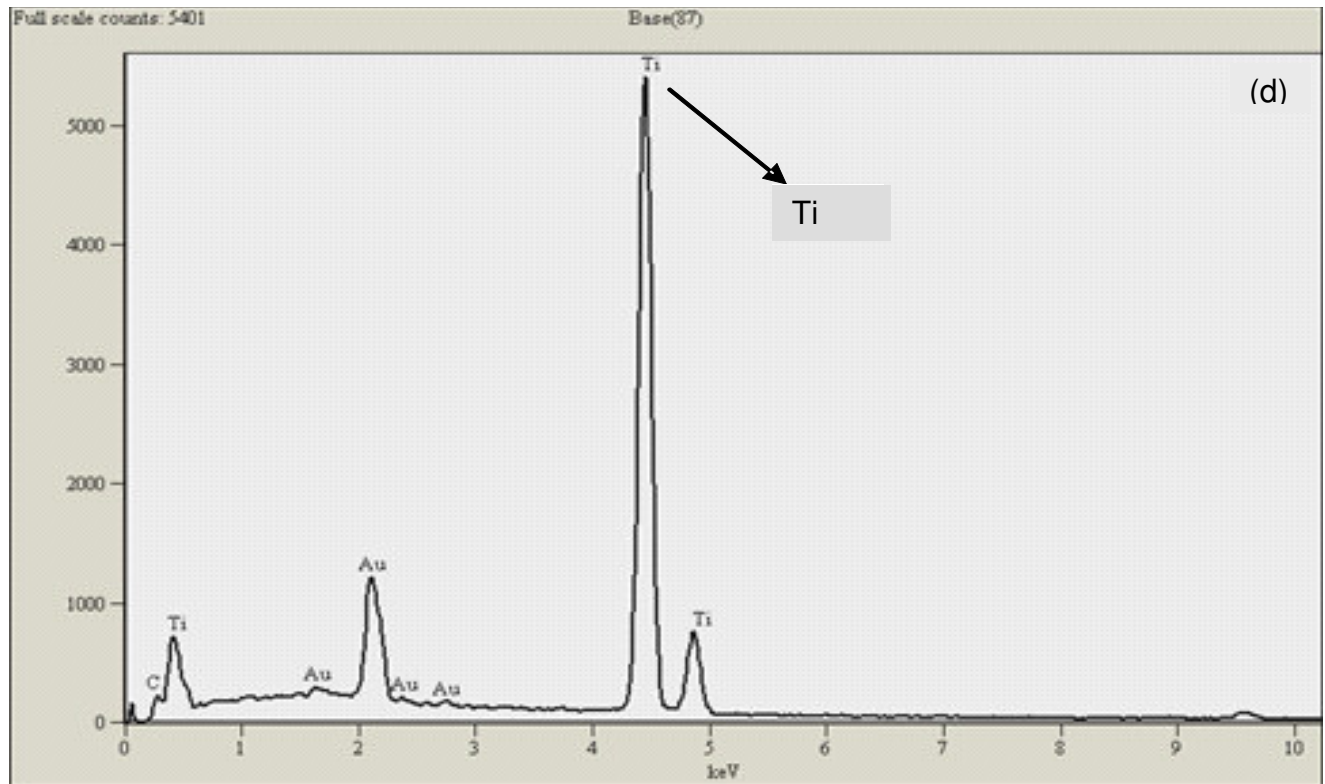


Figure 11. EDX examination and analysis of the samples (a) Full HA (b) 75% HA + 25% Ti (c) 50% Ti + 50% HA (d) Full Ti.

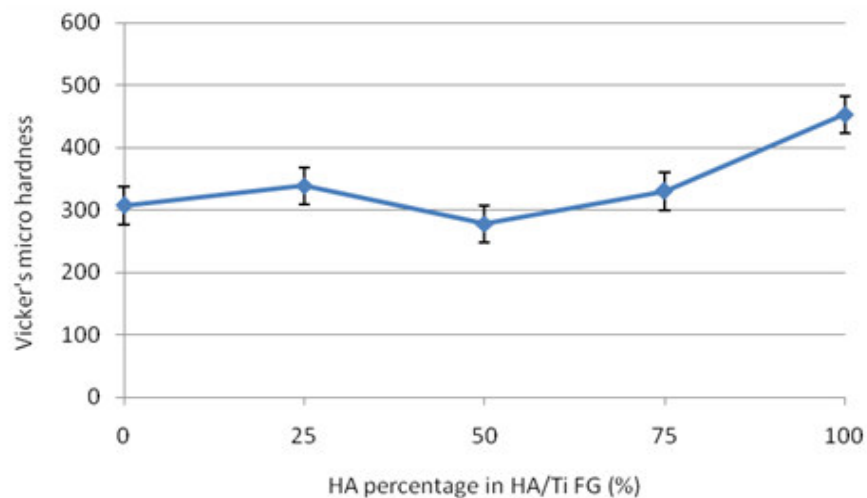


Figure 12. Vicker's Hardness against HA percentage of HA/Ti FG.

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