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Optimal design and fabrication of hydroxyapatite–Ti asymmetrical functionally graded biomaterial

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Abstract

Hydroxyapatite (HA)–Ti asymmetrical functionally graded biomaterial (FGM) combining the excellent biocompatible properties of HA ceramic and the good mechanical properties of titanium metal was designed optimally and fabricated in this paper. The thermo-elastic properties of the uniform HA–Ti composites with various mixing ratios corresponding to each graded layer of the FGM were tested firstly. The experimental results show thermal expansion coefficients of HA–Ti composites increase with the rise of testing temperature or the content of HA ceramic and aren't affected by the allotropic transformation of $\alpha \rightarrow \beta$-Ti phase at 882.5 °C, while there is no a direct corresponding relationship between elastic modulus and the mixing ratio of HA–Ti composites. Then the optimal graded compositional distribution exponent n for HA–Ti asymmetrical FGM is acquired by the thermal stress relaxation design and structure optimization, which is 0.9. Finally the perfect HA–Ti asymmetrical FGM with the optimum graded composition was fabricated by hot pressing successfully. The tested values of residual thermal stress in the sintered FGM samples by X-ray stress analyzer are basically consistent with the theoretically calculated ones.

Keywords: Functionally graded biomaterial; Optimal design; Titanium; Hydroxyapatite

1. Introduction

Hydroxyapatite (HA)–Ti system functionally graded biomaterials (FGMs) with the gradual distribution of components can eliminate the macroscopic interface existing between the HA coatings and titanium alloys, which make full use of the excellent bioactivity of HA and the high strength and toughness of Ti metal [1–8]. So far, both HA–Ti asymmetrical FGM with a asymmetrically distributing compositional profile varying gradually from Ti side to HA side [2,3,5,6] and HA–Ti symmetrical FGM with a symmetrically distributing compositional profile [7,8] have been developed successfully by our group using powder metallurgical method. The mechanical properties, fracture behaviors and the relaxing characteristics of thermal residual stress of these FGMs have also been reported correspondingly.

As discussed previously, the change of ambient temperature could lead to the existence of additional residual thermal macroscopic stress and strain in each graded layer besides the thermo-elastic deformation of the whole FGM due to the heterogeneous characteristic along the thickness direction of FGM [9–11]. The sintering temperatures are far higher than the utilizing ones (or the body temperatures) of HA–Ti FGMs. As a result, the yielding of residual thermal macroscopic stress in the FGM could not be avoided, which will play an important role on the preparation and properties of HA–Ti FGMs. In our previous studies, it was found that HA–Ti symmetrical FGM with a compositional profile pre-designed has always many microcracks on the surfaces [7], while the perfect HA–Ti symmetrical FGM with the optimum graded composition can be prepared by the thermal stress relaxation design and structure optimization [8]. Although there are no microcracks on the surface of HA–Ti asymmetrical FGM, the compositional profile pre-designed is not the optimum for the relaxation of thermal residual stress in

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the FGM due to the presence of the maximal residual tensile stress in Ti–60vol.% HA region of the FGM with the poor strength and toughness [6]. Thus the optimal design of HA–Ti asymmetrical FGM should be made.

In this paper, the thermo-elastic properties of HA–Ti composites with various mixing ratios corresponding to each graded layer of HA–Ti asymmetrical FGM were tested firstly, which are essential for the structure optimization of the FGM. Then the optimal design of HA–Ti asymmetrical FGM was made. Finally, HA–Ti asymmetrical FGM with the optimum graded composition was fabricated by hot pressing. The residual thermal stresses in the sintered FGM sample were tested by X-ray stress analyzer (XSA).

2. Optimal design model of FGM

Fig. 1 shows the analysis model for FGM plate with a thickness of h, which consists of n layers of infinite macroscopic boards. To analyze the elastic properties of FGM plate simply and conveniently, the following hypotheses should be made: (1) The hypothesis of consistent deformation between layers: each layer bonds tightly and is deformed consistently with its contiguous layers; (2) The hypothesis of invariable straight normal: the normal on the median plane of FGM plate keeps vertical before and after the deformation; (3) The hypothesis of $\sigma_z = 0$: the positive stress in the direction of thickness is too little to be taken into account; (4) The hypothesis of the plane stress state: each layer in the FGM may be considered in the plane stress state approximatively. The HA–Ti system composite materials with very homogeneous chemical compositions and microstructure stand in linear elastic stage and present intergranular fracture without macroscopic plastic deformation [1,2]. At the same time, the dimension of thickness is far less than those of the plate surface in the FGM. Thus the above-mentioned hypotheses are in reason.

Based on the above analysis model, the elastic properties of FGM were analyzed by thermo-elastic mechanics. The following analytic expression of the residual thermal macroscopic stress during the fabrication process at an arbitrary point in FGM was gained.

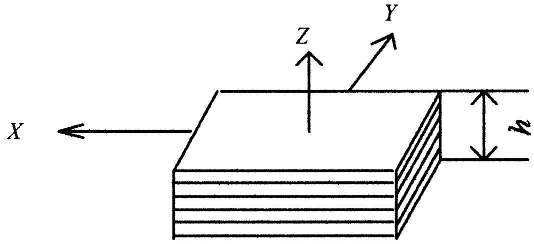


Fig. 1. The analysis model for FGM plate.

The detailed theoretical discussion may refer to Ref. [1].

$$\{\sigma^{R}\} = [Q](\{\varepsilon^{0T}\} + z\{\kappa^{T}\} - \{\alpha\}\Delta T), \quad (1)$$

where $\{\sigma^{R}\}$ is the matrix of residual thermal stress, $[Q]$ the matrix of the stiffness of the positive axis, $\{\varepsilon^{0T}\}$ the matrix of the thermal strain of the median plane, $\{\kappa^{T}\}$ the matrix of thermal deformation curvature, $\{\alpha\}$ the matrix of thermal expansion coefficient, ΔT the difference between the fabricating temperature and the room one.

3. Experimental procedure

3.1. Raw materials and powder processing

The raw materials used were titanium powders and HA powders. The chemical composition of the titanium was (wt.%): Ti 99.3, Fe 0.039, O 0.35, N 0.035, C 0.025, Cl 0.034, H 0.024 and Si 0.0018. The HA was prepared by the reaction between $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$. Its Ca/P ratio was $1.67 \pm 2.0\%$. Sizing by means of Laser Particle Sizer (OMEC LS-POP(III)) showed the Ti particles had a average size of 45.2 μm (93.64 wt.% of Ti particles were in the range 37.0–60.0 μm), whereas the average size of HA particles is 1.75 μm (82.12 wt.% of HA particles were found to be between 0.35 and 3.70 μm). There are significant agglomerations of HA powders shown by scanning electron microscopy. The starting powders with different HA–Ti mixing ratios were first blended by ball milling for 12 h. Then the mixed powders were stacked layer by layer in a steel die according to the optimized compositional profile and compacted at 200 MPa. Thus the green compacts were hot pressed at 1100 °C under a pressure of 20 MPa in nitrogen atmosphere for 30–90 min with a heating rate of 10 °C min^{-1} and a cooling rate of 6 °C min^{-1}. The uniform HA–Ti composites (non-FGM) with various mixing ratios corresponding to each graded layer of the FGM were also produced in the same way.

3.2. Characterization

HA–Ti composites were cut into rectangular specimens about $3 \times 4 \times 36$ mm^3 in dimension using a diamond saw. A total of 24 samples (4 ones for each composition group) were obtained. Thus elastic modulus of HA–Ti composite materials was determined by three-point bending tests. Thermal expansion coefficient of HA–Ti composite materials was tested by Thermal Analyzing System (TAS100 type) with a testing temperature scope of 100–900 °C and a heating rate of 10 °C min^{-1}. The residual thermal macroscopic stress in FGM during the fabrication process was tested layer by layer using 0–45° method by XSA (AST-X2001 type). The testing conditions include the X-ray power of

30 kV/6.6 mA and the angle resolving power of 0.029° per point. The X-ray peak used to determine the stress is the highest Ti peak in the 2θ range of 125–162°. The tested samples were mechanical grinded and polished firstly, then corroded by a solution of $HF+HNO_3$, which could erase the influence of grinding stress.

4. Results and discussion

4.1. Thermo-elastic properties of HA–Ti composites

It is necessary for the structure optimization of HA–Ti asymmetrical FGM to acquire the thermo-elastic properties of the uniform HA–Ti composites with various mixing ratios corresponding to each graded layer of the FGM, such as thermal expansion coefficient, elastic modulus and Poisson's ratio.

Fig. 2 shows thermal expansion coefficient of HA–Ti composites with various mixing ratios corresponding to each graded layer of the FGM at different temperatures. It could be found that thermal expansion coefficients of HA–Ti composites increase with the rise of testing temperature or the content of HA ceramic.

The macroscopic thermal expansion behavior of the composite is often correlated with the composition, the configuration and the distribution of its constitutional phases directly. At the same time, the phase transformation of the components during the process of the change of the temperature should be considered because the change of the volume accompanying the phase transformation may result in the abnormal thermal expansion behavior of the composite. It should be noted that although the allotropic transformation of $\alpha \rightarrow \beta$-Ti phase occurs when the temperature increases up to 882.5 °C, there is no an abrupt change of thermal expansion coefficient of pure titanium or HA–Ti composites in the testing temperature range from 20 to 900 °C. This phenomenon suggests that the allotropic transformation of titanium has little effect on its thermal expansion behavior.

Elastic modulus of HA–Ti composites with various mixing ratios corresponding to each graded layer of the FGM was tested and listed in Table 1. Obviously there is no a direct corresponding relationship between elastic modulus and the mixing ratio of HA–Ti composites. For HA–Ti composites fabricated by powder metallurgical method, it was found that their elastic modulus changes corresponding to the relative density in Ref. [1]. So comparing with the mixing ratio, the relative density seems to play a more important role on elastic modulus of the HA–Ti composites. Elastic modulus of Ti–80vol.% HA composite is minimum. It is interesting that elastic modulus of pure HA (110.89 GPa) is similar to that of pure Ti (107.95 GPa), which can reduce elastic mismatches between HA and Ti, and diminish the microcracks generated during the fabrication of HA–Ti FGM. Poisson's ratio of HA–Ti composites listed in Table 1 was estimated by the mixing law.

4.2. Optimal design of HA–Ti asymmetrical FGM

The graded compositional distribution function of HA–Ti asymmetrical FGM is shown as the following,

$$f_{HA}(\xi) = \begin{cases} 0 & \xi < L_0 \\ \left(\dfrac{\xi - L_0}{1 - L_0 - L_1}\right)^n \times 100\% & L_0 < \xi < 1 - L_1, \\ 100\% & \xi > 1 - L_0 \end{cases} \quad (2)$$

where $f_{HA}(\xi)$ is the volume fraction of HA ceramic which changes with the distance ξ in the FGM, n the compositional distribution exponent, L_0 the thickness of pure titanium layer in the FGM, L_1 the thickness of

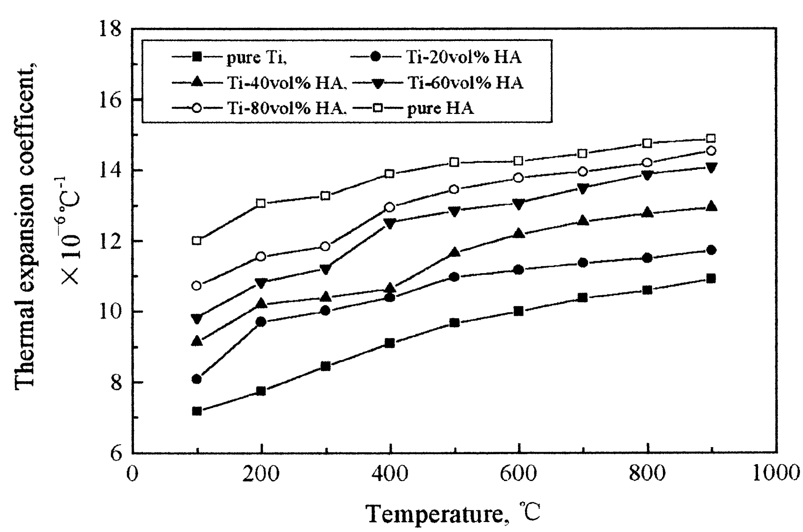


Fig. 2. Thermal expansion coefficient of HA–Ti composites at different temperatures.

Table 1
Elastic modulus, thermal expansion coefficient (20–900 °C) and Poisson's ratio of HA–Ti composites

Materials	Elastic modulus (Gpa)	Thermal expansion coefficient (10^{-6} °C^{-1})	Poisson's ratio
Pure HA	110.89	14.87	0.28
Ti–80vol.% HA	75.91	14.53	0.292
Ti–60vol.% HA	79.25	14.08	0.304
Ti–40vol.% HA	87.71	12.94	0.316
Ti–20vol.% HA	102.64	11.72	0.328
Pure Ti	107.95	10.9	0.34

pure HA layer in the FGM. The dimensionless variable ξ could be acquired by the following expression:

$$\xi = z/d, \quad (3)$$

where z is the coordinate along the thickness direction of FGM as shown in Fig. 1. The origin $z_0 = 0$ corresponds to the outer side of pure titanium graded layer in the FGM. d is the thickness of FGM along the graded direction. If the coordinate system z is translated into the coordinate system ξ, the origin $\xi_0 = 0$ corresponds to the outer side of pure titanium graded layer in the FGM. The situation $\xi = 1$ corresponds to the outer side of pure HA graded layer in the FGM. L_0 and L_1 are also dimensionless variables. Fig. 3 shows the compositional continuous distributions of HA–Ti asymmetrical FGM dependent on n. Fig. 4 shows the compositional continuous distributions and the corresponding stepwise-simulated distributions of HA–Ti asymmetrical FGM. On the premise that the number of the graded layers in the FGM is given, the value of the compositional distribution exponent n can be adjusted by changing the thickness of each graded layer.

The optimal design of this FGM is to determine the graded compositional distribution function when the residual thermal macroscopic stress during the fabrication process is minimum and has the optimal distribution. The magnitude of L_0 and L_1 in the compositional distribution function should be pre-established according to the actual requirements of hard tissue replacement towards FGMs. So the optimal design of HA–Ti asymmetrical FGM is to determine the compositional distribution exponent n [1].

The difference between the sintering temperature of FGM (1100 °C) and the room one (25 °C) is −1075 °C. The optimal design of HA–Ti asymmetrical

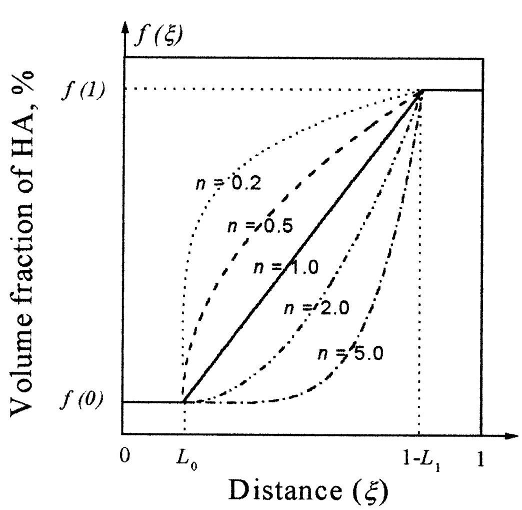
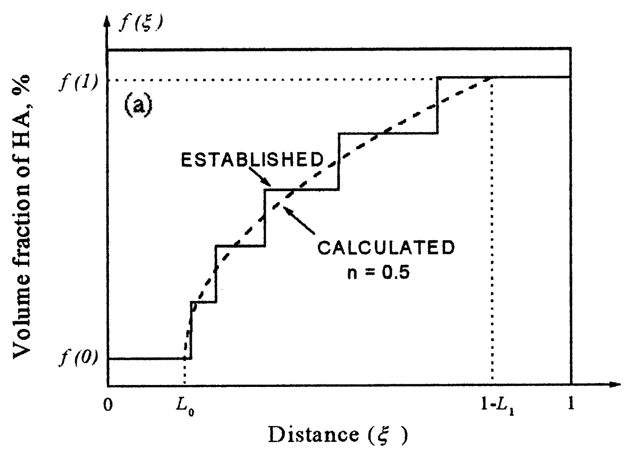


Fig. 3. Compositional continuous distributions of HA–Ti asymmetrical FGM dependent on n.



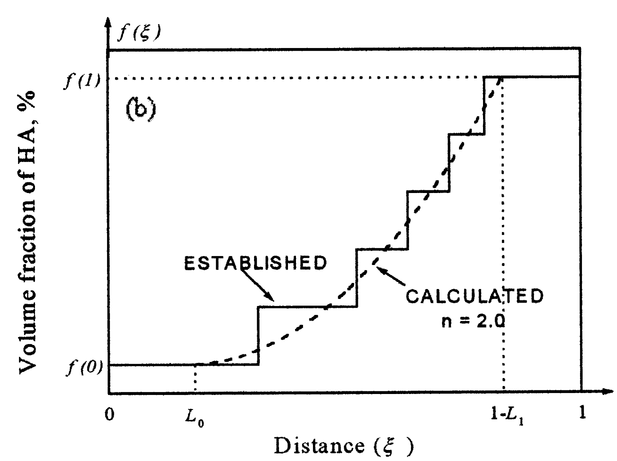


Fig. 4. Compositional continuous distributions and the corresponding stepwise-simulated distributions of HA–Ti asymmetrical FGM (a) $n < 1$; (b) $n > 1$.

FGM was made by the classical lamination theory and thermo-elastic mechanics as discussed in Section 2. The compositional distribution exponent n is optimized between 0.1 and 10 with an optimized step of 0.1. The necessary thermo-elastic properties of HA–Ti composites were listed in Table 1. The steps and results of the optimal design of HA–Ti asymmetrical FGM are shown as follows.

4.2.1. The optimization on the maximum tensile stress in HA–Ti asymmetrical FGM

Fig. 5 shows the changes of the maximum tensile stress in HA–Ti asymmetrical FGM with the compositional distribution exponent n for different L_0. It is obvious that when L_0 is 0.25, the valley point of the maximum tensile stress in HA–Ti asymmetrical FGM appears at $n = 0.9$. Consequently the compositional distribution exponent n of HA–Ti asymmetrical FGM may be determined near 0.9. Moreover, the compositional distribution exponent n corresponding to the valley point of the maximum tensile stress always shifts to a lower value when the thickness of pure titanium layer L_0 increases, while the value of the valley point of the maximum tensile stress increases with the rise of the thickness of pure titanium layer L_0. As a result, the residual thermal stress in the FGM will reach a higher level if the thickness of pure titanium layer L_0 increases.

4.2.2. The optimization on the center position of the maximum tensile stress in HA–Ti asymmetrical FGM

HA–Ti asymmetrical FGM consists of several HA–Ti composite graded layers with various mixing ratios. Each graded layer has the different ability to endure tensile stress. Thus the situation where the maximum tensile stress appears will play an important role on the fabrication and the application of HA–Ti asymmetrical FGM. As the toughness of titanium metal is far higher than that of HA ceramic, the center position of the maximum tensile stress in the FGM must be situated in the graded layer with a high content of metal phase by adjusting the compositional distribution exponent n. The change of the center position of the maximum tensile stress in HA–Ti asymmetrical FGM with the compositional distribution exponent n when L_0 is 0.25(1/4) is shown in Fig. 6. In our previous studies [6], it was found that both residual thermal stress and strain in the FGM during the fabrication process always reach their peak values at two sides of the interface between every two graded layers. To discuss conveniently, the position with the serial number ‘1’ in the Y-coordinate of Fig. 6 denotes the outer side of pure titanium graded layer in the FGM. In the same way, the position with the serial number ‘2’ denotes the side of pure titanium graded layer near Ti–20vol.% HA graded layer, and the position with the serial number ‘3’ denotes the side of Ti–20vol.% HA graded layer near pure titanium graded layer. Other positions in Fig. 6 are also defined analogously. It is found that there are four possible graded layers where the maximum tensile stress will appear, namely pure titanium graded layer corresponding to the position with the serial number ‘1’ when n is between 0.9 and 3.0, Ti–60vol.% HA graded layer corresponding to the position with the serial number ‘7’ when n is between 0.2 and 0.8, Ti–80vol.% HA graded layer corresponding to the position with the serial number ‘9’ when n is 0.1, and pure HA graded layer corresponding to the position with the serial number ‘11’ when n is between 3.1 and 10. Obviously when the compositional distribution exponent n is 0.9, the maximum tensile stress in the FGM will appear in pure titanium graded layer with the highest toughness, and the graded compositional distribution in the FGM can meet the requirement of the optimal design that the residual thermal macroscopic stress during the fabrica-

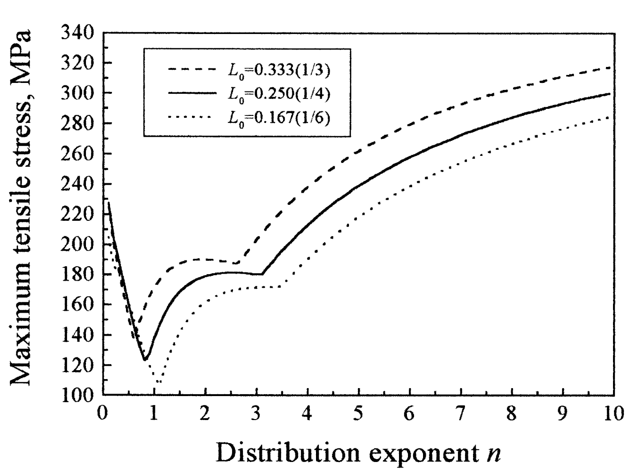


Fig. 5. Changes of the maximum tensile stress in HA–Ti asymmetrical FGM with the compositional distribution exponent n.

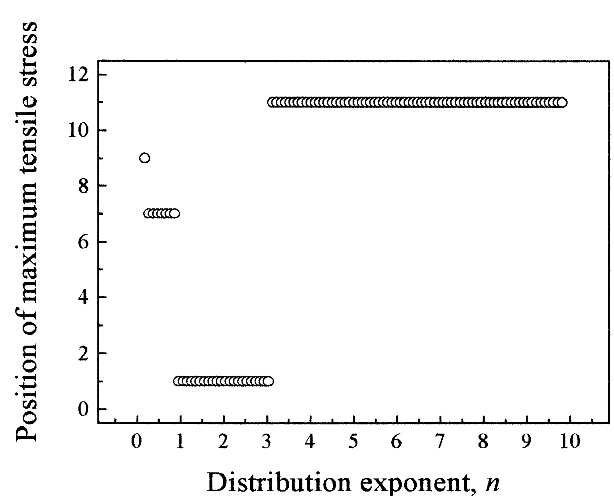


Fig. 6. The change of center position of the maximum tensile stress in HA–Ti asymmetrical FGM with the compositional distribution exponent n.

tion process is minimum and has the optimal distribution.

4.2.3. *The optimization on the maximum tensile stress in pure HA and Ti–60vol.% HA graded layers*

From the discussion in Section 4.2.2, it is found that the maximum tensile stress in the FGM appears mainly in the graded layer of pure titanium, Ti–60vol.% HA or pure HA. Unfortunately both Ti–60vol.% HA layer and pure HA layer have a poor toughness. They are the fragile regions to endure the tensile stress in the FGM. Thus it is necessary to study the maximum tensile stress in pure HA and Ti–60vol.% HA graded layers. Fig. 7 shows the changes of the maximum tensile stress in pure HA and Ti–60vol.% HA graded layers with the compositional distribution exponent n. When n is 0.9, the maximum tensile stresses in pure HA and Ti–60vol.% HA graded layers are 37.9 and 115.4 MPa, respectively, while the maximum tensile stresses in overall HA–Ti asymmetrical FGM is 127.4 MPa and appears in pure titanium layer. If the compositional distribution exponent n shifts to a lower value, the maximum tensile stresses in pure HA graded layer will decrease and reach its valley point (24.4 MPa) when n is 0.6. It is beneficial for pure HA graded layer in the FGM. However, the maximum tensile stresses in Ti–60vol.% HA graded layer with a similarly poor toughness will increase markedly to 145.4 MPa as a consequence. At the same time, Ti–60vol.% HA graded layer replaces pure Ti graded layer as the center position of the maximum tensile stress in HA–Ti asymmetrical FGM. Obviously the shift of the compositional distribution exponent n to a lower value is unreasonable. If the compositional distribution exponent n shifts to a higher value, the maximum tensile stresses in Ti–60vol.% HA graded layer will decrease gently and reach its valley point (88.9 MPa) when n is 1.8. Simultaneously the center position of the maximum tensile stress in HA–Ti asymmetrical FGM is also in pure titanium graded layer. However, the maximum tensile stresses in pure HA graded layer will increase to 106.9 MPa. At the same time, the maximum tensile stress in overall HA–Ti asymmetrical FGM will increase markedly to 176.5 MPa as a consequence. Thus the shift of the compositional distribution exponent n to a higher value is also unreasonable.

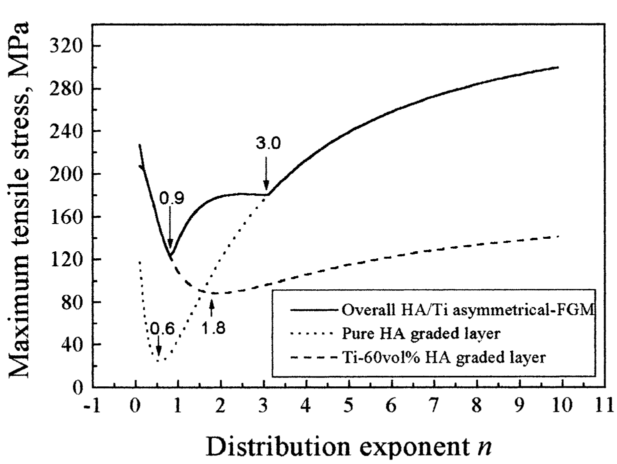


Fig. 7. Changes of the maximum tensile stress in pure HA and Ti–60vol.% HA graded layers with the compositional distribution exponent *n*.

In conclusion, the optimal graded compositional distribution exponent n for HA–Ti asymmetrical FGM is acquired by the thermal stress relaxation design and structure optimization, which is 0.9.

4.2.4. *Fabrication and residual thermal stress measurement of HA–Ti asymmetrical FGM*

HA–Ti asymmetrical FGM with the optimum graded composition was fabricated by hot pressing under the optimal sintering technics [2]. Its thickness along the graded direction h, L_0, L_1 and n are 6 mm, 0.25(1/4), 0.083(1/12), and 0.9, respectively. The sintered sample has no bending deformation and microcracks parallel to the graded direction of the FGM on the surfaces.

The residual thermal stresses at different situations along the graded direction in HA–Ti asymmetrical FGM with the optimum graded composition were tested by XSA and shown in Fig. 8. It is found that the whole pure HA graded layer in the FGM is acted on by the residual compressive stress, which can block the propagation of microcracks effectively. There are not any microcracks present in pure HA layer of the sintered FGM samples. The residual thermal stress state at different positions of pure Ti layer is different. The outer position of pure Ti layer is acted on by the large tensile stress, while the inner situation of pure Ti layer near Ti–20vol.% HA layer is acted on by the compressive stress. The residual compressive stress acts on Ti–20vol.% HA graded layer on the whole. All other graded layers of Ti–40vol.%, Ti–60vol.% and Ti–80vol.% HA

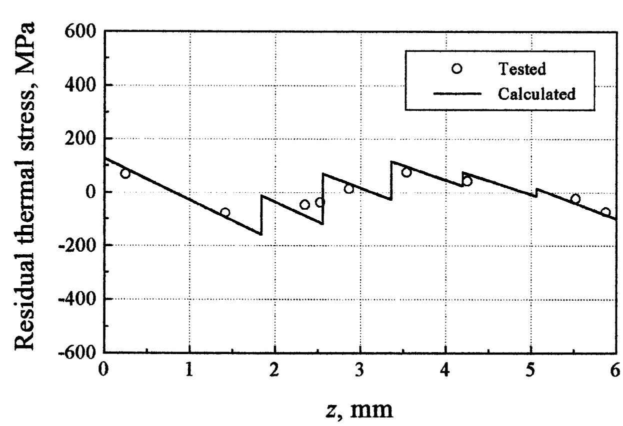


Fig. 8. Residual thermal stress in HA–Ti asymmetrical FGM with the optimum graded composition.

are acted on by the small tensile stress. The above tested values of residual thermal stress in the sintered FGM samples are basically consistent with the theoretically calculated ones.

5. Conclusions

The study of optimal design and fabrication of HA–Ti asymmetrical FGM leads to the following important conclusions.

(1) Thermal expansion coefficients of HA–Ti composites increase with the rise of testing temperature or the content of HA ceramic and aren't affected by the allotropic transformation of $\alpha \rightarrow \beta$-Ti phase at 882.5 °C, while there is no direct corresponding relationship between elastic modulus and the mixing ratio of HA–Ti composites.

(2) The optimal graded compositional distribution exponent n for HA–Ti asymmetrical FGM is acquired by the thermal stress relaxation design and structure optimization, and is 0.9.

(3) HA–Ti asymmetrical FGM with the optimum graded composition was fabricated by hot pressing successfully, and has no bending deformation and microcracks parallel to the graded direction of the FGM on the surfaces. The tested values of residual thermal stress in the FGM are basically consistent with the theoretically calculated ones.

As discussed above, the perfect HA–Ti asymmetrical FGM could be acquired by the thermal stress relaxation design and structure optimization. The osteoconductivity of HA–Ti asymmetrical FGM with the optimum graded composition will be reported before long.

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