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Dynamic Young's Modulus and Mechanical Properties of Ti–Hf Alloys

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Ti–Hf alloys are expected to have lower modulus and higher strength than pure Ti since. Hf has been suggested to have the potential to enhance the strength and to reduce the Young's modulus of Ti alloys at the same time. In the present study, binary Ti–Hf alloys with Hf contents from 5 to 40 mass% were designed and fabricated. The effects of Hf content on the microstructures, dynamic Young's modulus and mechanical properties of Ti–Hf alloys were investigated with the aim of biomedical applications. The microstructures were examined using a scanning electron microscopy and an X-ray diffraction analysis. The experimental results indicate that all the studied Ti–Hf alloys exhibit lamellar HCP martensite (α') structure under the given solution treatment, and increasing Hf content can gently reduce the Young's modulus but strongly enhance the strength of Ti–Hf alloys.

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1. Introduction

The average age and life expectancy of the human being has continuously increased since 1950, and the increasing trend is predicted to accelerate in the future.[1)] This leads to the ever-increasing demand for biomedical implant materials in our times and in the future. For example, worldwide, over 500000 total hip replacement surgeries are performed each year.[2)] Ti and its alloys have been widely used in the medical field since 1950s.[3)] However, the current bio-Ti alloys possess too high elastic modulus compared with a human bone, and hence can potentially lead to premature failure of bones.[4,5)]

The biomaterials for har tissue should possess an excellent biocompatibility, superior corrosion capacity, good fatigue property, high strength and low elastic modulus (near to that of a human bone to the greatest extent). In order to achieve those goals, considerable efforts have been devoted by material scientists and engineers. On the basis of the first principal calculation using a discrete variation cluster method (DVM), Song *et al.*[4,5)] have calculated the binding energies between titanium and various alloying elements, from which the strength and modulus are then estimated. They suggested that element Hf has the potential to enhance the strength and to reduce the modulus of Ti alloys at the same time.

Hf, which belongs to the IVa group together with Ti, is known to show very similar physical and chemical properties to those of Ti, and most of these properties are desirable for biomedical materials. For example, Ti and Hf have been proven to have good biocompatibility and osteoconductivity in both soft and hard tissues.[6)] The Ti–16Nb–10Hf alloy has been already developed for biomedical applications in the United States.[3)] Thus, Ti–Hf alloys have the potential for biomedical application. Up to now, a little study on Ti–Hf alloys has been done although it is of significance to investigate the Young's modulus and mechanical properties of Ti–Hf alloys. The effects of Hf content and heat treatment on the mechanical properties of Ti–Hf alloys were reported in the previous study,[7)] but without the associated information of microstructure and Young's modulus values.

The purpose of the present study is to investigate the effect of Hf content on the dynamic Young's modulus and mechanical properties of Ti–Hf alloys, attempting to find a binary Ti–Hf alloy that gives a good balance of low Young's modulus and high strength for biomedical applications, and also to provide useful data for developing new Ti alloys since the information of binary alloys plays important roles in developing new alloys.

2. Experimental Procedure

2.1 Materials preparation

The Ti–Hf alloys with Hf contents from 5 to 40 mass% (hereafter, 'mass%' will be referred to as '%') were prepared from high purity sponge Ti (99.5%) and chip Hf (99.95%) in the appropriate proportions. Before melting, a definite amount of oxygen getter was melted in the furnace, which had been evacuated and flushed five times with purified argon. Melting was carried out in a high purity argon atmosphere by a non-consumable tungsten electrode tri-arc furnace with water-cooled copper hearth. Owing to the big difference in density (Ti: 4.51 g/cm^3, Hf: 13.1 g/cm^3) between the two pure metals, and owing to the relatively large two phase (liquid and solid) field in the binary Ti–Hf phase diagram,[8,9)] the oval ingots of the designed alloys were melted more than ten times, and each time were held in the molted state for 3–4 minutes. At the same time, they were flipped between each melting to further promote the chemical homogeneities.

All the ingots were homogenized in vacuum at 1273 K for 21.6 ks to eliminate the as-cast microscopic segregation, and then rolled into the plates of 3 mm thick by a total thickness reduction of 80%. The blank specimens with a size of $3 \times 12 \times 57\,mm^3$ used for measurement of the dynamic Young's modulus and mechanical properties were cut from the rolled plates along the longitudinal direction, and those with a size of $3 \times 10 \times 10\,mm^3$ were used for phase identification analysis. All the specimens were subjected to a solution treatment at 1223 K, which is above β transus temperature, for 3.6 ks followed by a rapid quenching in ice water.

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Table 1 Measured average densities of the studied Ti–Hf alloys.

Alloy code	Density (g/cm^3)
Ti–5% Hf	4.64
Ti–10% Hf	4.79
Ti–15% Hf	4.97
Ti–20% Hf	5.14
Ti–30% Hf	5.51
Ti–40% Hf	5.93

Table 2 Chemical compositions of Ti–10% Hf alloy.

Element	mass%
Hf	9.83
O	0.103
Ti	Bal.

The compositions of the designed alloys were checked by comparing the weights of the initial materials with those of the ingots. The weight loss rates were found to be between 0.17~0.6%. The average densities of the designed alloys (Table 1) were measured by the measurement device for the dynamic Young's modulus, the differences between the calculated and measured densities were found to be between 0.2~1.5%. These comparisons indicate that the actual composition of each alloy is close to its nominal composition. On behalf of the designed alloys, the wet chemical and gas analysis of Ti–10% Hf alloy was carried out for checking the true chemical compositions of the alloy. The result is shown in Table 2, which confirms the above inference.

2.2 Material characterization

The microstructures of the studied alloys were investigated by a scanning electron microscopy (SEM). The samples for the microstructural characterization were ground, polished and etched in a solution composed of 5 vol% HF, 10 vol% HNO_3 and 80 vol% H_2O. The phase identification was performed on bulk samples using an X-ray diffraction (XRD) analysis operated at 40 kV and 30 mA at room temperature.

2.3 Young's modulus measurement

Dynamic method to measure elastic properties is commonly employed because of the non-destructive nature of the measurement, simple operating procedures and geometrically simple specimens. This method is based on the measurement of the fundamental resonant frequencies of the material during vibration to determine its elastic properties.[10,11] The dynamic modulus measured by this method is more accurate than the static modulus measured by a tensile test. Hence, the dynamic method was used to determine the modulus of Ti–Hf alloys.

Rectangular bar specimens with a cross-section of 10 mm × 2 mm and a length of 55 mm were machined from the blank specimens. They were ground, polished, and then used to determine the dynamic Young's modulus by the resonance vibration method at room temperature. The specimen was supported horizontally at its nodal points by two pairs of fine nickel wires. The specimen was driven electrostatically in flexural vibration. The vibration amplitude was recorded as a function of frequency. The dynamic Young's modulus, E, was calculated according to the following equation:[12)]

$$E = 0.9694 mL^3 f_r^{\,2}/(wd^3)$$

where m, L, w, d and f_r, are the mass, the length, the width, the thickness of specimens, and the resonance frequency, respectively.

For each designed Ti–Hf alloy, 3 pieces of specimens were used for the measurement of the dynamic Young's modulus in order to minimize the experimental errors caused by the measurement and possible chemical inhomogeneity.

2.4 Tensile test

Tensile specimens with a thickness of 2 mm, a width of 3 mm and a gage length of 12 mm of which longitudinal directions are parallel to rolling direction were machined from the blank specimens, and then ground and polished. The strain gage was attached at the gage section of each specimen to measure the strain change during tensile test. For each designed Ti–Hf alloy, 3 pieces of specimens were prepared. The uniaxial tensile tests were conducted at a crosshead speed of 8.33×10^{-6} m/s at room temperature in air using an Instron type machine. Hence, the ultimate tensile strength, yield strength at 0.2% offset and elongation at fracture were determined.

3. Results and Discussion

3.1 Phase constitution and microstructure

The XRD analysis results are shown in Fig. 1. It can be seen that the crystal structures of all the studied Ti–Hf alloys rapidly quenched from the β field exhibit the same HCP structure, and no second phase is detected. Since this allotropic transformation of BCC to HCP structure is formed by a rapid quenching from the β field without a diffusion of solute, it is designated as martensite.[9,13,14)] There are two types of martensites in Ti alloys. One is marteniste α' with HCP structure, and the other is marteniste α'' with ortho-

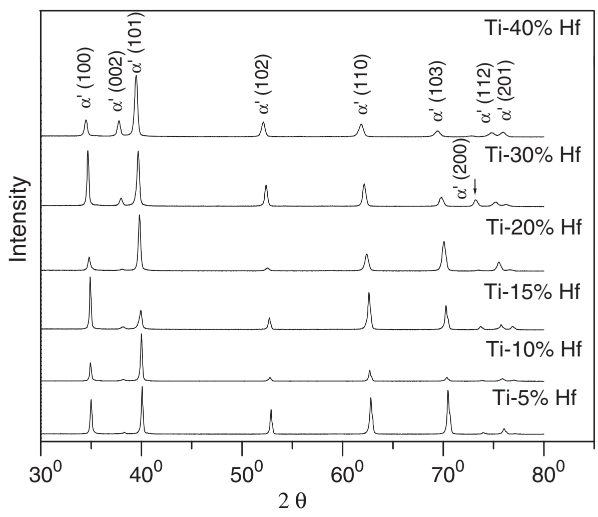

Fig. 1 XRD patterns of Ti–Hf alloys in bulk materials.

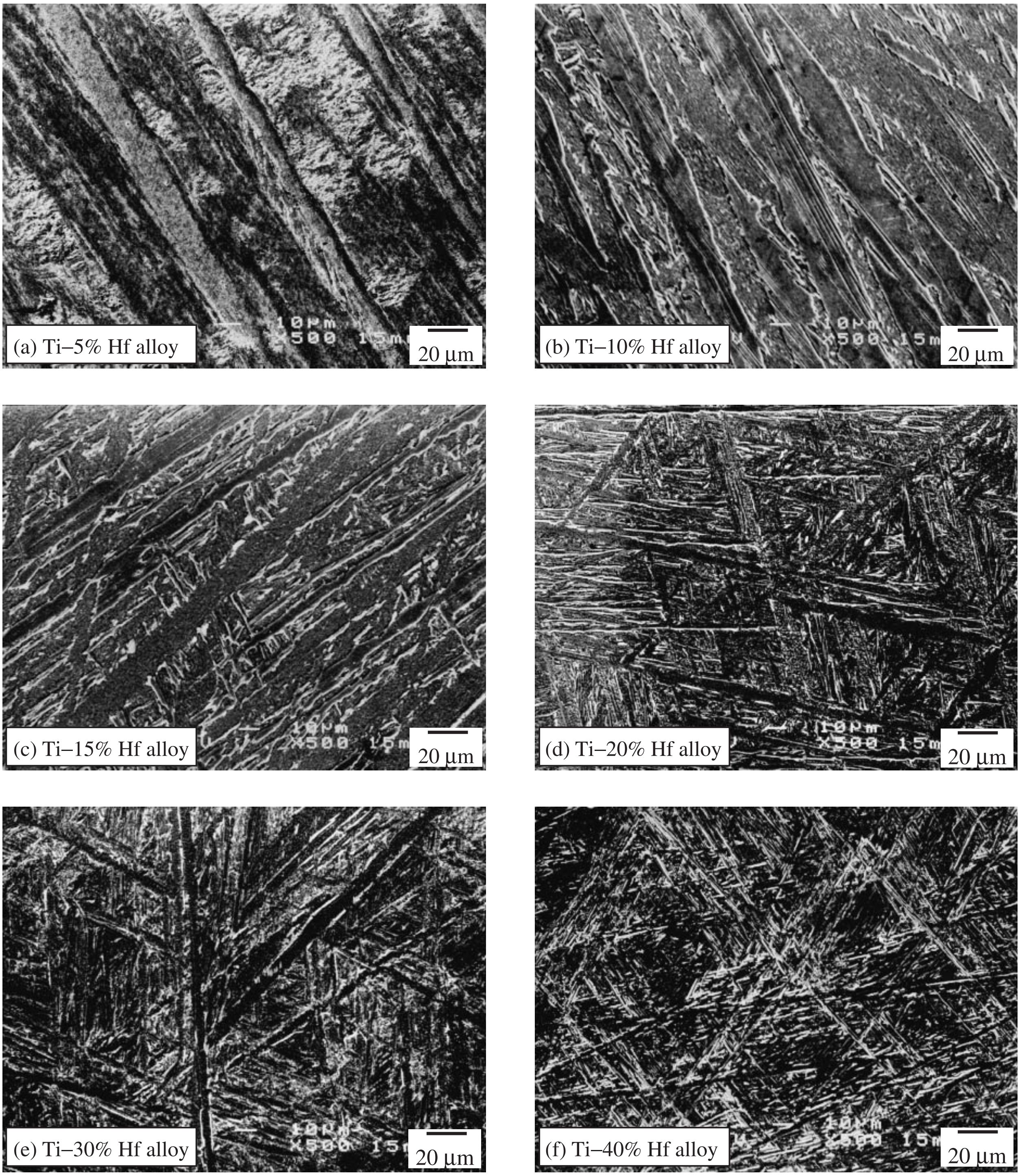

Fig. 2 Microstructures of Ti–Hf alloys by SEM.

rhombic structure. Their formation depends on chemical composition and quenching rate from the β field.[9,13,14] The previous studies found that the martensite α'' only occurs in some binary Ti alloys such as Ti–Mo, Ti–Nb and Ti–Ta alloys.[8,9,13,14] The present results of XRD analysis indicate that only the martensite α' exists in the quenched Ti–Hf alloy, which is consistent with the previous investigation.[9]

The microstructures of the transverse section of the studied Ti–Hf alloys are shown in Fig. 2. These observations are in good agreement with the results of the XRD analysis as mentioned above. It is clear that lamellar martensite α' is formed in all the studied Ti–Hf alloys. Parallel but coarse arrays of plates exist in the Ti–5% Hf, 10% Hf and 15% Hf alloys as shown in Figs. 2(a), (b) and (c), respectively. With increasing Hf content, the martensite α' becomes finer, and the arrays of martensite α' change from the single direction into the multiple ones as shown in Figs. 2(d), (e) and (f). In addition, the acicular martensite α' structures in the Ti–40% Hf alloy (Fig. 2(f)) get entangled by one another. Generally speaking, the phase transformation of martensite is usually accompanied by a volume expansion, and the resistance due to the volume expansion to growth of α' phase is enhanced by

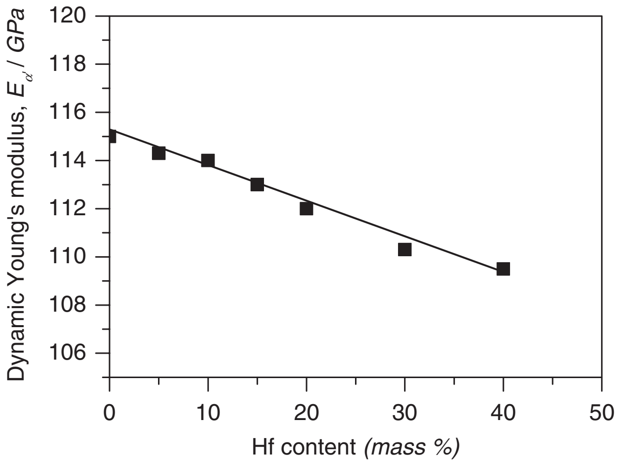

Fig. 3 Variation of Young's modulus, $E_{\alpha'}$ and Hf content (mass%).

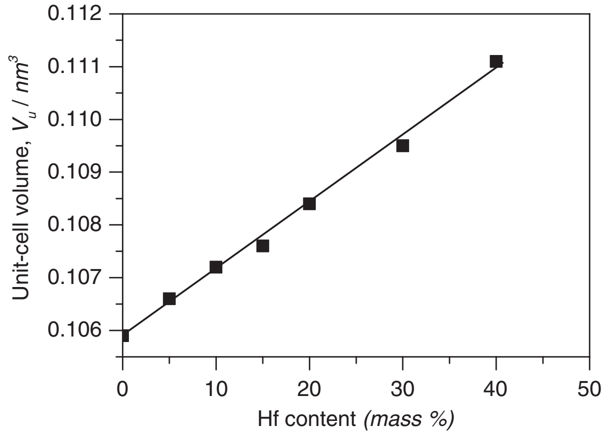

Fig. 4 Variation of unit-cell volumes, V_u and Hf content (mass%).

alloying elements. Thus, the martensite in Ti–Hf alloys gets finer and its arrays exhibit multiple orientations with increasing Hf contens.

3.2 Effect of Hf content on Young's modulus of Ti–Hf alloys

The measured dynamic Young's modulus of quenched Ti–Hf alloys is summarized in Fig. 3 as a function of Hf content. It can be seen that the dynamic Young's modulus gently decreases with increasing Hf content, and reaches the minimum value of 109.5 GPa at 40% Hf. The nearly linear relationship between the dynamic Young's modulus of Ti–Hf alloys and Hf content is obtained according to Fig. 3, as described below for 0–40% Hf:

$$E_{\alpha'}(\mathrm{GPa}) = 115 - 0.15 \times (\mathrm{Hf}\ \%)$$

It is well known that the Young's modulus, one of the intrinsic natures of materials, is determined by the bonding force among atoms. This bonding force is not only related to crystal structure but also to distances among atoms, and can be affected by alloying addition, heat treatment and plastic deformation.[15–17] Since the same heat treatment and plastic deformation were carried out in the present study, and the Young's modulus is not sensitive to grain size and morphology of materials,[12,15,18,19] for the present alloy with martensite α', the elastic modulus mainly depends on its chemical composition, *i.e.* Hf content. Element Hf has a bigger atom radius than element Ti,[8] thus, the degree of lattice distortion in the quenched alloy increases with addition of Hf content when the crystal structure is kept unchanged. This distortion degree inevitably leads to the change in the lattice parameters and unit-cell volumes of the alloy. Hence, the resulting variation in distances among atoms alters the modulus of the quenched alloys. The lattice parameters of the martensite α' phase in the present Ti–Hf alloys can be determined by the analysis of XRD patterns. The unit-cell volumes of martensite α' phase are then calculated based on the above lattice parameters, and are plotted with the variation of Hf content as shown in Fig. 4. It can be seen from Fig. 4 that the unit-cell volume of martensite α' nearly linearly expands with increasing Hf content. Since the bigger the unit-cell volume, the weaker the binding force among the alloying atoms and the matrix atoms,[4,5] the decreased Young's modulus of martensite α' with increasing Hf content is related to the increased unit-cell volume with Hf content. Further investigation based on the combination of Fig. 3 and Fig. 4 reveals that the Young' modulus of HCP structure (α') keeps a nearly linear relationship with its unit-cell volume.

3.3 Effect of Hf content on mechanical properties of Ti–Hf alloys

The measured tensile strength, yield strength and elongation at fracture are summarized in Fig. 5. The strength of all the studied Ti–Hf alloys is higher than that of pure titanium. It can be seen that the tensile strength is 454 MPa at 5% Hf, and gradually increases with increasing Hf content up to 30%. Then it drastically increases and reaches the highest value of 1110 MPa at 40% Hf.

It is considered that the change in the strength is due to the change in the microstructures caused by Hf content. As mentioned above, the degree of lattice distortion in the quenched alloy increases with increasing Hf content. Accordingly, the effect of solid solution strengthening in the quenched alloy is also improved. Additionally, the finer microstructure (Figs. 2(d), (e) and (f)) contributes to the increased strength of the quenched alloy with increasing Hf content. The drastic increase in strength of the Ti–40% Hf alloy is possibly related to its entangled acicular structures

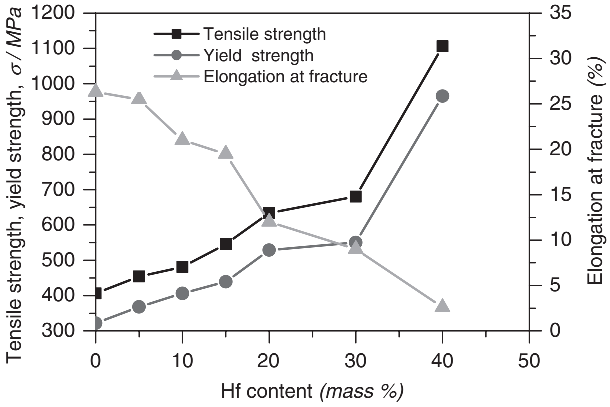

Fig. 5 Variation of mechanical properties and Hf content (mass%).

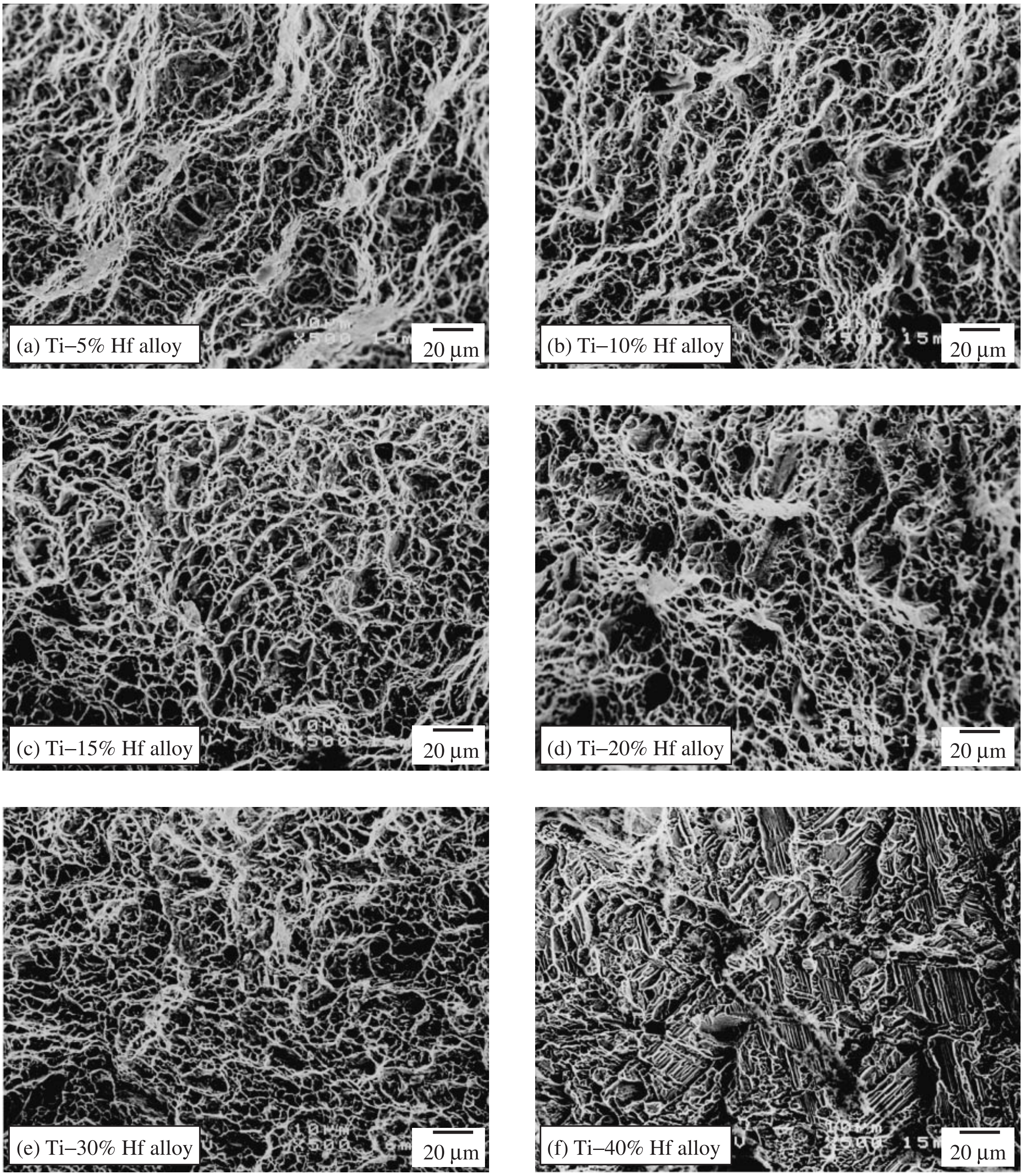

Fig. 6 SEM fractographs of tensile fractured Ti–Hf alloys.

(Fig. 2(f)). On the contrary, the elongation at fracture decreases with increasing Hf content. This phenomenon is consistent with the ordinarily observed strength-ductility relationship, *i.e.* when the yield strength increases, the ductility accordingly decreases. However, the obvious decrease in the ductility of Ti–40% Hf alloy suggests its different failure mode. The fracture surfaces of the tensile specimens were examined by an SEM as shown in Fig. 6. It can be seen that the failure modes for all the studied Ti–Hf alloys except the Ti–40% Hf alloy are by the ductile transgranular fracture modes at room temperature. In contrast, the Ti–40% Hf alloy shows mainly a cleavage-like appearance (Figs. 6(f)), which indicates the brittle fracture behavior.

The previous investigations in Ti–V, Ti–Nb, Ti–Mo[13,20,21] and Ti–Ta alloys[22,23] demonstrate that the β-isomorphous elements V, Nb, Mo and Ta have a strong effect on the elastic modulus and mechanical properties of binary Ti alloys. However, the present results indicate that the β-isomorphous element Hf can slightly reduce the elastic modulus but strongly increase the strength of Ti–Hf alloys. Those discrepancies among the previous and present results about

Table 3 Properties of some implant materials and the typical Ti–Hf alloy.

Alloy code	Modulus (GPa)	Tensile strength (MPa)	Ratio of strength-to-modulus
ASTM F75[24] (Co–Cr–Mo)	220	655–690	3–3.1
V316[24] (Stainless steel)	379	965	2.6
Ti–6Al–4V[24]	124	896	7.2
Ti–6Al–7Nb[25]	114	900–1050	7.89–9.21
Ti–13Nb–13Zr(Aged)[25]	79–84	973–1037	11.58–13.13
Ti–40% Hf [Present study]	110	1110	10.1

the elastic modulus could be caused by the intrinsic effect of different alloying elements on the modulus of the alloys.[4,5)]

As mentioned in the introduction, the biomedical implant materials are required to have high strength and low modulus. In orthopedic applications, a useful parameter is the elastic admissible strain, defined as the strength-to-modulus ratio. The higher the admissible strain, the more desirable the materials for such applications.[4,5] A brief summary of Young's modulus and mechanical properties of some implant materials together with the typical Ti–Hf alloy is listed in Table 3. It is noticed that Ti–40% Hf alloy has obviously higher strength-to-modulus ratio than the existing implant materials such as ASTM F75, V316 and Ti–6Al–4V alloy which is regarded as a standard biomaterial, and has close strength-to-modulus ratio compared with the newly developed Ti alloys; Ti–6Al–7Nb and Ti–13Nb–13Zr. Thus, Ti–40% Hf alloy has the potential for biomedical applications from the viewpoint of high elastic admissible strain. However, on the other hand, Ti–40% Hf alloy still possesses much higher elastic modulus than a human bone, and has poor ductility, which indicates a high manufacturing cost. Therefore, Ti–40% Hf alloy is not an ideal candidate as a biomedical implant material.

Since Nb, having a β phase stabilizing effect, is regarded as the most effective alloying element to reduce the Young's modulus,[4,26] Ti–40% Hf based ternary alloy containing a amount of Nb is expected to be a hopeful alloy with a good combination of high strength and low modulus. It is also expected that the ductility of proposed alloy will be improved because the β phase introduced by β phase stabilizer has a good ductility.[13,15] Hence, our future work will shift to the research on Ti–40% Hf–Nb ternary alloys.

4. Summary

The effects of Hf content on the microstructures, dynamic Young's modulus and mechanical properties of Ti–Hf alloys were investigated. The results of the present study are summarized below:

(1) All the studied Ti–Hf alloys exhibit lamellar HCP martensite (α') structure under the given solution treatment.

(2) Increase of Hf content can gently reduce the dynamic Young's modulus but strongly enhance the strength of Ti–Hf alloys.

(3) Ti–40% Hf alloy has the highest strength-to-modulus ratio among all the studied Ti–Hf alloys.

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