Materials Science and Engineering C 29 (2009) 36–43

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Structure, mechanical properties and grindability of dental Ti–10Zr–X alloys

Wen-Fu Ho [a], Chung-Hsiao Cheng [b], Chang-Hung Pan [c], Shih-Ching Wu [d,e], Hsueh-Chuan Hsu [d,e,*]

[a] Department of Materials Science and Engineering, Da-Yeh University, Taiwan, ROC
[b] Prosthetic Division of Taichung Veterans General Hospital, Taiwan, ROC
[c] Department of Mechanical and Automation Engineering, Da-Yeh University, Taiwan, ROC
[d] Department of Dental Laboratory Technology, Central Taiwan University of Science and Technology, Taiwan, ROC
[e] Institute of Biomedical Engineering and Material Science, Central Taiwan University of Science and Technology, Taiwan, ROC

ARTICLE INFO

Article history:
Received 6 November 2007
Received in revised form 8 April 2008
Accepted 9 May 2008
Available online 16 May 2008

Keywords:
Titanium alloy
Structure
Mechanical property
Grindability

ABSTRACT

This study aimed to investigate the structure, mechanical properties and grindability of a binary Ti–Zr alloy added to a series of alloying elements (Nb, Mo, Cr and Fe). The phase and structure of Ti–10Zr–X alloys were evaluated using an X-ray diffraction (XRD) for phase analysis and optical microscope for microstructure of the etched alloys. Three-point bending tests were performed using a desk-top mechanical tester. Grindability was evaluated by measuring the amount of metal volume removed after grinding for 1 min at each of the four rotational speeds of the wheel (500, 750, 1000 or 1200 m/min). Results were compared with c.p. Ti, which was chosen as a control. Results indicated that the phase/crystal structure, microstructure, mechanical properties and grindability of the Ti–10Zr alloy can be significantly changed by adding small amounts of alloying elements. The alloying elements Nb, Mo, Cr and Fe contributed significantly to increasing the grinding ratio under all grinding conditions, although the grinding rate of all the metals was found to be largely dependent on grinding speed. The Ti–10Zr–1Mo alloy showed increases in microhardness (63%), bending strength (40%), bending modulus (30%) and elastic recovery angle (180%) over those of c.p. Ti, and was also found to have better grindability. The Ti–10Zr–1Mo alloy could therefore be used for prosthetic dental applications if other conditions necessary for dental casting are met.

1. Introduction

Due to their light weight, excellent corrosion resistance, biocompatibility and mechanical properties, pure titanium and its alloys have been widely used for many biomedical applications. For example, pure titanium is used for hip cup shells, dental crowns and bridges, endosseous dental implants and plates for oral maxillofacial surgery [1–3]. However, the fact that pure titanium has a high melting temperature and high reactivity with oxygen and impurities at elevated temperatures makes it difficult to cast [4]. Moreover, reducing the melting temperature of titanium could decrease the risk of inadequate mold filling and porosity which results from the considerable temperature difference between the molten alloy and the much cooler investment [5]. One method of achieving this is to use titanium alloys, which exhibit solid solution hardening and have lower fusion temperatures and better ductility than c.p. Ti [6,7]. In fact, many titanium alloys have been developed for dental use, and their properties have been extensively studied [1,6,8–10], mainly to improve the strength and castibility of titanium.

The recent development of the CAD/CAM method represents a great advancement over casting technology [11]. However, the poor machinability of titanium is an obstacle to practical dental applications. If titanium prostheses are fabricated by CAD/CAM, the tool life is short and the processing time is long [6,12]. Consequently, there is a need for further development of new dental materials especially suited for machining. Although there may be several ways to improve grindability, one well documented method is through alloying [13–17]. In fact, a great deal of effort has been devoted to the study of new dental materials suited for machining, such as Ti–Cu [13,14], Ti–Ag [14], Ti–Nb [15], Ti–Hf [16], Ti–Au [17] and Ti–Cr–Cu [18].

Of all the various titanium alloys, the Ti–6Al–4V alloy has been put forward as a possible replacement for commercially pure titanium (c.p. Ti) due to its higher strength and adequate corrosion resistance [1]. However, there has been speculation that the release of Al and V ions from the alloy might cause some long-term health problems [19–21]. Therefore, the development of new Ti alloys with good mechanical properties, but without Al or V content is important for biomedical applications.

It is well known that the properties of Ti alloys are sensitive to their phases/crystal structure, and certain phases may be stabilized by the addition of alloying elements. Thus, the mechanical properties of titanium might be enhanced through alloying [22]. A good candidate for alloying is Zr, which is a neutral element when dissolved in Ti and

* Corresponding author. Department of Dental Laboratory Technology, Central Taiwan University of Science and Technology, No. 11, Buzih Lane, Beitun District, Taichung, Taiwan 40605, ROC. Tel.: +886 4 22391647x7422.
E-mail address: hchsu@ctust.edu.tw (H.-C. Hsu).

0928-4931/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2008.05.004

has high solubility in both α Ti and β Ti. Zr can enhance strength and improve the plasticity of alloys, guaranteeing fine processing properties [23]. In our previous research [24], we developed a Ti–10Zr alloy, with higher hardness and better grindability than unalloyed titanium. However, its strength and elastic recovery capability (springback) were not sufficient for clinical dental applications.

Two types of β stabilizer were added to the Ti–10Zr alloy in the present study. The β-isomorphous elements, Nb and Mo were included, while β-eutectoid elements, Cr and Fe were chosen [25]. In every case the added elements comprised 1 wt.% of the alloy. As Ho et al. [26] argued, the phase/crystal structure, microstructure and mechanical properties of Ti–7.5Mo alloy can be significantly changed by small amounts (1 wt.%) of alloying additions. Furthermore, these Ti–10Zr–X alloys are considered to be suitable as biomaterials since they do not contain elements such as Al or V. Therefore, the major goal of this research was to improve the mechanical properties and grindability by adding 1 wt.% of a variety of alloying elements to the Ti–10Zr alloy, and to judge the potential of new alloys for practical dental applications.

2. Experimental procedures

Alloying elements selected for the study include Zr, Nb, Mo, Cr and Fe, which were all 99.9% pure. For the sake of simplicity, throughout the text "Ti–10Zr" refers to "Ti–10 wt.% Zr" and "Ti–10Zr–1X" refers to "Ti–10 wt.% Zr–1 wt.% X", where X is a given alloying element. The series of Ti alloys, including Ti–10Zr, Ti–10Zr–1Nb, Ti–10Zr–1Mo, Ti–10Zr–1Cr and Ti–10Zr–1Fe, were prepared from 99.9% pure titanium, using a commercial arc-melting vacuum-pressure-type casting system (Castmatic, Iwatani Corp., Japan). The melting chamber was first evacuated and purged with argon. An argon pressure of 1.5 kgf/cm^2 was maintained during melting. Appropriate amounts of each metal were melted in a U-shaped copper hearth with a tungsten electrode. The ingots were re-melted five times prior to casting to improve chemical homogeneity. Prior to casting, the ingots were melted once again in an open-based copper hearth under an argon pressure of 1.5 kgf/cm^2. The difference in pressure between the two chambers allowed the molten alloys to instantly drop into the graphite mold.

The cast alloys were sectioned using a Buehler Isomet low-speed diamond saw to obtain specimens for experimental purposes. Surfaces of the alloys for microstructural study were mechanically polished using a standard metallographic procedure to a final level of 0.3 μm with alumina powder and then etched in a solution of water, nitric acid, and hydrofluoric acid (80:15:5 in volume). Microstructure of the etched alloys was examined using an optical microscope (BH2, Olympus, Japan). X-ray diffraction (XRD) for phase analysis was conducted using a diffractometer (XRD-6000, Shimadzu, Japan) operated at 30 kV and 30 mA. Ni-filtered CuKα radiation was used for this study. Phase was identified by matching each characteristic

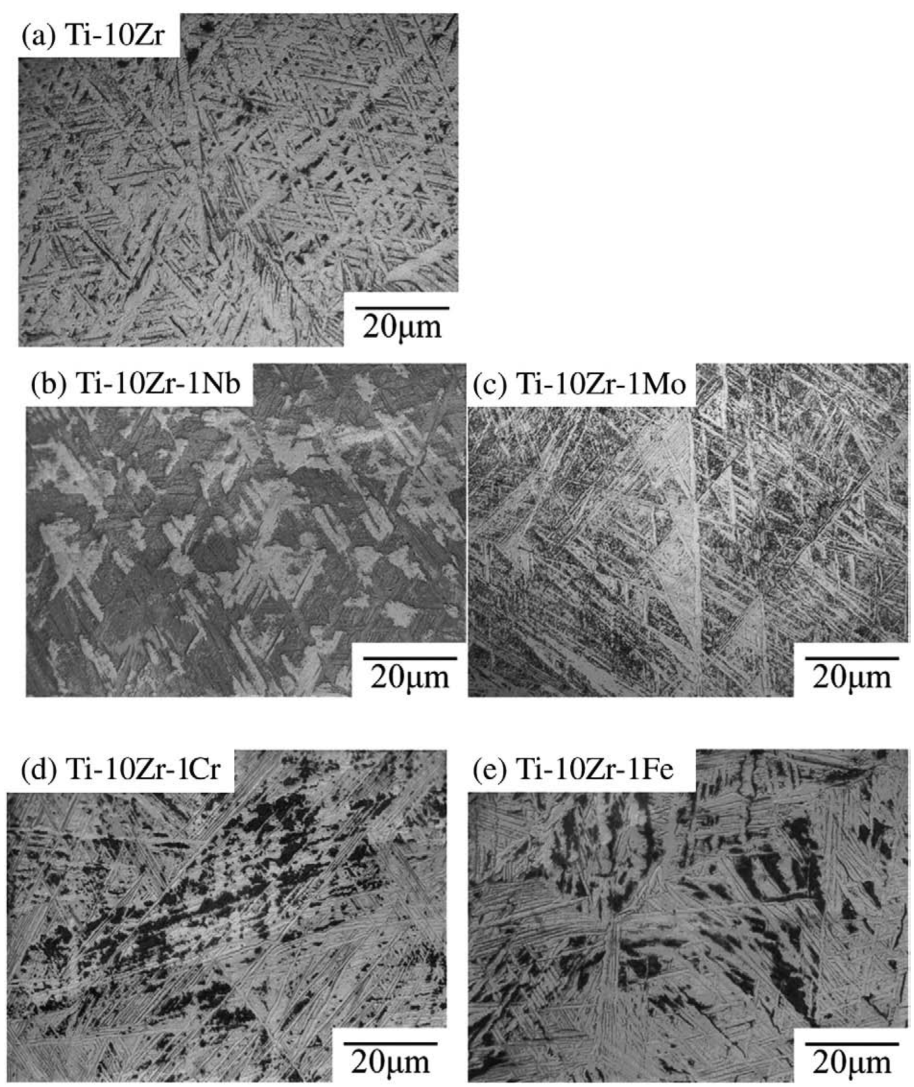

Fig. 1. Light micrographs of Ti–10Zr and Ti–10Zr–1X alloys.

peak with the JCPDS files. The microhardness of polished alloys was measured using a microhardness tester (MVK-E3, Mitutoyo, Japan) at 100 gm for 15 s.

Three-point bending tests were performed using a desk-top mechanical tester (AG-IS, Shimadzu, Japan) at a crosshead speed of 0.5 mm/min. The bending strengths were determined using the equation, $\sigma = 3PL/2bh^2$ [27], where σ is the bending strength (MPa), P is the load (kg), L is the span length (mm), b is the specimen width (mm), and h is the specimen thickness (mm). The dimensions of all specimens were: $L = 30$ mm, $b = 5.0$ mm and $h = 1.0$ mm. The modulus of elasticity was calculated from a load increment and the corresponding deflection increment between the two points on the straight line as far apart as possible, using the equation: $E = L^3 \Delta P / 4bh^3 \Delta\delta$, where E is the modulus of elasticity in bending (Pa), ΔP is the load increment as measured from preload (N), and $\Delta\delta$ is the deflection increment at mid-span as measured from preload. The average bending strength and modulus of elasticity were taken from at least 5 tests under each condition. The elastic recovery (springback) capability for each material was calculated from the change in deflection angle corresponding to the removal of loading. The specimen was unloaded at the pre-set bending deflection of 8 mm. Details can be found in Ho et al. [28].

The method used in previous studies by several other researchers [13–17,29–31] was adopted to evaluate grindability. A silicon carbide (SiC) wheel (G11, Shofu, Kyoto, Japan) (diameter 13.1 mm, thickness 1.75 mm) on an electric dental hand-piece (Ultimate 500, NSK Nakanishi Inc., Japan) was used to grind the specimens. Each specimen was placed on the test apparatus, as referred to in a previous study by Ohkubo et al. [31], so that the edge of the wheel made contact with the specimen at 90°. By applying a force of 100 gf, the specimens were ground at one of the four rotational speeds of the wheel (500, 750, 1000 or 1200 m/min). The specimen and grinding wheel were housed in a closed compartment during grinding so that any metal chips generated could be collected.

The amount of metal removed (mm^3) in 1 min was calculated from the density, previously measured using Archimedes' principle [31], and the weight loss of the specimen. The grinding test was performed six times for each kind of metal at every grinding speed and a new wheel was applied for every test. The diameter and weight of each wheel were measured before and after grinding. Grindability was evaluated from the volume of metal removed per minute (grinding rate), and the volume ratio of metal removed compared to the wheel material lost, which was calculated from the diameter loss of the wheel (grinding ratio). Thus, the grinding rate represents ease of metal removal, whereas the grinding ratio is a measure of wheel life [16]. At each of the four grinding speeds, three specimens were used to evaluate the grindability of each kind of metal. The test was repeated three times for each specimen at each grinding speed. After testing, the ground surfaces of the metals were examined using optical microscopy (BH2, Olympus, Japan). The surface of the chips resulting from the metal grinding was examined using a scanning electron microscopy (SEM; S-3000N, Hitachi, Japan).

In this study, the experimental alloys were fabricated using a graphite mold instead of a dental investment mold, which meant that the alloys did not exhibit α-case. However, according to the results of Ohkubo et al. [31], there is no appreciable difference in the grindability between c.p. Ti with α-case and without α-case when a silicon carbide (SiC) wheel is used. All the results in this study were analyzed using two-way ANOVA and Duncan's multiple comparison test at $p < 0.05$ level.

3. Results and discussion

3.1. Phase and microstructure

Typical etched microstructures of Ti–10Zr and the Ti–10Zr–1X alloys under optical microscopy are shown in Fig. 1. As shown in Fig. 1a, the Ti–10Zr alloy displayed hexagonal α phase with coarse lath structures. When 1 wt.% Nb was added, the microstructure was similar to the Ti–10Zr alloy with coarse lath type structures (Fig. 1b). With the addition of 1 wt.% Mo, Cr or Fe, the alloys showed large amounts of fine martensitic laths (Fig. 1c–e), as was shown by Kobayashi et al. [32] and Kobayashi et al. [33]. This effect was especially apparent in the Ti–10Zr–1Mo alloy. A similar result was also observed by Collings [34], who proposed that, when small amounts of β-stabilizing elements were added to titanium, a martensitic structure with a distorted hexagonal crystal lattice would be obtained. This structure was referred to as α′ phase.

The XRD patterns of Ti–10Zr and the series of ternary Ti–10Zr–1X alloys are shown in Fig. 2. The Ti–10Zr alloy was comprised entirely of a hexagonal α phase. The alloying elements Nb, Mo, Cr and Fe used in this study are all known to act as β stabilizers [25]. However, the addition of small amounts of Nb or Mo did not cause a noticeable phase change. When 1 wt.% Nb or Mo was introduced into the Ti–10Zr alloy, the XRD patterns remained essentially unchanged. However, when 1 wt.% β-stabilizer Cr or Fe was added, a small amount of β phase was retained, indicating that Cr or Fe has a stronger effect than Nb or Mo on the stabilization of β phase. Although traces of β phase in the Ti–10Zr–1Cr and Ti–10Zr–1Fe alloys can be seen on the X-ray diffraction patterns, the small amounts of retained β structure were not easily observed under an optical microscope and were not deemed to be significant.

3.2. Mechanical properties

Microhardness values of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys are shown in Fig. 3. ANOVA test results showed significant overall differences among the microhardness values of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys ($p < 0.05$). All the Ti alloys had significantly higher microhardness values than that of c.p. Ti (186 HV) ($p < 0.05$). The microhardness value of Ti–10Zr alloy was 266 HV, and those of the Ti–10Zr–1X alloys ranged from 264

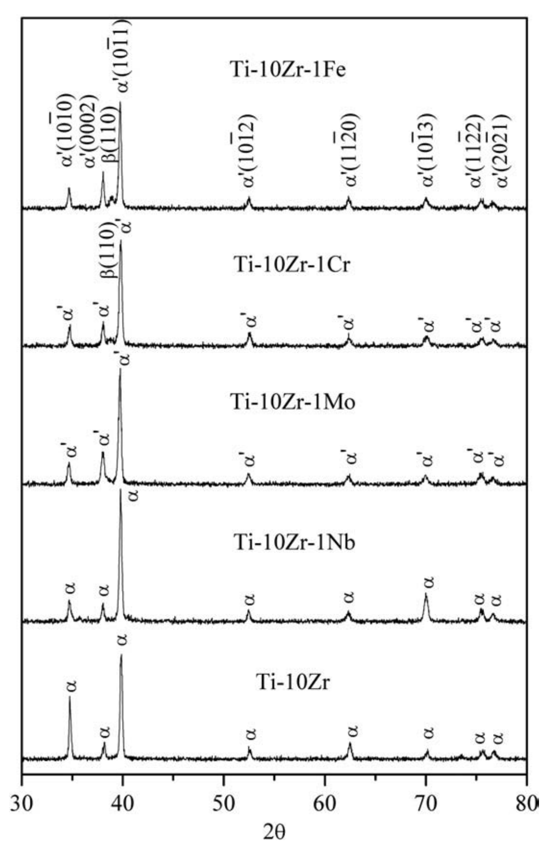

Fig. 2. X-ray diffraction patterns of Ti–10Zr and Ti–10Zr–1X alloys.

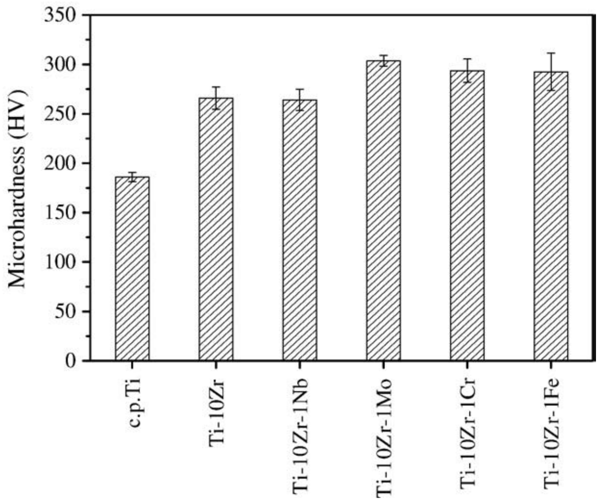

Fig. 3. Microhardness of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys.

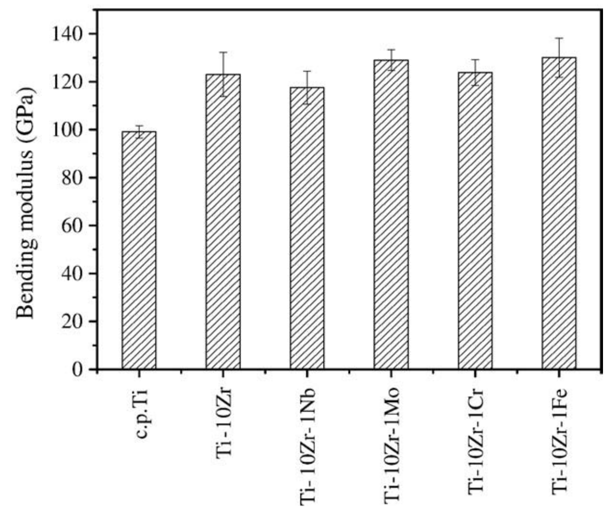

Fig. 5. Bending moduli of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys.

HV (Ti–10Zr–1Nb) to 304 HV (Ti–10Zr–1Mo). Ti–10Zr–1Mo, Ti–10Zr–1Cr and Ti–10Zr–1Fe had the highest microhardness values of all the metals tested, significantly higher than c.p. Ti, Ti–10Zr and Ti–10Zr–1Nb ($p<0.05$). The microhardness value of Ti–10Zr–1Mo exceeded that of Ti–10Zr by 14% and c.p. Ti by 63%.

As with microhardness, the bending strengths of all the Ti alloys were significantly higher than that of c.p. Ti (844 MPa) ($p<0.05$) (Fig. 4). Variations in the alloys' bending strength showed a similar trend to that of microhardness. With the exception of Ti–10Zr–1Nb, all the ternary alloys had higher strengths than that of the binary Ti–10Zr alloy ($p<0.05$). With the addition of 1 wt.% Nb, bending strength decreased from 989 MPa for Ti–10Zr to 943 MPa for Ti–10Zr–1Nb. By contrast, the addition of 1 wt.% Cr or Fe caused increased bending strengths of 1080 and 1076 MPa, respectively. It is worth noting that the Ti–10Zr–1Mo alloy had the highest strength ($p<0.05$), and its bending strength (1177 MPa) was higher than that of Ti–10Zr by 20% and c.p. Ti by 40%. As indicated in an early report of Davis et al. [35], molybdenum is very effective in producing the acicular-type martensite structure. In this case, the acicular structure probably increased as a result of a solute-induced decrease in Martensite transformation start (Ms) temperature [36]. As seen here, the fine acicular martensitic structure of the Ti–10Zr–1Mo alloy resulted in a greater hardness and strength than those of c.p. Ti and Ti–10Zr.

The bending moduli of Ti–10Zr and all Ti–10Zr–1X alloys were higher than that of c.p Ti ($p<0.05$) (Fig. 5). When 1 wt.% Mo or Fe was added, the bending modulus increased to some 130 GPa higher than that of c.p. Ti by 30%. This is important because a higher elastic modulus is required to minimize the elastic deformation when using titanium for dental prostheses that are subject to comparatively high stress, such as bridges and partial denture frameworks. A higher elastic modulus is also favorable for machining titanium [37]. By contrast, a low elastic modulus results in large deflection even if a material has high yield strength.

Fig. 6 shows the means of the elastic recovery capability of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys. With the exception Ti–10Zr–1Nb, the superior mechanical properties of Ti–10Zr–1X alloys are also demonstrated in their high elastic recovery capability, That is, Ti–10Zr–1Mo, Ti–10Zr–1Cr and Ti–10Zr–1Fe alloys exhibited significantly higher ($p<0.05$) elastic recovery capability than Ti–10Zr–1Nb, Ti–10Zr and c.p. Ti, as well as higher bending modulus. High elastic recovery capability of a metal is essential for many load-bearing implant and dental applications. It is worth noting that the elastic recovery capability of Ti–10Zr–1Mo alloy was significantly higher ($p<0.05$) than all other Ti alloys and c.p. Ti. In

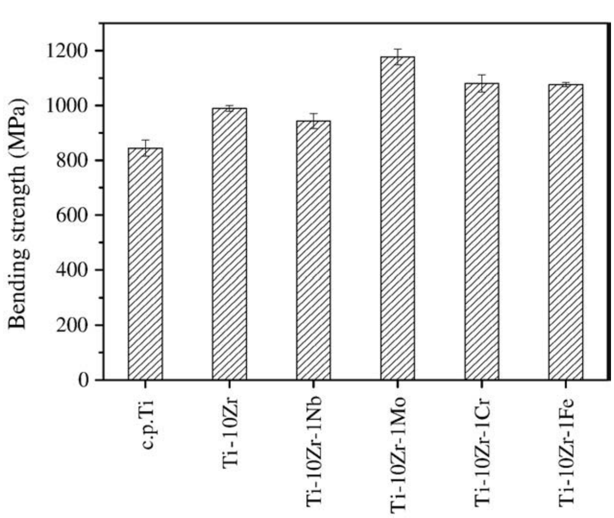

Fig. 4. Bending strengths of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys.

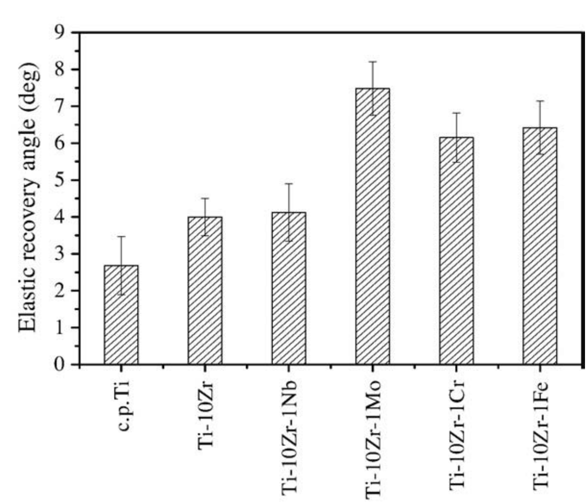

Fig. 6. Elastic recovery angles of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys.

particular, the elastic recovery angle of Ti–10Zr–1Mo was higher than that of Ti–10Zr by 87% and that of c.p. Ti by as much as 180%. Significantly, the bending modulus of the Ti–15Mo alloy was lower than all the other β-phase Ti–Mo alloys, whereas it demonstrated the lowest elastic recovery capability. Although, in general, high modulus seems to lead to low elastic recovery, the trend in this study is not the case. Although the reason is not immediately apparent, a similar result was also observed by Ho et al. [26] and raises the need for further study.

3.3. Grindability

The grinding rates of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys at four different grinding speeds are shown in Fig. 7(a). The grinding rate of all the Ti alloys and c.p. Ti showed a tendency to increase at higher grinding speed, but decrease at 1200 m/min. For all the alloys, a test of multiple comparison was also conducted using Duncan's multiple range test. Results show that grinding rates at 1200 m/min were significantly lower ($p<0.05$) than those at 1000 m/min. At the grinding speed of 500 m/min, the grinding rates for the Ti–10Zr–1Cr and Ti–10Zr–1Fe alloys were notably higher than those of c.p. Ti and Ti–10Zr ($p<0.05$). For example, the grinding rate of the Ti–10Zr–1Fe alloy at 500 m/min was approximately 1.59 times higher than that of c.p. Ti and 1.57 times higher than that of Ti–10Zr. In addition, the grinding rates of all the Ti–10Zr–1X alloys were significantly higher ($p<0.05$) than that of c.p. Ti at the grinding speeds of 750 and 1000 m/min. It is notable that the ease of grinding these alloys appeared to be dependent on grinding speed. The grinding rates of all the metals in this study tended to increase as the grinding speed increased from 500 m/min, which is reasonable, given that the grinding speed determines the distance the wheel edge travels on the surface of the specimen per unit of time. However, grinding rates at 1000 m/min were significantly higher than those for the highest speed of 1200 m/min. This resembles a similar result seen in another titanium alloy system [16]. Although further study is needed, it is possible that the condition of the grinding wheel deteriorates at the speed of 1200 m/min.

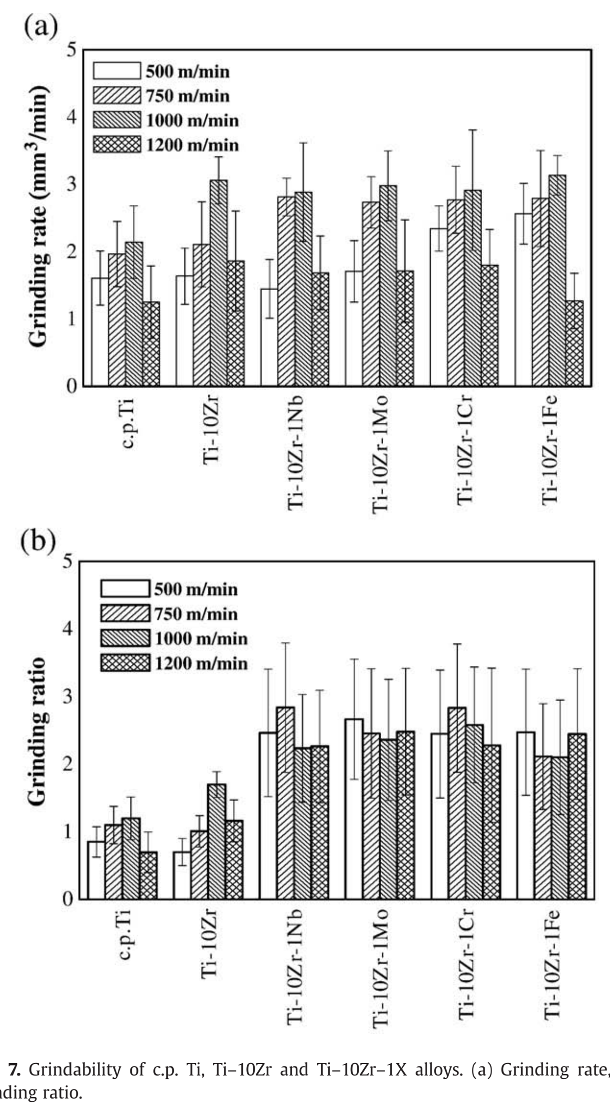

Fig. 7. Grindability of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys. (a) Grinding rate, (b) grinding ratio.

The grinding ratios of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys are shown in Fig. 7(b). The grinding ratios of all the Ti–10Zr–1X alloys were significantly higher ($p<0.05$) than those of c.p. Ti and Ti–10Zr at all grinding speeds. However, there were no significant differences in the grinding ratios of the Ti–10Zr–1X alloys. This is important because tool life can be predicted based on an evaluation of the grinding ratio. A higher grinding ratio signifies lower tool wear for the same volume of metal removed [16]. Ratios varied widely for all the metals tested, probably because both the volumes of the metal ground and wheel material lost were very small. It is worth noting that, the alloying elements Nb, Mo, Cr and Fe contributed significantly to improving the grinding ratio under all grinding conditions.

Takeyama [38] showed that higher strength and hardness of a material generally make machining of the material more difficult. However, in this study, Ti–10Zr–1Cr and Ti–10Zr–1Fe alloys both had higher hardness values and bending strength than that of c.p. Ti, but they also had higher grinding rates, especially at the speed of 500 m/min. On the other hand, Ti–10Zr–1Nb had the lowest hardness and strength of all the Ti–10Zr–1X alloys, but its grinding rates were similar to those of the other Ti–10Zr–1X alloys. In early studies, researchers [39–41] discussed grindability in terms of the hardness of metals. Nevertheless, in the present study there appeared to be no correlation between the volume loss and the hardness of the metals. This result was also in agreement with that reported by Ohkubo et al. [31] who tested c.p. Ti and Ti–6Al–4V alloy. In fact, it seems that hardness and strength are not the principal reasons for better grindability. According to Kikuchi et al. [14], elastic modulus appeared to have no relation to grindability. Nevertheless, the relatively low elastic modulus of titanium causes chatter vibration or deformation of the workpiece during machining [42]. Therefore, Kikuchi et al. suggested that titanium alloys with higher elastic modulus are more suitable for machining [14]. In this study, all the Ti–10Zr–1X alloys had higher elastic moduli than that of c.p. Ti. Thus, from the view point of modulus, the Ti–10Zr–1X alloys are more suitable for dental machining. This study showed that the exact mechanisms which affect the grindability of various alloys are complex and would merit further study.

3.4. Observation of metal chips and ground surfaces

Typical metal chips that resulted from grinding at 500 m/min and 1000 m/min are shown in Fig. 8. Although no quantitative analysis was performed, the size of the metal chips produced at the grinding speed of 500 m/min generally appeared somewhat larger than those at 1000 m/min. However, there were no clear differences in the appearance of the metal chips of the Ti–10Zr and Ti–10Zr–1X alloys. In general, finer metal chips indicate that materials are more suitable for grinding than those which produce larger metal chips [17].

Fig. 9 shows optical micrographs of the ground surfaces of the metals at 500 and 1000 m/min. Grinding marks were observed for all the metals and speeds. There were no pronounced differences in the appearance of the ground surfaces of c.p. Ti and Ti alloys at 500 m/min. Grinding adhesion was observed to a greater degree for c.p. Ti and Ti–10Zr alloy ground at 1000 m/min. In addition, grinding burns could also be found for c.p Ti and Ti–10Zr. As can be seen in other research [14,15,17], the grinding burn typically found on titanium and titanium

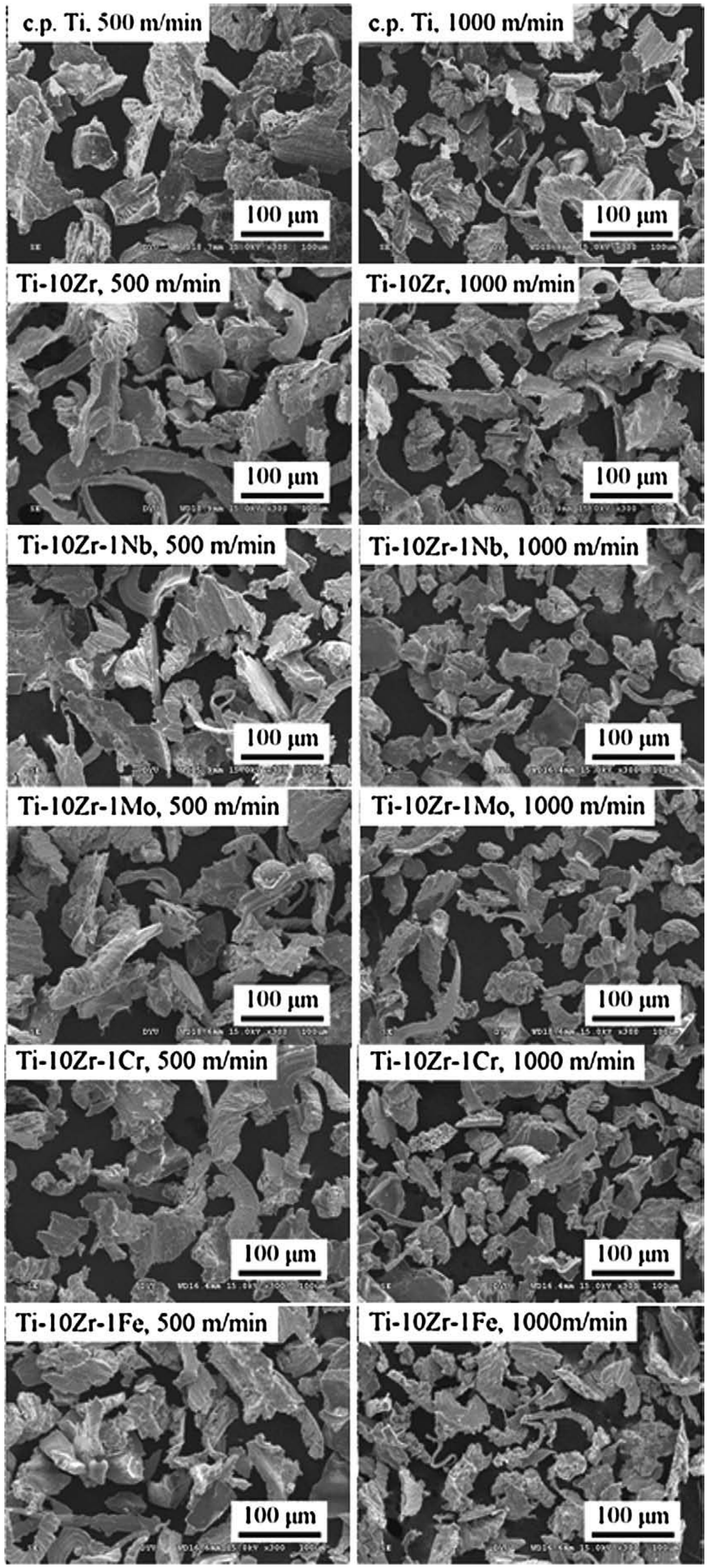

Fig. 8. SEM micrographs of metal chips resulting from grinding at 500 and 1000 m/min.

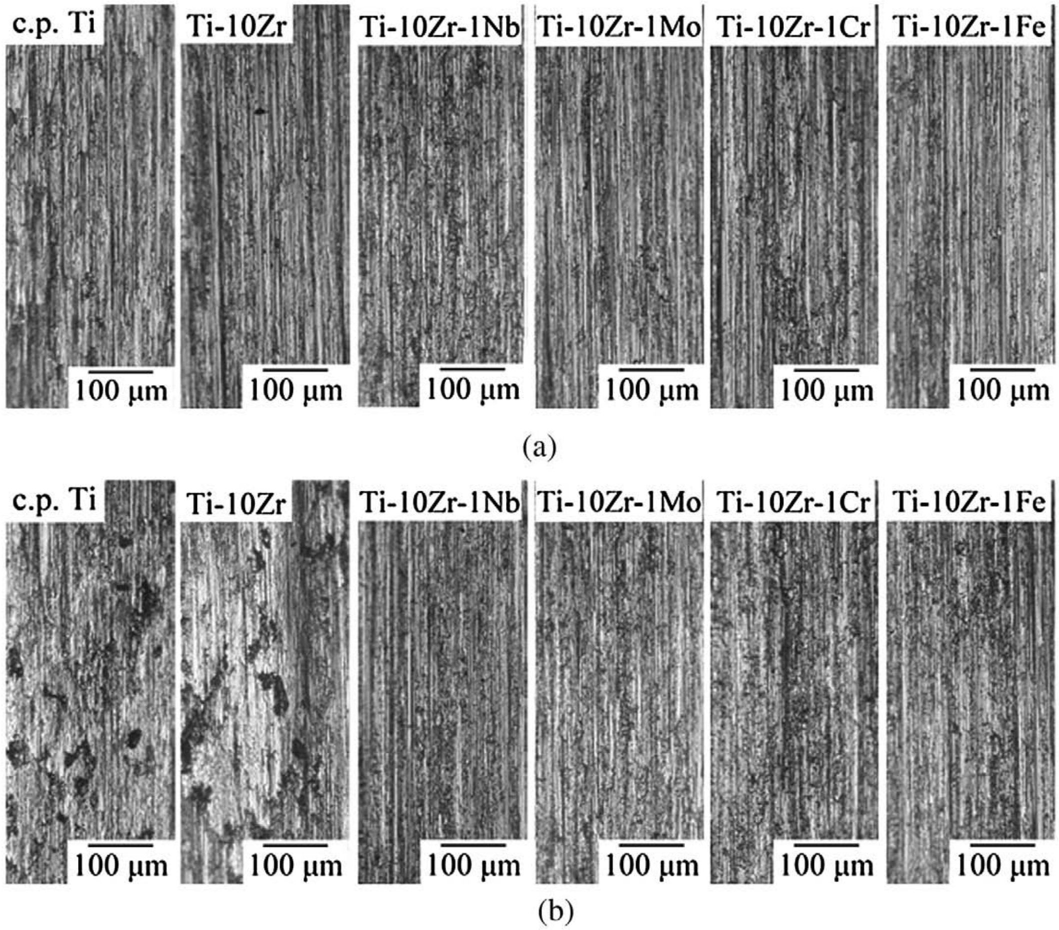

Fig. 9. Grinding surfaces of c.p. Ti, Ti–10Zr and Ti–10Zr–1X alloys at (a) 500 m/min, and (b) 1000 m/min.

alloys results from high-speed grinding. In addition, appreciable sparking was occasionally observed during the grinding test, especially at a high grinding speed.

4. Conclusions

The microstructure of Ti–10Zr–1Nb was similar to that of Ti–10Zr but with coarse lath type formations. Ti–10Zr–1Mo, Ti–10Zr–1Cr and Ti–10Zr–1Fe all showed fine martensitic lath morphology, and which was most apparent for Ti–10Zr–1Mo. The Ti–10Zr–1Mo alloy exhibited the highest microhardness and strength of all the metals in this study. Ti–10Zr–1Mo, Ti–10Zr–1Cr and Ti–10Zr–1Fe exhibited significantly higher elastic recovery capability and bending modulus than Ti–10Zr–1Nb, Ti–10Zr and c.p. Ti. At the higher grinding speeds of 750 and 1000 m/min, all the Ti–10Zr–1X alloys showed better grindability than c.p. Ti. The grinding ratios of all the Ti–10Zr–1X alloys were far higher than those of c.p. Ti and Ti–10Zr.

In conclusion, the authors found that the addition of small quantities of alloying metals significantly improved the mechanical properties of Ti–10Zr alloys, and of all the alloys tested in this study, Ti–10Zr–1Mo showed the most potential for clinical dental applications such as dental prostheses as it possesses the best balance of superior mechanical properties and machinability.

Acknowledgements

The authors acknowledge the financial support from Taichung Veterans General Hospital and Da-Yeh University through the projects TCVGH-DYU968307 and ORD-9607.

References

[1] E.P. Lautenschlager, P. Monaghan, Int. Dent. J. 43 (1993) 245.
[2] H. Nakajima, T. Okabe, Dent. Mater. J. 15 (1996) 77.
[3] R.R. Wang, A. Fenton, Quintessence Int. 27 (1996) 401.
[4] O. Okuno, A. Shimizu, I. Miura, J. Jpn. Soc. Dent. Mat. Dev. 4 (1985) 708.
[5] S. Zinelis, A. Tsetsekou, T. Papadopoulos, J. Prosthet. Dent. 90 (2003) 332.
[6] O. Okuno, H. Hamanaka, Dent. Jpn. 26 (1989) 101.
[7] A. Shimizu, J. Jpn. Soc. Dent. Mat. Dev. 5 (1986) 122.
[8] M. Hattori, K. Hasegawa, M. Yoshinari, E. Kawada, Dent. Mater. J. 20 (2001) 16.
[9] Y. Takada, H. Nakajima, O. Okuno, T. Okabe, Dent. Mater. J. 20 (2001) 34.
[10] M. Takahashi, M. Kikuchi, Y. Takada, O. Okuno, Dent. Mater. J. 21 (2002) 270.
[11] F. Duret, J.L. Blouin, B. Duret, J. Am. Dent. Assoc. 117 (1988) 715.
[12] H. Nakajima, T. Okabe, Dent. Mater. J. 15 (1996) 77.
[13] M. Kikuchi, Y. Takada, S. Kiyosue, M. Yoda, M. Woldu, Z. Cai, O. Okuno, T. Okabe, Dent. Mater. 19 (2003) 375.
[14] M. Kikuchi, M. Takahashi, T. Okabe, O. Okuno, Dent. Mater. J. 22 (2003) 191.
[15] M. Kikuchi, M. Takahashi, O. Okuno, Dent. Mater. J. 22 (2003) 328.
[16] M. Kikuchi, M. Takahashi, H. Sato, O. Okuno, M.E. Nunn, T. Okabe, J. Biomed. Mater. Res. B. Appl. Biomater. 77 (2005) 34.
[17] M. Takahashi, M. Kikuchi, O. Okuno, Dent. Mater. J. 23 (2004) 203.
[18] M. Koike, M. Itoh, O. Okuno, K. Kimura, O. Takeda, T.H. Okabe, T. Okabe, J. Mater. Eng. Perform. 14 (2005) 778.
[19] P.R. Walker, J. LeBlanc, M. Sikorska, Biochemistry 28 (1989) 3911.
[20] S. Yumoto, H. Ohashi, H. Nagai, S. Kakimi, Y. Ogawa, Y. Iwata, Int. J. PIXE 2 (1992) 493.
[21] S. Rao, T. Ushida, T. Tateishi, Y. Okazaki, S. Asao, Biomed. Mater. Eng. 6 (1996) 79.
[22] E.W. Collings, in: J.L. Water, M.R. Jackson, C.T. Sims (Eds.), Alloying, ASM International, Metals Park, Ohio, 1988, p. 257.
[23] Y. Zhentao, Z. Lian, Mater. Sci. Eng., A. 25 (2006) 438.
[24] W.F. Ho, C.H. Lai, W.K. Chen, H.C. Hsu, S.C. Wu, Proc. 6th Int. Symp. on Titanium in Dentistry, The Society for Titanium Alloys in Dentistry, Kyoto, Japan, 2007, p. 121.
[25] M.J. Donachie, Titanium: A Technical Guide, 2nd ed., ASM International, Materials Park, Ohio, 2000, p. 15.
[26] W.F. Ho, C.P. Ju, J.H. Chern Lin, AFS Trans. 99 (1999) 853.
[27] A. Guha, 9th edn., Metals Handbook, vol. 8, ASM International, Metals Park, Ohio, 1985, p. 133.
[28] W.F. Ho, C.P. Ju, J.H. Chern Lin, Biomaterials 20 (1999) 2115.

[29] M. Taira, M. Okazaki, J. Takahashi, M. Yamaki, J. Oral Rehabil. 24 (1997) 527.
[30] I. Watanabe, C. Ohkubo, J.P. Ford, M. Atsuta, T. Okabe, Dent. Mater. 16 (2000) 420.
[31] C. Ohkubo, I. Watanabe, J.P. Ford, H. Nakajima, T. Hosoi, T. Okabe, Biomaterials 21 (2000) 421.
[32] E. Kobayashi, S. Matsumoto, H. Doi, T. Yoneyama, H. Hamanaka, J. Biomed. Mater. Res. 29 (1995) 943.
[33] S. Kobayashi, K. Nakai, Y. Ohmori, Mater. Trans. 42 (2001) 2398.
[34] E.W. Collings, in: R. Boyer, G. Welsch, E.W. Collings (Eds.), Materials Properties Handbook: Titanium Alloys, ASM International, Materials Park, Ohio, 1994, p. 1053.
[35] R. Davis, H.M. Flower, D.R.F. West, J. Mater. Sci. 14 (1979) 712.
[36] J.C. Williams, Titanium Science and Technology; Proceeding, Metallurgical Society of AIME, Plenum Press, New York, 1973, p. 1433.
[37] H.E. Chandler, 9th edn., Metals Handbook, vol. 16, ASM International, Materials Park, Ohio, 1989, p. 844.
[38] H. Takeyama, T. Yoshikawa, T. Takada, J. Jpn. Soc. Preci. Eng. 41 (1975) 392.
[39] R. Grajower, I. Kurz, M.S. Bapna, Dent. Mater. 2 (1986) 187.
[40] M.H. Reisbick, B.F. Bunshah, J. Dent. Res. 52 (1973) 1138.
[41] W.J. O'Brien, Dental Materials: Properties and Selection, Quintessence Publishing Company, Chicago, 1989, p. 515.
[42] E.O. Ezugwu, Z.M. Wang, J. Mater. Process. Technol. 68 (1997) 262.