Ti–Ge binary alloy system developed as potential dental materials

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Abstract: As-cast Ti–xGe (x = 2, 5, 10, 20 wt %) binary alloys were produced in this work, and various experiments were carried out to investigate the microstructure, mechanical properties, in vitro electrochemical and immersion corrosion behaviors as well as cytotoxicity with as-cast pure Ti as control, aiming to study the feasibility of Ti–xGe alloy system as potential dental materials. The microstructure of Ti–xGe alloys changes from single α-Ti phase to α-Ti + Ti5Ge3 precipitation phase with the increase of Ge content. Mechanical tests show that Ti–5Ge alloy has the best comprehensive mechanical properties. The corrosion behavior of Ti–xGe alloys in artificial saliva with different NaF and lactic acid addition at 37°C indicates that Ti–2Ge and Ti–5Ge alloys show better corrosion resistance to fluorine-containing solution. The cytotoxicity test indicates that Ti–xGe alloy extracts show no obvious reduction of cell viability to L-929 fibroblasts and MG-63 osteosarcoma cells, similar to pure Ti which is generally acknowledged to be biocompatible. Considering all these results, Ti–2Ge and Ti–5Ge alloys possess the optimal comprehensive performance and might be used as potential dental materials.© 2012 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 100B: 2239–2250, 2012.

Key Words: Ti–xGe alloys, microstructure, mechanical properties, corrosion, cytotoxicity


INTRODUCTION

Metal and alloy systems used in the clinical dentistry for rehabilitation include gold alloys, palladium-based alloys, Co-Cr alloys, Ni-Cr alloys, CP Ti, Ti–6Al–4V, and Ti–6Al–7Nb (ISO5832-11), in which gold, palladium-based, and Co-Cr alloys, Ni-Cr alloys, CP Ti, Ti–6Al–4V, and Ti–6Al–7Nb (ISO5832-11), in which gold, palladium-based, and Co-Cr alloys have a long history, but gold and palladium are costly while Co, Ni, and Cr are toxic.1,2

Titanium and its alloys have been widely used as dental materials, due to their excellent corrosion resistance and superior biocompatibility.3 The development of new titanium alloys are still needed for improvement of the current ones. On the one hand, the low strength and poor wear resistance of pure Ti restrict its use in a number of applications, especially where the high mechanical performance is required, e.g., removable partial denture framework. On the other hand, alloying strengthened Ti alloys (Ti–6Al–4V and Ti–6Al–7Nb) have been considered to be acceptable with excellent mechanical performance; however, their metal ion leaching and corresponding toxicity of vanadium and aluminum were also reported.4,5 Therefore in the past few years, some new ternary and multicomponent Ti alloys like Ti–13Nb–13Zr (ASTM F1713-1996) and Ti–12Mo–6Zr–2Fe (ASTM F1813-1997) were developed by choosing the biocompatible alloying elements, meanwhile plenty of Ti–X binary alloys were also developed, such as Ti–Mo,6 Ti–Nb,7 Ti–Ta,8 Ti–Zr,9 Ti–Hf,10 Ti–Sn,11 Ti–Pd,12 Ti–Au,13 Ti–Ag,14 Ti–Cu,15 Ti–Cr,16 and so forth.

Titanium casting technology for dentistry has made great progress during the past 20 years,17 yet the casting of Ti and Ti alloys is still not a simple task as it always involves in several challenges, such as high melting temperature, affinity with interstitial elements, and considerable activity with mould materials.18 It is hard to perform the casting as well as to obtain the homogeneous composition when the high melting point metals (such as Mo, Nb, Ta, Zr, Hf) are added as alloying elements. Thus, it is of practical
significance to find new titanium alloys to lower the casting difficulties.

To our knowledge, there has been no report on Ti–Ge alloy system as a dental casting alloy as yet. There are several good reasons for us to explore the feasibility of Ti–Ge binary alloy system as dental materials: (1) according to the Ti–Ge phase diagram, 

\[ \text{Ti} \text{–Ge phase diagram} \]

Ti alloyed with Ge has a comparatively lower melting temperature, which might greatly favor the casting procedure. (2) As the density of Ge is only 5.32 g/cm³, much lower than that of the frequently used alloying elements (Mo, Nb, Ta, Zr, Hf, Pd, Sn, Au, Ag, Cu, Cr, etc.), the very light dentures or bridges can be manufactured to alleviate the burden of the castings on the alveolar bone and remained teeth. This is crucial to the large-scale rehabilitation of the upper jaw. (3) Though Ge is not a necessary element for human, it indeed widely exists in our body and other organisms. Hamilton et al. examined the concentration and distribution of Ge in healthy human tissues, and found a small amount of Ge distributed in many tissues, e.g. kidney, blood, brain, liver, and lung. Further, a lot of studies showed that Ge has the antitumor effect, immunomodulative activity, and antimitogenic properties as well as some favorable physiological effects in the form of organic or inorganic compounds. Despite this, Ge was also reported to be a cumulative toxin causing serious and potentially fatal, adverse effects on the kidneys. However, Ge toxicity was largely associated with consumption of inorganic germanium dioxide as a dietary supplement. Thus, element Ge may still be considered an element of rather low risk to human.

In the present study, four as-cast Ti-xGe alloys were designed and produced, with the microstructure characterization, mechanical tests, corrosion tests, as well as in vitro cytotoxicity evaluation conducted to study their feasibility as potential materials for dental applications. Nowadays, the efforts are made to improve mechanical properties and replace Ti alloys the toxic or potentially toxic elements with nontoxic elements. Though diverse Ti alloys are under research nowadays, seldom has been commercially used in dentistry. Even for Ti-6Al-4V and Ti-6Al-7Nb alloys, their element toxicity and hypersensitivity are major concerns. Since pure Ti remains to be the predominant material for dental implant, as-cast pure Ti was used as a control throughout for better comparison.

**MATERIALS AND METHODS**

**Materials preparation**

Ti (purity: 99.86%) wires and Ge (purity: 99.99%) ingots, provided by Beijing Cuibolin Nonferrous Metal Technology Developing Co. Ltd., China, were used to produce as-cast pure Ti and Ti-xGe (x = 2, 5, 10, 20, in mass percentage) ingots, weighing approximately 80 g each. The experimental alloys were melted in an vacuum arc-melting furnace (manufactured by Sky Technology Development Co. Ltd., Chinese Academy of Sciences, Shenyang, China) with a nonconsumable tungsten electrode and water-cooled copper crucible under vacuum atmosphere (5 × 10⁻³ Pa). Each ingot was overturned and remelted six times for homogenization. The ingots were cut into strip samples (40 mm × 2 mm × 1 mm) for tension test (gauge length 15 mm, nonstandard specimens), square samples (10 mm × 10 mm × 1 mm) for corrosion, wear, and cytotoxicity tests and rectangular samples (10 mm × 5 mm × 1 mm) for immersion test, by wire cut electric discharge machine (BDK 7725, Dimenghengda Mech. & Elec. Co. Ltd., Beijing, China). Each sample was mechanically grinded up to 2000 grit, ultrasonically cleaned in acetone, ethanol, and distilled water and then dried in open air. For cytotoxicity tests, the samples were sterilized by ultraviolet radiation for at least 2 h.

**Microstructure characterization**

X-ray diffraction (XRD) measurements were carried out (X’Pert Pro diffractometer operated at 40 kV and 30 mA with Cu-Kα radiation) in order to identify the phase constitution and the corrosion products after immersion test. Microstructure of the samples (mechanically grinded up to 2000 grit and then immersed in artificial saliva for 10 days) was observed by backscattered electron imaging and secondary electron imaging techniques using the scanning electron microscope (SEM, CamScan MX2600FE, UK).

**Mechanical properties tests**

**Tensile test.** The tensile tests were carried out at a strain rate of 3%/min utilizing Instron 3365 universal test machine. At least three effective measurements (only those fractured within the gauge length section were counted as effective measurement and used for data analysis) were taken for each group.

**Microhardness test.** A digital hardness tester (HVS-1000) was utilized to examine the Vickers microhardness of samples. A load of 200 g was dwelt for 15 s, repeating five times in different positions of each sample to get an average value.

**Wear test.** All wear tests were performed at room temperature using a ball-on-flat tribometer, in dry condition and lubricated condition with artificial saliva, respectively. The commercially available silicon nitride ceramic ball (Φ 6 mm, Si₃N₄) was used as the mating ball. The grinding ball ran in circles with a diameter of 6 mm, a frequency of 2 Hz, and a loading force of 4 N, so as to simulate the wear conditions of human teeth. Each sample underwent the wear test for 0.5 h and then the wear debris and wear tracks were observed by SEM. Further analysis of the wear debris composition was conducted with EDS. Weight losses were measured with the electric balance (Sartorius CP225D 0.01 mg). At least three samples were tested to ensure the repetition of the experimental results.

**Electrochemical measurements**

All electrochemical measurements were performed on CHI660C electrochemical working station (CHI, Chenhua, China) at 37°C in the following two electrolytes with pH adjusted to 5.8 by adding NaOH. The first electrolyte was Fuyama Mayer artificial saliva (NaCl 0.4 g/L; KCl 0.4 g/L;
CaCl₂ 0.6004 g/L; NaH₂PO₄·2H₂O 0.78 g/L; KSCN 0.300 g/L; Na₂S·9H₂O 0.005 g/L; urea 1.000 g/L). The second one was Fuayama Mayer artificial saliva added with 0.2% NaF since fluoride concentration (in terms of NaF) in some commercial toothpastes and prophylactic gels could vary in the range of 0.1 to 2.0 wt %, while the corresponding pH value ranged from 5.5 to 7.0. Since human saliva is rich in oxygen, both the two electrolytes were naturally aerated for simulation of clinical conditions.

The open-circuit potential (OCP) was recorded for 1 h in each electrolyte for samples to reach a steady state within the two electrolytes. Then potentiodynamic polarization measurements were carried out in these two artificial solutions with a scan rate of 1 mV/s from −0.8 V to +2.0 V. A three-electrode cell was used. The counter electrode was a platinum electrode and the reference electrode was saturated calomel electrode (SCE). The samples were embedded in epoxy resin and an area of 1 cm² was exposed to the solution. At least three samples were tested to ensure the repetition of the experimental results.

**Immersion test**
Immersion test was carried out according to the ASTM-G31-72. Four immersion solutions were prepared: (1) artificial saliva, (2) artificial saliva with 0.2% NaF, (3) artificial saliva with 0.3% lactic acid, and (4) artificial saliva with both 0.2% NaF and 0.3% lactic acid (all additives were in weight percentage), with pH values of 5.8, 5.8, 2.5, and 4.0, respectively. Lactic acid was selected to resemble the extremely acidic condition, such as exposure to acidic beverages or regurgitation or the presence of dentobacterial plaque. Bacteria in active dental plaque generates a powerful, tooth mineral destroying mixture of lactic, acetic, and other metabolic acids, at a pH of 4.0 or lower. Each sample, with the total exposed surface area of 1.3 cm², was immersed in 25 mL testing solution and kept in water bath of 37°C. After immersion of 10 days, the samples were removed, gently rinsed with distilled water, and dried at room temperature. The metal ion release for each group was analyzed by using inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Electron Corp.). Surface morphology, composition, phase constitution of experimental samples after immersion testing were characterized by SEM, energy-disperse spectrometer (EDS), and XRD, respectively.

**Cytotoxicity test**
Cytotoxicity tests were carried out according to ISO 10993-5:2009 using the indirect contact method (extracts). Murine fibroblast cells (L-929) and human osteosarcoma cells (MG63) were cultured in Dulbecco’s modified Eagle’s medium (DMEM), supplemented with 10% fetal bovine serum (FBS), 100 U mL⁻¹ penicillin and 100 µL mL⁻¹ streptomycin at 37°C in a humidified atmosphere of 5% CO₂. Extracts were prepared using DMEM serum free medium as the extraction medium with the surface area of extraction medium ratio 1.25 mL/cm² in a humidified atmosphere with 5% CO₂ at 37°C for 72 h. The supernatant fluid was withdrawn and centrifuged to prepare the extraction medium, then refrigerated at 4°C before the cytotoxicity test. DMEM medium was used as negative control and 10% DMSO/DMEM medium as positive control. Cells were incubated in 96-well cell culture plates with 5 × 10³ cells/100 µL medium in each well and incubated for 24 h to allow attachment. The medium was then replaced with 100 µL extracts. After incubating the cells in a humidified atmosphere with 5% CO₂ at 37°C for 1, 2, and 3 days, respectively, 10 µL MTT was added to each well. The samples were incubated with MTT for 4 h at 37°C, then 100 µL formazan solubilization solution (10% SDS in 0.01M HCl) was added in each well overnight in the incubator in a humidified atmosphere. The spectrophotometric absorbance of the samples was measured by microplate reader (Bio-RAD680) at 570 nm with a reference wavelength of 630 nm.

**Statistical analysis**
The experimental data were expressed as mean and standard deviation. One-way analysis of variance (ANOVA) was conducted with SPSS11.5 to evaluate the difference in mechanical properties and cell viabilities of as-cast pure Ti (the control group) and Ti-xGe alloys. Statistical significance was defined as ≤0.05. Student-Newman–Keuls (q test) would be done between the experimental and control groups if statistical significance was confirmed between groups using ANOVA.

**RESULTS**
Phase constitution and microstructure of as-cast Ti-xGe binary alloys
Figure 1 presents the XRD patterns of the as-cast Ti-xGe alloys at room temperature. It can be seen clearly that with the increasing of Ge, the phase constitution evolves from single α-Ti phase to a mixture of α-Ti phase and the secondary phase of Ti₅Ge₃. The low-Ge alloys such as Ti-2Ge and Ti-5Ge alloys display a single α-Ti phase feature, while Ti-10Ge alloy has shown several weak peaks of Ti₅Ge₃, which demonstrates its α-Ti + Ti₅Ge₃ dual phase constitution.
For Ti–20Ge alloy, the numerous and typical peaks of Ti₅Ge₃ indicate its large quantity in this alloy.

The microstructure of the Ti–xGe alloys at room temperature was also examined using SEM, as shown in Figure 2. Figure 2(a) shows that Ti–2Ge alloy has typical granular equiaxed microstructure of single α-Ti phase. However, for Ti–5Ge alloy, as displayed in Figure 2(b), there are some small particles of Ti₅Ge₃ evenly distributed in the matrix. Figure 2(c) presents the microstructure of Ti–10Ge alloy, with Ti₅Ge₃ secondary phase distributing along the grain boundary or directionally arranging in lines inside the α-Ti grain. A large amount of Ti₅Ge₃ particles disperse totally disorderedly on the α-Ti matrix for Ti–20Ge alloy, as illustrated in Figure 2(d).

**Mechanical properties of as-cast Ti–xGe binary alloys**

**Tensile strength and microhardness.** Figure 3(a) shows the tensile properties of as-cast Ti–xGe alloys, with as-cast pure Ti as control. It can be seen that the addition of Ge into pure Ti firstly brings about an upward tendency in yield strength and ultimate tensile strength, which reaches a maximum of 486 MPa and 745 MPa (p < 0.05), respectively.
for the Ti–5Ge alloy. However, a further increase of Ge content up to 10 wt % or even more leads to a decrease in strength ($p < 0.05$). Ti–5Ge alloy shows significantly improved strength and comparable elongation (16.4%) to that of as-cast pure Ti (18.5%). The hardness of as-cast pure Ti and the four Ti–$x$Ge alloys is shown in Figure 3(b). As can be seen, the addition of Ge greatly improves ($p < 0.05$) the hardness of the four Ti–$x$Ge alloys, even for the lowest addition of 2 wt %.

Wear resistance. Figure 4 presents the weight losses of as-cast pure Ti and Ti–$x$Ge alloys after sliding wear tests in unlubricated condition and lubricated condition with artificial saliva. It is obvious that the weight loss decreases with the increase of Ge content in Ti–$x$Ge alloys under the dry wear condition while that in the lubricated condition decreases ($p < 0.05$) at first and then comes to a stable level. Ti–20Ge alloy shows the best wear resistance ($p < 0.05$) in dry wear condition while Ti–5Ge alloy displays the lowest weight loss ($p < 0.05$) in the lubricated condition with artificial saliva.

Figure 5 illustrates the typical wear tracks of as-cast pure Ti and Ti–5Ge alloy samples. Wear debris and its composition of Ti–5Ge alloy have also been shown in Figure 5(e,f). Adhesive wear modes include scoring, galling, seizing, and scuffing. Plowing is one of the typical mechanisms of abrasive wear. Plowing occurs when material is displaced to the side, away from the wear particles, resulting in the formation of grooves that do not involve direct material removal. A high content of oxygen in the wear debris proves the typical oxidative wear. Hence, the results demonstrate that the wear mechanism of Ti–$x$Ge alloys in dry condition is a mixture of adhesive wear, abrasive wear, and oxidative wear which is due to the high affinity of Ti to oxygen. The lubrication of artificial saliva alleviates the wear, especially abrasive wear and oxidative wear. However, it brings about a new wear mechanism, namely corrosive wear.

Electrochemical corrosion behavior of as-cast Ti–$x$Ge binary alloys

Figure 6 shows the varying tendency of open circuit potential (OCP) with respect to the time in artificial saliva and that with 0.2% NaF for as-cast pure Ti and four Ti–$x$Ge alloys. In both solutions, the OCP curves take on an upward trend and become stable gradually. The final OCP in the
artificial saliva after 3600 s immersion for all the alloys are positive than that in the artificial saliva with 0.2% NaF. Further, the OCP for pure Ti drops dramatically from a stable value of −0.15 V in the artificial saliva to some −0.6 V in the fluoridated artificial saliva.

Figure 7 shows the experimental potentiodynamic polarization curves of as-cast pure Ti and Ti–xGe alloys in the artificial saliva with two different NaF concentrations (0% and 0.2%). The calculated passivation current density (I_p) for pure Ti, Ti–2Ge, Ti–5Ge, Ti–10Ge, and Ti–20Ge alloys in artificial saliva were 3.69 ± 0.31, 4.11 ± 0.47, 3.86 ± 0.76, 16.28 ± 5.80, and 16.30 ± 7.38 μA cm², respectively; and in artificial saliva with 0.2% NaF 25.01 ± 2.28, 4.87 ± 1.07, 4.59 ± 1.02, 36.49 ± 12.64, and 66.49 ± 13.60 μA cm², respectively. It can be seen that (i) the alloying of element Ge into Ti decreases the corrosion potentials of the materials in the artificial saliva without NaF, which is in agreement with the OCP results; (ii) in artificial saliva with 0.2% NaF, the corrosion-resistance of the experimental materials all deteriorated; however, Ti–2Ge and Ti–5Ge alloys came into passivation state more easily; (iii) there is an obvious breakdown potential for pure Ti around 1.0 V in the NaF added artificial saliva.

Immersion corrosion behavior of as-cast Ti–xGe binary alloys

Table I presents the ion releases of as-cast pure Ti and Ti–xGe alloy in four immersion solutions after 10 days immersion. In artificial saliva, both Ti and Ge ions were not detected (below the detection limit of the equipment—1 ppb) after 10 days immersion, while in the acidified artificial saliva, only Ti ions were detected, with an extremely low concentration of no more than 1.3 μg/cm² after 10 days immersion for all the experimental materials. In artificial saliva with 0.2% NaF, both Ti and Ge ions were detected, which were much higher than those detected in the artificial saliva with 0.3% lactic acid. A sharp release of Ti (over 5000 μg/cm²) and Ge ions (over 100 μg/cm²) was found in the artificial saliva with both lactic acid and NaF.

The corroded surfaces of as-cast pure Ti and Ti–xGe alloys after 10 days immersion have also been analyzed with XRD as shown in Figure 8. Obvious changes could be found for samples immersed in the acidified and fluoridated artificial saliva: A layer of TiO₂ has been demonstrated to form on the surface of pure Ti and Ti–2Ge alloy, displaying mainly the TiO₂ peaks and weak α-Ti peaks. Ti–5Ge alloy shows peaks of α-Ti, TiO₂, and GeO₂. Ti–10Ge and Ti–20Ge
alloys display strong $\alpha$-Ti and Ti$_5$Ge$_3$ peaks as well as some weak peaks of TiO$_2$ and GeO$_2$. The EDS results in Table II have revealed the existence of oxygen on all corroded surfaces, which further demonstrate the existence of TiO$_2$ and GeO$_2$ passivation layers. The surface of Ti–5Ge alloy after the immersion test indicates the highest oxygen content.

Cytotoxicity tests of as-cast Ti–xGe binary alloys

Figure 9 shows the viability of cells cultured in 100% extracts of as-cast pure Ti and Ti–xGe alloys for 1, 2, and 3 days. It could be seen that the mean cell viability of the two cell lines for all the experimental alloys is above 90% after 3 days culture. For L-929 cells, only the cell viability in Ti–20Ge alloy extracts decreases after 3 days culture ($p < 0.05$). For MG-63 cells, the cell viability in Ti–xGe alloy groups shows no significant difference from that in pure Ti group ($p > 0.05$). Meanwhile, it was found that both the two cells maintained normal spindle or polygonal morphology, while spherical and aberrant cell morphologies were seldom observed. According to ISO 10993-5:2009,\(^3\) the cytotoxicity grade of Ti–Ge alloys for L-929 fibroblast cells and MG63 osteosarcoma cells is 0 grade or 1 grade, same as pure Ti.

**DISCUSSION**

Due to the complications of the oral environment, a lot of strict requirements must be satisfied for materials used in prosthodontics and implant dentistry.

![X-ray diffraction patterns](image-url)

**FIGURE 8.** X-ray diffraction patterns of as-cast (a) pure Ti, (b) Ti–2Ge, (c) Ti–5Ge, (d) Ti–10Ge, (e) Ti–20Ge alloys after immersion in four artificial solutions (i. artificial saliva, ii. artificial saliva with 0.2% NaF, iii. artificial saliva with 0.3% lactic acid, iv. artificial saliva with 0.2% NaF and 0.3% lactic acid) for 10 days, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
Mechanical properties
To meet the demands of various dental applications such as the removable partial denture frameworks, artificial dental crowns, bridges, and implants, materials with high mechanical performances are required by different composition and processing designs.33 It may be noticed that Ti–5Ge alloy shows the lowest hardness but the highest YS, UTS, and elongation during the four as-cast Ti–xGe alloys. This could be explained by the effect of secondary phase in the matrix. Due to solution strengthening, hardness of Ti–2Ge alloy (conferred to be supersaturated solid solution at room temperature) is slightly higher than that of Ti–5Ge alloy having low volume fraction of precipitated secondary phase. Then an increase of the secondary phase volume fraction owing to the increase of Ge leads to continuing increase in hardness. However, it is not the same with yielding strength and elongation, which are determined by the size and volume fraction as well as distribution pattern of the secondary phase. A model34 for the restraining effect of second-phase inclusions on an advancing crack front deriving from brittle matrix was presented which incorporated a parameter characterizing the relative ease of cutting through or circumventing the second phase, compared with matrix cracking. The model predicted a rapid increase in toughness with volume fraction of the secondary phase at dilute concentrations, and a maximum toughness at intermediate volume fraction. Large-size secondary phase particles could act as crack source and along grain boundary distributed secondary phase shall cause brittleness, which all contribute to deterioration of strength and elongation. The work of Kikuchi et al.35 on Ti–Cu alloys and Hsu et al.11 and Ho et al.36 on Ti–Sn and Ti–Cr alloys also demonstrated it. Ti–5Ge alloy developed in this work with fine Ti3Ge5 particles in low concentration distributing evenly in the α-Ti matrix shows the best mechanical properties with the average tensile strength of 745 MPa, elongation of 16.4% and the hardness of HV307. However, restricted by the small-size ingots, the tension samples had a rectangular shape instead of the recommended geometry with dumb-bell shape proposed by the relative ISO standard, which might lead to underestimation of the true tensile strength and elongation.

Figure 10 compares the tensile strength and elongation of as-cast Ti–Ge alloys and some clinically used as-cast dental metals and alloys. It can be seen that the tensile strength of Ti–Ge alloy ranges from 660 MPa to 750 MPa, which is lower than that of high Pd alloy,37 Ti–6Al–4V/Ti–6Al–7Nb38–40 but superior to that of Ti–Nb–Zr–X alloy,41 Ni–Cr alloy,42,43 and TA240,44 (an extensively used dental implant material of Nobel-Biocare, Straumann and Astra Tech, etc.45,46). Noticeably, the tensile strength of Ti–xGe alloys is comparable with that of type IV Au alloys47,48 and Co–Cr alloys49 while a higher elongation (maximum 22%) is also obtained for Ti–Ge alloy system.

Figure 11(a) shows the varying tendency of tensile strength along with the increasing of alloying elements content for some previously studied Ti–X binary alloy systems. It has been found that Ti–Mo alloy has the highest tensile strength in the seven selected Ti–X binary alloys.50 Single addition of Ag,51 Nb, Ta, or Hf has a very small strengthening effect, for example addition of Nb, Ta, or Hf up to 30 wt % only elevates the tensile strength to 600 MPa or so.7,52,53 However, an effective addition of Ge is no more than 7 wt %, much lower than that of Ag, Nb, Ta, or Hf. This may be due to the different strengthening mechanisms, for Ti alloys with Nb, Ta, or Hf (β isomorphous stabilizer alloying element), solution strengthening plays a key role, and for those with Ge or Cu (β eutectoid alloying element), dispersion strengthening predominates.

| TABLE II. Energy Dispersive Spectroscopy Surface Analysis of As-Cast Pure Ti, Ti–5Ge, and Ti–20Ge Alloys After Immersion in Artificial Saliva with 0.3% Lactic Acid and 0.2% NaF for 10 Days |
|---|---|---|
| Element | Pure Ti | Ti–5Ge | Ti–20Ge |
| Wt % | At % | Wt % | At % | Wt % | At % |
| O K | 05.37 | 14.29 | 09.13 | 23.14 | 03.59 | 10.84 |
| F K | 00.87 | 01.95 | 00.85 | 01.80 | 01.28 | 03.24 |
| Na K | 00.44 | 00.81 | 00.71 | 01.25 | 00.00 | 00.00 |
| Ti K | 93.32 | 82.95 | 83.15 | 70.36 | 66.06 | 66.58 |
| Ge K | – | – | 06.17 | 03.44 | 29.08 | 19.34 |

**FIGURE 9.** Cell viability of (a) L-929 cells and (b) MG-63 cells after 1, 2, and 3 days culture, respectively, in the extraction mediums of as-cast pure Ti and four Ti–xGe alloys. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
and Ti–5Ge alloys have much better corrosion resistance of biomedical titanium alloys is dependent on certain alloy and reduces the longevity of the restoration. Therefore, it is of primary importance to study the wear and corrosion behavior of newly developed Ti alloys.

Wear and corrosion resistance

In the oral environment, both wear and corrosion exist. Degradation of dental materials is generally seen as bad, since elements released into solution may have detrimental effects on local tissues or accumulate elsewhere in the body. Further, the corrosion process weakens the material and reduces the longevity of the restoration. Therefore, it is important to understand how these processes affect the behavior of materials in the body. Figure 11(b) compares the hardness of some Ti–X binary alloys reported by other researchers. It could be seen that hardness of Ti–30Ta is higher than HV300 while Ti–35Nb and Ti–20Ge alloys is significantly deteriorate the corrosion resistance of titanium in acidic fluoride-containing saline solution than commercial pure grade 2, type IV Au alloy, and Co-Cr alloy. Note that all tensile data were obtained for materials in as-cast state. (Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.)

Further, Figure 11(b) also roughly compares the passivation current density of some Ti–X binary alloys with pure Ti in their corresponding physiological solutions. It is easier for material with lower passivation current density to enter the passive state and maintain a lower corrosion rate, which indicates higher corrosion resistance. The corrosion resistance of Ti and its alloys largely depends on the fluoride concentration and the pH of the environmental solution that they are placed in. It was reported that Ti, Ti–6Al–4V, and Ti–6Al–7Nb alloys, which were commercially available as dental implants, were prone to corrosion in the presence of even a small amount of fluoride (0.05% NaF) with a low-level oxygen level below 0.1 ppm. So the comparisons were conducted with pure Ti in the same physiological solutions, respectively. It has been found that Ti–2Ge and Ti–15Mo6 show better corrosion resistance than pure Ti in their respective testing solutions, while Ti–30Hf alloy shows similar corrosion resistance to pure Ti in the modified Tani-Zucchi solution. There is a lack of direct comparison of corrosion resistance between Ti–30Ta alloy and pure Ti, however, Mareci et al.8 found the corrosion resistance of Ti–30Ta alloy in the saliva with 0.1 NaF is similar to that of Ti–6Al–7Nb. Ti–5Ag was found to show an inferior corrosion resistance to pure Ti in saliva with 1% NaF. Osorio et al. have also proved that the addition of Cu could significantly deteriorate the corrosion resistance of titanium in 0.9% NaCl solution due to the precipitation of Ti2Cu intermetallic compound. Unfortunately Ti–35Nb alloy indicates even a lower corrosion resistance in the same solution than Ti–5Cu. In addition, Ti–20Cr alloy, Ti–Pd, and Ti Pt alloys have been reported to show greater corrosion resistance in an acidic fluoride-containing saline solution than commercially pure Ti. Numerous previous studies have confirmed that the oxide layer on the surface of various Ti alloys

In the present study, since it shows elevated hardness to pure Ti and higher corrosion resistance than Ti–20Ge alloy. Further, Figure 11(b) also roughly compares the passivation current density of some Ti–X binary alloys with pure Ti in their corresponding physiological solutions. It is easier for material with lower passivation current density to enter the passive state and maintain a lower corrosion rate, which indicates higher corrosion resistance. The corrosion resistance of Ti and its alloys largely depends on the fluoride concentration and the pH of the environmental solution that they are placed in. It was reported that Ti, Ti–6Al–4V, and Ti–6Al–7Nb alloys, which were commercially available as dental implants, were prone to corrosion in the presence of even a small amount of fluoride (0.05% NaF) with a low-level oxygen level below 0.1 ppm. So the comparisons were conducted with pure Ti in the same physiological solutions, respectively. It has been found that Ti–2Ge and Ti–15Mo6 show better corrosion resistance than pure Ti in their respective testing solutions, while Ti–30Hf alloy shows similar corrosion resistance to pure Ti in the modified Tani-Zucchi solution. There is a lack of direct comparison of corrosion resistance between Ti–30Ta alloy and pure Ti, however, Mareci et al.8 found the corrosion resistance of Ti–30Ta alloy in the saliva with 0.1 NaF is similar to that of Ti–6Al–7Nb. Ti–5Ag was found to show an inferior corrosion resistance to pure Ti in saliva with 1% NaF. Osorio et al. have also proved that the addition of Cu could significantly deteriorate the corrosion resistance of titanium in 0.9% NaCl solution due to the precipitation of Ti2Cu intermetallic compound. Unfortunately Ti–35Nb alloy indicates even a lower corrosion resistance in the same solution than Ti–5Cu. In addition, Ti–20Cr alloy, Ti–Pd, and Ti Pt alloys have been reported to show greater corrosion resistance in an acidic fluoride-containing saline solution than commercially pure Ti. Numerous previous studies have confirmed that the oxide layer on the surface of various Ti alloys

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consists of predominant TiO₂ and small amount of oxide of the alloy elements. In the present study, XRD and EDS results after immersion corrosion also demonstrated this. The better corrosion resistance of Ti-20Cr alloy was reported to result from the formation of a chromium oxide-rich surface film. It was also found that the addition of over 0.5 wt % Pd or Pt to Ti promoted a localized cathodic reaction in the acidic fluoride-containing saliva, which accelerated spontaneous passivation of the Ti surface at the anodic area by forming TiO₂ layer, which accounted for the superior corrosion resistance of Ti-Pd and Ti-Pt alloys. The reason that Mo addition improves the corrosion resistance of its Ti alloys remains not very clear. It is the same with Ti-xGe alloys, hence, an overall investigation shall be conducted on the corrosion mechanism of Ti-xGe alloys in our further study to clarify the excellent corrosion resistance of Ti-xGe alloy with Ge content no more than 5 wt %.

**Biosafety**

Health effects of dental materials can be subdivided into systemic toxicity, local toxicity, and allergic reactions. Besides, the substances leaching from materials should also be evaluated for their potential risk of causing a teratogenic effect and the possible influence on reproductive ability. The present in vitro cytotoxicity results show that the cytotoxicity grade of Ti–2Ge and Ti–5Ge alloy extracts for L-929 fibroblast cells and MG63 osteosarcoma cells after 3 days culture is 0 grade. There is no significant difference between these two alloys and pure Ti. According to our ion release results, Ge ion release for Ti–2Ge and Ti–5Ge alloys is no more than 205 µg/cm² in the harshest environment after 10 days immersion. Take an implant with 3 cm² area into consideration, which is big enough for an all-metal crown or a dental implant surface area. Ti–2Ge and Ti–5Ge alloys should have a Ge ion release of no more than 62 µg/day, which is much lower than the daily intake of Ge from foods for human, because the typical daily dietary intake of Ge is 0.4 to 1.5 mg.

**Practicability**

When the comprehensive properties have satisfied the requirements, practicability is the deciding factor for a new material to be applicable in the clinical dentistry. (i) Density (Au > Ta > Hf > Pd > Ag > Mo > Cu > Nb > Sn > Cr > Zr > Ge > Ti); light weight of titanium alloy implants plays a noticeable role in patient perception of the efficacy of the device implanted in the body. Ge has a density of 5.32 g/cm³ close to that of pure Ti (4.52 g/cm³) while the densities of Au, Ta, Mo, and Nb reach 19.3, 16.4, 10.2, and 8.57 g/cm³, respectively. When the large-scale rehabilitation of the upper jaw is demanded, Ge shows a tremendous advantage over the other alloying elements, because light weight should add to the easiness of wearing the dental prostheses. (ii) Melting point (Ta > Mo > Nb > Hf > Cr > Zr > Ti > Pd > Cu > Au > Ag > Ge > Sn); High melting point of the alloying elements (2996°C/Ta, 2610°C/Mo, 2467°C/Nb, 1852°C/Zr) will increase the difficulty of melting procedure and the reactivity of Ti with mold materials, which fails to ensure homogenization of the ingot and the quality of the casting. The low melting point of Ge (938°C) shall facilitate the casting process of titanium since it could lower the liquidus and solidus temperatures even at a low addition of Ge. (iii) Prices (Au > Pd > Ge > Hf > Ag > Ta > Nb > Co > Mo > Ni > Sn > Zr > Cr > Ti > Cu); the applications of gold alloys and palladium alloys are limited by the extremely high prices of gold and palladium elements while casting titanium and its alloys for dental rehabilitation are limited by the need for special casting machines and the difficulties of casting procedure. Though the price of Mo, Nb, Ta, Zr, Hf elements is lower than that of Ge, this economic advantage can be offset, considering the greater difficulty of casting these titanium alloys alloying with Mo, Nb, Ta, Zr, or Hf and the lower addition of Ge.

**CONCLUSIONS**

In this study, as-cast Ti–xGe (x = 2, 5, 10, 20 wt %) alloys were studied as potential dental materials and the following conclusions can be drawn:

1. With the increase of Ge content, the microstructure of the as-cast Ti–xGe alloys changes from single α-Ti phase to α-Ti + Ti₃Ge₂ precipitation phase. Hardness and wear resistance have been significantly increased by alloying of Ge. Ti–5Ge alloy possesses the best comprehensive mechanical properties.
2. Ti–2Ge and Ti–5Ge alloys show a favorable corrosion resistance like pure Ti in artificial saliva and even an improved resistance to fluorine ions in contrast with pure Ti. Immersion tests show that Ti alloying with Ge of no more than 5 wt % will not significantly deteriorate the immersion corrosion property and the Ge releases are also in an acceptable range.
3. The cytotoxicity results indicate that the cytotoxicity grade for as-cast pure Ti and Ti–xGe alloys is 0 grade or 1 grade, basically showing no toxicity to Murine fibroblast cells (L-929) and human osteosarcoma cells (MG63).
4. As-cast Ti–2Ge and Ti–5Ge alloys possess the best comprehensive properties in all the experimental as-cast Ti–xGe binary alloys in the present work. Hence, as-cast Ti–xGe alloy with Ge addition no more than 7 wt % is proposed to be acceptable as dental materials.

**REFERENCES**


