Ti–Ga binary alloys developed as potential dental materials

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A B S T R A C T
In this study, the microstructure, mechanical properties, castability, electrochemical behaviors and cytotoxicity of as-cast Ti–Ga alloys with pure Ti as control were systematically investigated to assess their potential application in dental field. The results of OM and XRD showed that the microstructure of all experimental as-cast Ti–Ga alloys exhibited single α-Ti phase at room temperature. Mechanical tests indicated that the tensile strength, Young's modulus, microhardness and wear resistance were improved monotonically with the increase of Ga content. The castability test showed that Ti–2Ga alloy increased the castability value of pure Ti by 14.2(±3.8)% (p < 0.05). The electrochemical behaviors in both artificial saliva solutions indicated that the studied Ti–Ga alloys showed better corrosion resistance than pure Ti. The cytotoxicity test suggested that the studied Ti–Ga alloys produced no significant deleterious effect to L929 fibroblast cells and MG63 osteosarcoma cells, similar to pure Ti, indicating an excellent in vitro biocompatibility. The cell morphology test showed that both L929 and MG63 cells process excellent cell adhesion ability on all experimental materials. Considering all these results, Ti–2Ga alloy exhibits the optimal comprehensive performance and has potential for dental applications.

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1. Introduction

In the last few decades, metallic biomaterials have been widely used in hard tissue restoration and replacement because of their reliable mechanical performance. Their application includes load-bearing orthopedics, heart valve prosthesis, prosthetic joints, stents, dental implants, denture frameworks, crowns and bridges, etc. [1,2].

Among the metallic biomaterials, gold alloys and palladium-based alloys have the longest history in dentistry [3,4], but the high cost of elements gold and palladium limits their widespread application to a great extent. Though Co–Cr alloys and Ni–Cr alloys lower the cost, the elements Co, Ni and Cr are recognized as high risk elements with their incompatibility problems [5,6]. Therefore, their application in dentistry has to be declined. Ti and its alloys have many advantages (e.g., low density, high specific strength, excellent corrosion resistance and superior biocompatibility) compared with the above-mentioned alloys, so they are more expected to be used in the orthopedic and dental fields [2,7].

However, Ti alloys still need developing and improving when they are used in dentistry. On the one hand, the low strength and the poor wear resistance of pure Ti restrict its application in many respects, especially for load bearing application; on the other hand, although Ti–6Al–4V and Ti–6Al–7Nb alloys have acceptable mechanical performance due to alloying strengthening, both Al and V ions have been reported to be associated with long-term health problems, such as Alzheimer disease, neuropathy and osteomalacia [8–11]. Therefore, Al and V-free Ti alloys have been developed extensively in response to these concerns in recent years, such as Ti–Mo [12,13], Ti–Nb [14,15], Ti–Zr [16,17], Ti–Ta [18], Ti–Hf [19], Ti–Sn [20], Ti–Ag [21], Ti–Au [22], Ti–Pd [17,23], Ti–Cu [24], Ti–Ge [25], and Ti–In [26]. Some of the above-mentioned alloying elements such as Mo, Nb, Zr, Ta and Hf are refractory metals, and if they are selected as the alloying elements of pure Ti, it is still difficult to cast and obtain the homogenous composition. Ti has a high melting point (1668 °C) and is prone to oxidation at high temperature. These two characteristics restrict its applications in dentistry severely [27,28]. Therefore, if the melting temperatures of Ti alloys can be lowered by adding fusible metals, the casting procedure will become easier.

Galium (Ga) is one of the metals (with cesium, mercury, and francium) that are liquid at or near-normal room temperature, and its melting point is 29.8 °C [29]. It is also notable that Ga has a large liquid range and a low vapor pressure at high temperature, which makes it not easy to volatilize during the melting process. According to the Ti–Ga phase diagram [30], Ti alloyed with Ga has a comparatively lower melting temperature, which might greatly favor the casting procedure. As early as the 1930s, Ga was suggested as an alternative to mercury...
in dental alloys [31]. Afterwards, Ga-containing alloys such as Galloy (Southern Dental Industries, Melbourne, Australia) and gallium alloy GF (Tokuriki Dorten Co. Ltd., Tokyo, Japan) have been developed for clinical use. Chandler et al. [31] evaluated the effect of Ga ion and its concentration (0.001–1.0 mmol/L) on L929 mouse fibroblast cells. The results demonstrated that Ga ion has no significant cytotoxicity. Besides, Ga has already approved by Food and Drug Administration (FDA) to treat hypercalcemia of malignancy, which is effective in suppressing bone resorption and concomitant elevated plasma calcium [32]. What’s more, the bactericidal effect of Ga3+ makes Ga a potentially promising new antibiotic for treating and preventing localized infections [33].

Recently, the biological features of Ga have fascinated scientists to study them in different glass systems [34,35]. However, there was no systematic study on Ti–Ga alloy system as biomedical materials so far. The use of Ga in dentistry has a long history, and Ti acts as one of the most popular metals in biomaterials, so the study of Ti–Ga alloys for dental application is promising. In the present study, three Ti–Ga binary alloys had been designed and fabricated, with the microstructure, mechanical properties, castability, electrochemical behaviors as well as in vitro cytotoxicity being evaluated to study their feasibility as potential materials for dental applications, with pure Ti as control.

2. Materials and methods

2.1. Materials preparation

The as-cast pure Ti and Ti–Ga alloys with nominal compositions (2, 5 and 10 wt.% Ga) were prepared from sponge Ti (99.5% in purity) and high-purity Ga (99.99% in purity). The experimental alloys were melted in a high-vacuum arc-melting furnace (Physcience, OE Co., Ltd. Beijing, China) with a non-consumable tungsten electrode and water-cooled copper crucible under an argon atmosphere. Each ingot was overmelted and re-melted six times to improve its chemical homogeneity. The chemical compositions of the resulting Ti–Ga alloys were analyzed by inductively coupled plasma atomic emission spectrometer (Agilent 7525-ES ICP-AES) for element Ga under the instruction of standard QB-H2-01-1996 and titration method (YS/T514.1-2009) for element Ti. The measured Ga contents for nominal Ti–2Ga, Ti–5Ga, and Ti–10Ga alloys are 2.25, 5.26, and 10.56 wt.%, respectively. Different specimens were cut by electro-discharge machining for various tests.

2.2. Microstructure characterization

The microstructure of the experimental materials was examined using an optical microscopy (OM, BX51M, Olympus, Japan). After being mechanically polished via a standard metallographic procedure, the specimens were etched in a solution of hydrofluoric acid, nitric acid and water (5:15:80 in volume ratio). X-ray diffraction (XRD, DMAX specimens were etched in a solution of hydro using an optical microscopy (OM, BX51M, Olympus, Japan). After being cut by electro-discharge machining for various tests.

2.3. Mechanical properties tests

The strip specimens (40 mm × 3 mm × 2 mm) of as-cast pure Ti and Ti–Ga alloys were prepared for tensile test. The tensile test was performed on universal testing machine (Instron5969, USA) with an initial strain rate of 5 × 10−4 s−1 at room temperature. The Young’s modulus is determined according to ASTM E111–97 [36], which calculates the Young’s modulus from the ratio between the tensile stress and the corresponding strain up to the proportional limit of the alloys. For each material, at least five duplicate specimens were tested. The Vickers microhardness of as-cast pure Ti and Ti–Ga alloys was measured at the loading of 200 g for 15 s, with a digital microhardness tester (HMV-2T, Shimadzu, Japan), and repeating eight times in different positions of each specimen to get an average value.

The wear performance of as-cast pure Ti and Ti–Ga alloys was evaluated at room temperature using a ball-on-flat tribometer in dry condition and lubricated condition with artificial saliva, respectively. The composition of artificial saliva can be seen in Section 2.5. The square sheet specimens (15 mm × 15 mm × 1 mm) of as-cast pure Ti and Ti–Ga alloys were used in the test. The commercially available silicon nitride ceramic ball (Φ6 mm, Si3N4) was selected as the mating ball. The grinding ball ran in circles with a diameter of 6 mm, the frequency of 2 Hz and the loading force of 4 N, in order to simulate the wear conditions of human teeth [37]. Each specimen underwent the wear test for 0.5 h and then the tracks were observed by SEM (Hitachi S-4800 SEM, Japan). The weight losses were measured with the accurate electric balance (Sartorius CP225D, Germany). At least three duplicate specimens for each material were tested to ensure the repetition of the experimental results.

2.4. Castability test

The castability of as-cast pure Ti and Ti–Ga alloys was carried out by modified Whitlock’s method [38]. The schematic view of mesh-pattern wax mold is shown in Fig. 4(a). In this study, the wax mesh with 100 square shaped spaces of 2 mm × 2 mm was selected. The bilateral wax runner bars of 2.5 mm diameter were attached to both edges of the wax mesh. The dominate wax runner bar with 5 mm diameter and 5 mm length was attached to the corner of wax mesh. After the mesh-pattern wax mold was obtained, it was mounted in a silicone ring and poured with a magnesia and silica-based dental investment material (SYMBION TD, Nissin Dental Products Inc., Japan). The investment material was mixed at a ratio of 100 g powder to 18 ml liquid according to the manufacturer’s instructions. A pure Ti casting system (SYMION CAST, Nissin Dental Products Inc., Japan) was used for casting the series of materials and an argon pressure of 1.5 Pa was maintained during the casting.

The castability value was calculated by Whitlock’s formula. It can be illustrated in Fig. 4(a) that the wax mesh provides a grid with 100 open squares and 200 segments. After casting, the number of complete cast segments was counted, divided by 200, and multiplied by 100% to obtain a percentage designated as “castability value”, as shown in Eq. (1). The segment was deemed to be complete or incomplete according to the previous work [38].

\[
\text{Castability value (\%)} = \frac{\text{Number of complete cast segments}}{200} \times 100\% \quad (1)
\]

2.5. Electrochemical measurements

The electrochemical measurements of as-cast pure Ti and Ti–Ga alloys were conducted on CHI660C electrochemical working station (CHI, Chen Hua, China) at 37 °C. Two kinds of artificial saliva were chosen as corrosion test electrolytes in this study, which were prepared freshly from the analytic grade agents and de-ionized water. The first electrolyte was modified Fusayama–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 1.00 g/L) [39]. The fluoride concentration (in terms of NaF and/or Na2PO3F) in commercially available toothpastes and mouthwashes is varying in the range of 0.02–0.15 wt.%. Therefore, the second electrolyte was Fusayama–Mayer artificial saliva added with 0.15% NaF. The specimens with an area of 1 cm² were grounded, polished and ultrasonically washed in acetone, alcohol and distilled water, sequentially. At least three duplicate specimens were prepared for each material. A platinum counter electrode and a saturated calomel electrode (SCE) reference electrode were used for electrochemical tests, and the specimen was used as working electrode. The open-
circuit potential (OCP) of each specimen was recorded for 2 h in each electrolyte. This period appeared to be sufficient for the OCP reaching a steady state within the two electrolytes. Electrochemical impedance spectroscopy (EIS) measurement was performed following the OCP test under a sinusoidal excitation signal of 0.01 V and a frequency range from $10^{4}$ Hz to $10^{-2}$ Hz. The impedance data were analyzed and fitted to appropriate equivalent electrical circuit using the ZSimpWin software. The potentiodynamic polarization test was measured from $-0.8$ V to $2.0$ V at a scan rate of 1 mV/s, after the above mentioned EIS test. Corrosion current density ($I_{corr}$) from polarization curves can be calculated by CorrView software.

2.6. Cytotoxicity test

The cytotoxicity test was carried out according to ISO 10993-5: 2009 [40]. Murine fibroblast cells (L929) and human osteosarcoma cells (MG63) were adopted to evaluate the cytotoxicity of as-cast pure Ti and Ti–Ga alloys by indirect method and direct seeding on the surfaces of specimens. L929 cells and MG63 cells were cultured in Dulbecco’s modified Eagle’s medium (DMEM) and minimum essential medium (MEM), respectively. Both media were supplemented with 10% fetal bovine serum (FBS), 100 U/ml penicillin and 100 μg/ml streptomycin. In the indirect method, extraction media of the studied materials were prepared using serum free cell culture medium (DMEM or MEM) with the extraction ratio (the ratio of specimen surface area to extraction medium) of 3 cm²/ml, and then incubated in a humidified atmosphere with 5% CO₂ at 37 °C for 72 h. The control groups involved the use of cell culture medium (DMEM for L929 cells and MEM for MG63 cells) as negative control and cell culture medium (DMEM for L929 cells and MEM for MG63 cells) containing 10% dimethylsulfoxide (DMSO) as positive control. Cells were incubated in 96-well cell culture plates at $5 \times 10^{5}$ cells/100 μl cell culture medium in each well and incubated for 24 h to allow attachment. After that, for the experimental groups, the cell culture medium of each well was replaced with 100 μl extraction medium; for the control groups, the cell culture medium of each well was replaced with 100 μl control medium. After then the cells were still cultured in a humidified atmosphere with 5% CO₂ at 37 °C for 1, 2 and 4 days, respectively. After the culture period, 10 μl 3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT, Sigma-Aldrich, USA) was added to each well. The specimens were incubated with MTT for 4 h at 37 °C in darkness, and then 100 μl formazan solubilization solution (10% sodium dodecyl sulfate (SDS) in 0.01 M HCl) was added in each well overnight. The spectrophotometric absorbance of the specimens was measured by microplate reader (Bio-RAD680, USA) at 570 nm with a reference wavelength of 630 nm.

In the direct assay, L929 cells and MG 63 cells with an initial density of $5 \times 10^{4}$ cells/ml were seeded on the sterilized sheet specimens in 24-well cell culture plates and then cultured 1, 2 and 4 days, respectively. After the culture period, the specimens with cells were rinsed gently with phosphate buffer saline (PBS) for three times and fixed in 2.5% glutaraldehyde for 2 h at room temperature, and then dehydrated in a gradient ethanol/distilled water mixture (50, 60, 70, 80, 90 and 100%) for 10 min each, dried in the air. Cellular attachment and detailed morphologies were observed by SEM after Au sputtering.

2.7. Statistical analysis

Statistical analysis was performed with SPSS 18.0 for Windows software (SPSS Inc., Chicago, USA). The all data were statistically analyzed using one-way analysis of variance (ANOVA), followed by the Tukey post hoc tests. A $p$-value < 0.05 was considered statistically significant, as indicated by an asterisk (*) in relevant figures.

3. Results

3.1. Microstructure and phase constitution of as-cast Ti–Ga alloys

Fig. 1 shows the microstructure and XRD patterns of as-cast pure Ti and Ti–Ga alloys at room temperature. As shown in Fig. 1(a), pure Ti, Ti–2Ga and Ti–5Ga alloys exhibit a typical as-cast morphology with serrated, irregular grain boundaries, indicating a rapid cooling process during casting. The structure of Ti–10Ga alloy is composed of relatively regular grains with no obvious straight grain boundaries. Fig. 1(b) shows that all Ti–Ga alloys have single α-Ti phase with hexagonal close packed (hcp) crystal structure.

3.2. Mechanical properties of as-cast Ti–Ga alloys

Fig. 2(a) shows the tensile properties of as-cast Ti–Ga alloys, with pure Ti as control. It can be seen that the addition of Ga into pure Ti increases the yield strength (YS, $\sigma_y$) and ultimate tensile strength (UTS, $\sigma_b$) ($p < 0.05$). The $\sigma_y$ and $\sigma_b$ of Ti–Ga alloys show an upward tendency with the increasing of Ga content, which reached a maximum of 614.3(± 21.9) MPa and of 700.8(± 11.3) MPa for Ti–10Ga alloy, respectively. However, the addition of Ga into pure Ti also brings about a slightly decline in the elongation, which Ti–2Ga alloy has a minimum value of 18.6(± 0.7)% ($p < 0.05$). Young’s moduli of pure Ti, Ti–2Ga, Ti–5Ga and Ti–10Ga alloys were measured accurately by using a strain gauge attached on the specimen, and their values are 103.1(±

![Fig. 1. Optical micrographs (a) and XRD patterns (b) of as-cast pure Ti and Ti–Ga alloys at room temperature.](image)
1.6), 106.8(±1.5), 110.5(±2.3) and 116.73(±1.1) GPa, respectively. It can be found that Young’s moduli of Ti–Ga alloys increase gradually with the increasing of Ga content. As shown in Fig. 2(b), the microhardness of as-cast pure Ti, Ti–2Ga, Ti–5Ga, and Ti–10Ga alloys are 179.5(±8.1), 254.1(±9.7), 286.1(±14.1), and 305.0(±20.6) HV, respectively. The addition of Ga greatly improves the microhardness of the Ti–Ga alloys, even for a lowest addition of 2%.

The weight losses of as-cast pure Ti and Ti–Ga alloys are shown in Fig. 3(a) as a function of Ga content. The weight losses of Ti–Ga alloys decrease with the increase of Ga content both in the dry condition and in the lubricated condition. It implies that the wear resistance of Ti–Ga alloys improves with the increasing Ga content. Fig. 3(b) displays the typical wear tracks of as-cast pure Ti and Ti–10Ga alloy specimens, which are similar with the wear tracks of other Ti–Ga alloys investigated in this study. As can be seen from the wear tracks, the wear surface morphology of pure Ti is rougher than that of Ti–10Ga alloy, especially in dry condition. Comparison of two different wear conditions, it can be found that there are more abrasive particles appeared on the wear surface in the dry friction condition.

3.3. Castability of as-cast Ti–Ga alloys

Fig. 4 shows the castability of as-cast pure Ti and Ti–Ga alloys. The images of mesh-pattern castings of experimental pure Ti and Ti–Ga alloys are shown in Fig. 4(b), it is obviously that the castings of Ti–2Ga alloy specimens have more complete casting segments than the others. Fig. 4(c) exhibits their castability values, that of as-cast pure Ti, Ti–2Ga, Ti–5Ga, and Ti–10Ga alloys are 79.7(±3.1), 91.0(±3.0), 75.7(±6.7), and 75.2(±6.3)%, respectively. It can be seen that Ti–2Ga alloy displayed the highest castability value, which improves the castability significantly.

3.4. Electrochemical properties of as-cast Ti–Ga alloys

The open circuit potential (OCP) curves for as-cast pure Ti and Ti–Ga alloys in artificial saliva (AS) and artificial saliva containing 0.15%NaF (ASF) are shown in Fig. 5(a) and (c), respectively. In both artificial saliva solutions, the OCPs of all experimental materials take on an upward trend and become stable gradually. Compared with pure Ti, the Ti–Ga alloys have nobler OCPs after immersing 2 h in both artificial saliva solutions. However, by comparing the two artificial saliva solutions, it can be found that the addition of fluoride (0.15%NaF) aggravates the corrosion behaviors of all experimental materials. The final OCPs for all experimental materials vary from −0.393 V (for pure Ti) to −0.293 V (for Ti–5Ga alloy) in artificial saliva, while from −0.583 V (for pure Ti) to −0.455 V (for Ti–2Ga alloy) in fluoride-containing artificial saliva.

Fig. 5(b) and (d) shows the experimental potentiodynamic polarization curves of as-cast pure Ti and Ti–Ga alloys after immersing 2 h in artificial saliva and that with 0.15%NaF, respectively. The calculated values of Icorr for pure Ti, Ti–2Ga, Ti–5Ga, and Ti–10Ga alloys in artificial saliva are 0.063(±0.011), 0.050(±0.008), 0.035(±0.006), and 0.092(±0.014) \(\mu\)A/cm\(^2\).
respectively; and in artificial saliva with 0.15% NaF solution are 4.89 (±0.26), 0.98 (±0.11), 0.89 (±0.07), and 1.28 (±0.09) μA/cm², respectively.

What's more, it can be evidently seen that the passive current densities ($I_{\text{pass}}$) obtained around the passive regions (0–1.2 V) of Ti–Ga alloys are lower than that of pure Ti in both artificial saliva solutions from Fig. 5(b) and (d).

Fig. 6 shows the Nyquist plots and Bode plots of as-cast pure Ti and Ti–Ga alloys after immersing 2 h in both artificial saliva solutions. As shown in Nyquist plots (Fig. 6(a) and (c)), the impedance spectra of all experimental materials are characterized by a large partial semicircle. The diameters of all Ti–Ga alloys’ semicircle are larger than that of pure Ti, which indicates that the Ti–Ga alloys have a nobler electrochemical characteristic due to the addition of Ga. As shown in Fig. 6(b) and (d), there are two distinct regions for all experimental materials characterized in Bode plots. In the high frequency range ($10^2$–$10^4$ Hz), a flat portion of curves (slope $\approx 0$) is observed in the Bode-magnitude plots, while the phase angle drops to 0° in the Bode-phase angle plots, which is due to the response of electrolyte resistance. In the broad low and middle frequency ranges, the spectra display a linear slope of about $-1$ in the Bode-magnitude plots. The phase angle values approximate $-85°$ in artificial saliva and $-80°$ in fluoride-containing artificial saliva, respectively. This indicates a typical passive film presented on the surface and a near-capacitive response for passive film characterized in both artificial saliva solutions [41,42].

3.5. Cytotoxicity of as-cast Ti–Ga alloys

Fig. 7 shows the cell viability of the murine fibroblast cells (L929) and human osteosarcoma cells (MG63) cultured in as-cast pure Ti and Ti–Ga alloys extraction media for 1, 2 and 4 days. It can be seen that, for L929 cells, the mean cell viabilities of the studied Ti–Ga alloys are slightly lower than those of negative group and pure Ti after each culture period. Meanwhile, the cell viabilities of both L929 and MG63 cells for all experimental materials are above 85% for each culture period.

Fig. 8 demonstrates the morphologies of L929 and MG63 cells cultured on as-cast pure Ti and Ti–10Ga alloy specimens for 1, 2 and 4 days. After 1 day culture, only a few cells can be observed on the surface of both pure Ti and Ti–10Ga alloy specimens. The cells shrink slightly and exhibit a poor adhesion on the experimental material surfaces, especially for L929 cells. With the prolonged culture time, the cells become denser and spread better. As can be seen from Fig. 8, the cells proliferate faster and adhered better on the surface of pure Ti than Ti–10Ga alloy, and it indicates that Ga has a slightly negative effect on cell proliferation. Good correspondence could be found between the direct observation and the indirect cell viability evaluation.

4. Discussion

4.1. Microstructure and mechanical properties

According to the Ti–Ga phase diagram [30], Ga is $\alpha$-stabilizing element that increases the allotropic transformation temperature from $\alpha$ (hcp) to $\beta$ (bcc) when dissolved in Ti. In addition, the solidification interval of Ti–Ga alloy is very narrow and the solubility of Ga in $\alpha$-Ti phase is up to 20 at.% (26.4 wt.%). This is the reason why all experimental as-cast Ti–Ga alloys exhibit single $\alpha$-Ti phase with hcp crystal structure at room temperature.

To meet the demand of denture frameworks or crowns, alloy with high mechanical performance is required. It can be noticed from Fig. 2 that all as-cast Ti–Ga alloys have higher strength and microhardness as well as slightly higher Young’s modulus compared to pure Ti, which is largely derived from solid solution strengthening of the Ga atoms in $\alpha$-Ti phase. Like that of Al, Ga acts as an $\alpha$-phase stable element of titanium, and with its atomic radius (1.30 Å) that is smaller than that
of Ti (1.40 Å) [43], it would be easy to cause lattice distortion when Ga atoms get into α-Ti lattice due to their atomic size mismatch. The Ga atoms act as obstacles to the motion of original dislocations and block the propagation of dislocations, thus improving the strength of Ti–Ga alloys. The addition of Ga (no more than 10 wt.%) into pure Ti brings about a decrease in elongation to some extent, Ti–2Ga alloy shows the minimum value of 18.6(±0.7)%, but it is also higher than that of the current clinical dental use materials (such as Co–Cr–Mo alloys, Ti–6Al–4V and Ti–6Al–7Nb alloys) [44,45].

When the metallic materials are used in human body, it is inevitably for the wear resistance to occur. High wear resistance will act as an advantage when the alloy is designed for denture frameworks or crowns. Generally speaking, the wear resistance is considered to be dependent on the specific alloy system, microstructure and microhardness [45]. In the same alloy system, the higher the microhardness and the harder the second phase, the better the wear resistance. Therefore, the wear resistance of Ti–Ga alloys increases with the increase of the Ga content in both dry condition and lubricated condition, and it accords with the increase of its microhardness.

As can be seen from the wear tracks in Fig. 3(b), the adhesive wear occurred, which includes scoring, galling, seizing, and scuffing. The wear surface of pure Ti specimen is very rough with severe micro-plowing and torn-off area. Micro-plowing is one of the typical mechanisms of abrasive wear. It 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. Compare with pure Ti, the wear surface morphology of Ti–10Ga alloy specimen is much smoother than that of pure Ti whether in dry condition or in lubricated condition. This is due to the Ti–10Ga alloy that possesses much higher strength and hardness, larger Young’s modulus, as well as lower plasticity. All of these characteristics make it be more resistant to wear than pure Ti. What’s more, the wear surface morphology of both materials presents fewer abrasive particles in lubricated condition than in dry condition, which implies the artificial saliva plays a good lubricating effect to reduce the wear degree. At the same time, artificial saliva acts as a corrosive liquid to corrode the specimen’s surface in the lubrication process. That is to say, when sliding wear occurs in artificial saliva, the lubrication and corrosion take place at the same time. In the present study, the addition of Ga improves the corrosion resistance of pure Ti in artificial saliva (see Section 4.3), therefore Ti–Ga alloys still possess better wear resistance than pure Ti in lubricated condition with artificial saliva.

Besides, the test was carried out in atmospheric condition, and the oxidative wear is inevitable. Hence, the results demonstrate that the wear mechanism of as-cast pure Ti and Ti–Ga alloys should be a mixture of adhesive wear, abrasive wear and oxidative wear. In the lubricated condition, abrasive wear is considered to have been alleviated due to the lubrication of artificial saliva. The result is consistent with our previous studies [25].

4.2. Castability

As seen in Fig. 4, it demonstrates that Ti–2Ga alloy possesses the highest castability value, which improved the casting performance of pure Ti significantly (p < 0.05). However, with further increase the content of Ga in pure Ti, the castability values of Ti–5Ga and Ti–10Ga...
alloys reduced, and even lower than that of pure Ti. The castability of an alloy is often associated with its ability to fill the mold, and mold filling is dependent on numerous factors, such as mold design, mold temperature, cooling rate, molten metal temperature, mold reaction, type of machine, applied pressure, surface tension (surface free energy) and oxide film of alloy [27]. In order to compare the castability of pure Ti with Ti–Ga alloys, the casting process parameters are fixed in this study, therefore, the factors affecting castability most likely are mold reaction, surface tension and oxide film of alloy. That is to say, the metal or alloy with slighter mold reaction, lower surface energy and more complete oxide film would have the better castability.

According to the casting theory, at the same degree of superheat, the liquidity of pure metal would be reduced by adding alloying elements, that is to say, the castability is also reduced. This is due to the solidification that no longer occurred in the solidification interface and the generation of the dendritic structure in the preliminary stage of the solidification process would make the molten metal flow more difficult [46]. This factor might satisfactorily explain why the castability value decreased in the studied Ti–Ga alloys except for Ti–2Ga alloy. Another possible factor is that adding alloying element changes the alloy's surface oxidation film characteristics, and further affects its castability. The oxidation film of the molten metal makes it present high surface tension. In the previous study [47], Papworth et al. found that adding 1 wt.% Mg in Al alloy changed its surface oxidation film from Al2O3 to MgAl2O4. MgAl2O4 is a kind of weak or thin oxidation film, which reduced the surface tension and increased the castability. In another paper [48], they studied the effect of Bi on the castability of Al alloy. It is found that the addition of Bi changes the morphology and disrupts the integrity of the initial alumina film. Bi improves the castability of the Al alloy by being incorporated into the oxide, which weakens the strength of the film and reduces the surface tension of the Al alloy. In this study, it is likely that Ga plays the same role of Bi, and adding 2 wt.% Ga into pure Ti changes the characteristic and integrity of the titanium dioxide film, which further improves its castability. When the content of Ga is increased to 5 wt.% or more, Ga plays a detrimental role on the castability of Ti–Ga alloys, based on casting theory. That is probably the reason why the castability of Ti–Ga alloys first increases and then decreases with the increase of Ga content.

4.3. In vitro corrosion resistance

In the oral environment, dental materials have to be provided with good corrosion resistance and excellent biocompatibility. The corrosion of dental materials can weaken their service life and the elements released from them may have detrimental effects on local tissues or accumulate elsewhere in the body. Therefore, it is very important to investigate the corrosion behavior and cytotoxicity of newly developed materials.

![Fig. 6. Representative EIS spectrum plots of as-cast pure Ti and Ti–Ga alloys. (a) Nyquist plots and (b) Bode plots in artificial saliva; (c) Nyquist plots and (d) Bode plots in artificial saliva with 0.15% NaF.](image)
Fig. 7. Cytotoxicity of (a) L929 and (b) MG63 cells cultured in as-cast pure Ti and Ti–Ga alloys extraction media for 1, 2 and 4 days.

Fig. 8. The morphology of L929 and MG63 cells cultured on as-cast pure Ti and Ti–Ga alloy specimens for 1, 2 and 4 days.
The OCP is the potential that the metal reaches equilibrium with the liquid environment, which varies as a function of the immersion time and finally stabilizes at a stationary value after a certain period of immersion [18]. The OCP results indicate that the addition of Ga makes the spontaneous passive film on the metallic surface more stable thermodynamically. Therefore, no matter in the artificial saliva contains 0.15% NaF or not, and the Ti–Ga alloys process the better corrosion resistance than pure Ti. Consistent with the OCP results, it can be found that all Ti–Ga alloys exhibit lower corrosion current densities ($i_{corr}$) and passive current densities ($i_{pass}$) than pure Ti in both artificial saliva solutions from Fig. 5(b) and (d).

Electrochemical impedance spectroscopy (EIS) is a tool used to analyze complex electrochemical systems through evaluation with equivalent circuit modeling. In the present study, the $R_e(Q,R_p)$ equivalent circuit model with only one time constant was proposed to fit the EIS data, which fitted in the case of a single passive film present on the metal surface [18]. The $R_e(Q,R_p)$ equivalent circuit is shown in Fig. 6(a). The parameter $R_e$ is the electrolyte resistance, $Q_p$ is the constant phase element (which represents a true capacitance, rather than an “ideal” capacitance C) and $R_p$ is the resistance of passive film. The parameters ($R_e$, $Q_p$, $n$, and $R_p$) obtained by the fitting procedure are listed in Table 1. It can be found that the $R_p$ of all Ti–Ga alloys is significantly higher than that of pure Ti, especially in the fluoride-containing artificial saliva. It suggested that the addition of Ga was beneficial for increasing the resistance of the passive film of Ti.

The above electrochemical test results indicated that the addition of Ga to pure Ti increases its corrosion resistance in both artificial saliva solutions. As we known, Ti and its alloys have a high corrosion resistance because they form a passive film on their surfaces. However, this corrosion resistance is significantly reduced in the presence of fluoride, which is also often clinically used in the prevention of dental caries. It was reported that Ti, Ti–6Al–4V and Ti–6Al–7Nb alloys, which were commercially available as dental materials, were prone to corrosion in the presence of even a small amount of fluoride (0.05% NaF) with a low oxygen level of 0.1 ppm [49]. In the present study, it is found that Ti–2Ga alloy and Ti–5Ga alloy show the best corrosion resistance in artificial saliva with and without 0.15% NaF, respectively. Ga has a high standard electrode potential than Ti [50]. In the previous studies, the Ti alloys containing noble metal elements (such as Ag, Pd and Ru) [21,51,52] usually showed an improved corrosion resistance than pure Ti. It was suggested that Ti is slightly dissolved during an initial stage of immersion and consequently the noble metal elements of the specimen surface may accumulate because of Ti loss. As a result, the potential of the alloy became further nobler than the critical potential for passivation of Ti, which made the alloys show improved corrosion resistance. In this study, the influence of Ga on corrosion resistance of Ti may be analogous to those noble metals. However, the real reason that Ga addition improves the corrosion resistance of its Ti alloys remains not very clear. Therefore, an overall investigation shall be conducted on the corrosion mechanism of Ti–Ga alloys in the further study.

### 4.4. Cytotoxicity

Cytotoxicity test is widely used to evaluate the in vitro biocompatibility of biomaterials. In vitro cytotoxicity tests are often conducted using L929 fibroblast cells and MG63 osteosarcoma cells. Ti is recognized as a non-toxic metal element and its surface can form easily a layer of stable passive film (TiO2), which makes Ti as superior biocompatibility. Even if the passive film is damaged, the film can be immediately rebuilt [2]. In addition, it was reported that Ga ion was not significantly toxic by cytotoxicity test [31]. The indirect test was used to evaluate the cytotoxicity of metal ions. In this study, the MTT results demonstrate that the cell viabilities of Ti–Ga alloys are just slightly lower than the negative control for both L929 and MG63 cells, which indicates that Ti and Ga ions exhibit low cytotoxicity. It can also be found from the cell morphology images that the cells adhere and spread out very well on the surface of studied material specimens. According to ISO 10993-5:2009 [40], the cytotoxicity grade of Ti–Ga alloys for L929 fibroblast cells and MG63 osteosarcoma cells is 0 or 1, similar as pure Ti. Thus, the studied Ti–Ga alloys were judged to be in vitro biocompatible.

### 5. Conclusion

In this study, the as-cast Ti–Ga alloys with Ga contents of 2, 5 and 10 wt.% were investigated for potential dental applications. Ga doesn't change the phase constitution of Ti. The strength, microhardness and wear resistance of Ti–Ga alloys increase monotonically with the increase of Ga content due to the solid solution strengthening. Adding a low content of Ga (2 wt.%), the castability of its Ti alloy is improved significantly. The addition of Ga into pure Ti improves the alloy corrosion resistance in both artificial saliva and fluoride-containing artificial saliva. Among them Ti–2Ga alloy and Ti–5Ga alloy exhibit the best corrosion resistance in artificial saliva with and without 0.15% NaF, respectively. The Ti–Ga alloys have no significant cytotoxicity for L929 fibroblast cells and MG63 osteosarcoma cells. Both cell lines process excellent adhesive ability on the surface of Ti–Ga alloys. Therefore, the above experimental results demonstrate that as-cast Ti–2Ga alloy has the best comprehensive properties in the present work, suggesting its potential application for dental material.

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