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Improvement on mechanical properties and corrosion resistance of titanium-tantalum alloys *in-situ* fabricated via selective laser melting

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Abstract

In this study, the role of tantalum (Ta) on the phase transformation, microstructure evolution, mechanical properties and corrosion resistance of titanium-tantalum (Ti-Ta) alloys *in-situ* fabricated via selective laser melting (SLM) was investigated. Ti-Ta mixed powders with different Ta ratios ranging from 0 to 25 wt. % were prepared by ball milling for the SLM process. With the increase of Ta content, the SLM-processed Ti-Ta alloys exhibits the microstructure evolution from the lath α grain to acicular α' + primary cellular β grains, accompanying with the gradual suppression of martensite transformation. The β -stabilized effect of Ta promotes the formation of β (Ti, Ta) solid solution phase in the alloys. The rise of Ta addition in SLM-processed Ti-Ta alloys contributes to the improvement on the tensile strength from 641 to 1186 MPa and the microhardness from 257 to 353 HV, which results from a combined effect of grain refinement strengthening and the solid solution strengthening. The Young's modulus decreases from 115-89 GPa due to the increasing amount of β phase. Additionally, the corrosion resistance of the Ti-Ta alloys is enhanced with few pits on the surfaces due to the increasing amount of Ta₂O₅ identified through X-ray photoelectron spectroscopy. These findings provide the knowledge and boost the further understanding on the SLM-processed Ti-Ta alloys as promising candidates for biomedical application.

Keywords: Titanium-tantalum alloys; selective laser melting; additive manufacturing; mechanical properties; corrosion resistance.

1. Introduction

The development in the sector of biomedical has facilitated the exploration for non-toxic and non-allergenic biomaterials [1, 2]. Titanium-tantalum (Ti-Ta) alloys have attracted increasing attention in bone implant applications due to their excellent biocompatibility, superb mechanical properties, high corrosion resistance and low cost [3-6]. Besides, the inclusion of Ta is beneficial to improving the biosafety and osteogenesis of Ti matrix. First, it improved the biosafety *in vivo* and eliminated the safety concerns from cytotoxic elements (such as Al and V) in other titanium alloys that would cause Alzheimer's disease after long-term applications [7-9]. Second, Ta was able to biologically bond to bones by forming a bone-like apatite coating accelerating the in-growth of bone [10], enhancing the biocompatibility and osteogenesis of Ti matrix. Moreover, the attachment, proliferation and differentiation of human osteoblasts on Ta discs were superior to those on bioinert pure Ti discs [11-13], and inflammatory response covered with thin fibrous connective tissues was not induced on Ta implants [14]. Finally, Ti-Ta alloys exhibited superior corrosion resistance by a protective passive film Ta_2O_5 without releasing any ions into adjacent tissues for long-term usage [15, 16], which is advantageous to the application in human body environment that is an extremely complicated electrolyte.

Researchers have made tremendous efforts for the preparation of Ti-Ta alloys by arc melting in a high-frequency induction furnace [6, 17, 18]. Owing to the great differences of melting point and density between Ti and Ta, Ti-Ta alloys were often melted for ten times to achieve a homogeneity of elemental distribution, which brought about a long processing period. It is noteworthy that the variation of Ta content plays a crucial role in the microstructure and mechanical properties of the prepared Ti-Ta alloys. Zhou et al. investigated the effect of Ta content (10-80 wt. %) on the elastic modulus and tensile strength of arc-melted Ti-Ta alloys [17]. It showed that Ti-30%Ta and Ti-70%Ta possessed the higher strength and lower modulus. Another study from Zhou et al. indicated that the addition of Ta with 10, 30 and 70 wt. % contents into Ti matrix simultaneously enhanced the strength, biocompatibility and corrosion resistance [19].

Besides, they found that the Ti-25% Ta sample exhibited the lowest elastic modulus and the highest ratio of strength to modulus (480 MPa / 64 GPa) among all the prepared Ti-Ta alloys, which resulted from the nanostructure with small grains [3]. Liu et al. developed Ti-Ta alloys with Ta addition from 20 to 30 wt. % by powder metallurgy. The Ti-Ta alloys achieved a good combination of low elastic modulus (74-84 GPa) and high tensile strength (1056-1251 MPa) and high biocompatibility [20]. Daniel et al. conducted a comparative corrosion study between Ti-Ta alloys with different Ta contents of 30, 40, 50 and 60 wt. % and Ti6Al7Nb alloys manufactured by levitation melting [15]. The results indicated the better corrosion properties of Ti-Ta alloys in fluoridated acidified saliva due to the spontaneously formation of Ta₂O₅.

Although conventional processes are capable to fabricate Ti-Ta alloy ingots with good performances, it is difficult to produce Ti-Ta alloy products with customized complex geometries particularly for bone implants [3]. Selective laser melting (SLM), a powder-bed-fusion additive manufacturing (AM) process, can manufacture complex metallic parts directly from CAD models in a layer-by-layer method using a high-energy laser beam [21]. SLM has been developed and validated for the manufacture of biomedical metals with refined cellular structures [22-24]. Dissimilar to the element segregation occurred in cast [25], SLM-processed alloys can achieve a homogeneous element distribution [1]. Sing et al. initiated a study on the Ti-Ta alloy using SLM [5]. Specifically, the Ta content of 50 wt. % was used to investigate the phase, microstructure and mechanical properties of the alloy. The Ti-50Ta alloy consisted of β phase and exhibited a high tensile strength of 924 MPa and lower Young's modulus compared to Ti and Ti6Al4V counterparts. The investigation on the effect of Ta content on the microstructure and properties of SLM-processed Ti-Ta alloys is still limited.

In this work, the effect of Ta ratio on phase components, microstructure, mechanical properties and corrosion resistance of Ti-Ta alloys manufactured by SLM was studied. Ti-Ta alloys with different Ta contents from 0 to 25 wt. % were *in-situ* fabricated via SLM. The influence of Ta content on the phase and microstructure evolutions of SLM-processed Ti-Ta alloys was discussed. The mechanical properties and corrosion resistance of the produced alloys were evaluated.

2.1. Material preparation

Gas-atomized commercial pure Ti (ASTM Grade 1, supplied by AP&C, Canada) and mechanically crushed Ta powders with the averaged particle size of 30.3 μm and 3.66 μm were used, respectively. The Ta powder with different ratios of 0, 6, 12, 18 and 25 wt. % was added into the Ti powder to prepare the mixed powders using ball milling (corresponding to Ti, Ti-6Ta, Ti-12Ta, Ti-18Ta and Ti-25Ta, respectively). The parameters of ball milling were set as ball-to-powder weight ratio of 4:1, rotation speed of 180 rpm and mixing time of 3 h in a ball grinder (QM-3SP, China). The morphologies and particle size distributions of mixed powders were shown in Fig. 1. It can be observed that irregular Ta powder particles distributed around the spherical Ti powder particles. Particle size distributions of the mixed powders were obtained using a laser diffraction particle size analyzer (Mastersizer 3000, UK). The average particle sizes of Ti-6Ta, Ti-12Ta, Ti-18Ta and Ti-25Ta powders are 29.4 μm , 31.6 μm , 30.5 μm and 29.0 μm , respectively.

Fig. 1. SEM morphologies of Ti-Ta powders with different Ta contents: (a) Ti, (b) Ti-6Ta, (c) Ti-12Ta, (d) Ti-18Ta, (e) Ti-25Ta, and (f) particle size distributions.

2.2. *In-situ* fabrication of Ti-Ta alloys by SLM

The SLM-125 machine (SLM Solutions, Lübeck, Germany) was utilized for the *In-situ* fabrication of Ti-Ta alloys from the prepared mixed powders. A fiber laser of

400W-Gaussian beam with a wavelength of 1064 nm was utilized. The spot size diameter of laser beam is approximately 80 μm . The schematic of SLM is illustrated in Fig. 2. The SLM processing was carried out in the chamber filled in argon with less than 500 ppm oxygen concentration to prevent the oxidation. Different laser power (220-380W) and scanning speed (600-1400 mm/s) were selected for the process optimization of the Ti-25Ta alloy. With the laser power of 340 W and the scanning speed of 1200 mm/s, the Ti-25Ta alloy achieved the highest relative density of 95%. Then the optimized parameters were utilized to fabricate Ti-Ta alloys with other Ta ratios. The scanning spacing was 0.07 mm and the layer thickness was 0.05 mm. The scanning vector of laser rotated 67° between two consecutive layers. Cubes with a dimension of 10 mm $\times$ 10 mm $\times$ 6 mm and tensile coupons with the length of 32 mm, width of 7 mm, height of 1.5 mm and the gauge length of 10 mm were fabricated, respectively [26]. After the fabrication, all the tensile specimens were removed from the substrate and were cut into the designed geometry using electrical discharge machining (EDM). The specimens were then cleaned using the distilled water, alcohol and acetone, followed by the surface grinding using sandpapers from 240 to 2000 meshes to remove the deformed layer caused by EDM.

Fig. 2. (a) Schematic of the SLM process and (b) tensile coupons of Ti-Ta alloys with different Ta contents in-situ fabricated by SLM.

2.3. Characterization

The phase identification was conducted by X-ray diffraction (XRD, XRD-7000S,

Shimadzu, Japan) Cu K α radiation at 40 kV and 30 mA. The diffraction angle of 2θ varied from 30° to 100° with a scan rate of 15° per minute. Specimens with different Ta contents were etched with Kroll's reagent (3 vol. % HF, 6 vol. % HNO₃ and 91 vol. % H₂O) at environmental temperature for 20 s after grinding and polishing. The microstructures of SLM-processed Ti-Ta alloys all features were observed by scanning electron microscopy (SEM, JSM-7600F, JOEL, Japan) equipped with an energy dispersive spectroscopy (EDS, X-Max 50, OIMS, UK) microprobe system. Chemical distributions on surfaces of Ti-Ta alloys were identified using EDS. The relative densities of the specimens were measured by the Archimedes method. Three samples were measured to obtain an average value for each Ta content.

2.4. Mechanical testing

The Vickers microhardness of Ti-Ta alloys with different Ta contents was characterized by a hardness test machine (430-SVD, Wilson Hardness, USA) with a load of 1.0 N and dwell time of 12 s. The tensile testing was conducted by a mechanical testing machine (Zwick/Roell Z020, Zwick, Germany) using a cross speed of 0.5 mm/min. Three samples were tested for each Ta ratio to obtain the yield strength and ultimate strength. The tensile fractures were then observed by SEM.

2.5. Electrochemical testing

Corrosion behaviors of SLM-processed Ti-Ta alloys with different Ta contents were investigated. The chemical composition of Ringer's solution consisted of 9 g/L NaCl, 0.42 g/L KCl, 0.2 g/L NaHCO₃ and 0.25 g/L CaCl₂, which was similar to the components of the body fluids [27]. The exposed surface area of the cubic specimens to the solution was approximately 1 cm². The electrochemical testing was performed on a CS310H electrochemical working station. A conventional three-electrode cell was composed of a working electrode (Ti-Ta alloys), a counter electrode (Pt plate) and a reference electrode (saturated calomel electrode, SCE). The pH value of the solution was kept 7.2 by adjusting the content of HCl or NaOH. The potentiodynamic polarization testing was performed using a scanning rate of 1 mV/s from -0.8 to $+1.5$

V after 1 h immersion in the solution.

The composition of formed passive film after polarization was estimated by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W). The surfaces of specimens were sputtered by Ar⁺ ions for 30 s to remove contaminants. The binding energies of electrons were adjusted by the peak of C 1s line (BE = 285 eV). XPS spectra were analyzed by a least-squares fit with XPSPEAK analytical software. The corrosive surface morphologies of Ti-Ta alloys were observed through SEM.

3. Results and discussion

3.1. Relative density

Fig. 3a shows that the relative densities of SLM-processed Ti-Ta alloys with different Ta contents are larger than 95%. The SEM morphology of the Ti-25Ta alloy indicates the existence of unmelted Ta particles and voids (Fig. 3b). The Ta particles are brighter than the adjacent Ti matrix due to the larger atomic number of Ta in comparison with Ti [28]. As schematized in Fig. 4, the energy density of the laser is sufficient to melt the Ti powder fully, but it may partially melt some larger Ta powder particles due to the much higher melting point of Ta (2996°C). The applied laser beam with Gaussian energy distribution outputs the inhomogeneous energy with the highest temperature located at the center and the lowest temperature at the edge [29]. When the laser with lower energy regions scans and melts the Ta powder, the partial melting of Ta occurs and unmelted Ta particles are retained in the solidified melt pool. It also indicates the insufficient time for Ta to diffuse into Ti matrix.

The consistency of the microstructure elucidates that the metallurgical bonding between unmelted Ta and Ti matrix is formed. No macro cracks can be observed around the unmelted Ta that is derived from the Ti-Ta mixed powder, but the unmelted Ta may serve as an origin of failure (i.e., fatigue). The pre-alloyed powders that are often used in SLM and electron beam melting, can exclude the microstructure inhomogeneity and releases parts with improved fatigue properties. However, the feedstock to produce a Ti-Ta pre-alloyed powder requires homogeneous Ti-Ta ingots, which experience ten or more times melting due to the great differences of melting point and density between

Ti and Ta. The high cost and long processing period pose a challenge to produce a Ti-Ta pre-alloyed powder through atomization.

Fig. 3. (a) Relative densities of SLM-processed Ti-Ta alloys with various Ta contents and (b) SEM morphology of SLM-processed Ti-25Ta alloy.

Fig. 4. Schematic diagram of the melting phenomenon of Ti-Ta alloys in SLM.

3.2. Phase identification

Fig. 5 shows the phase component of SLM-processed Ti-Ta alloys with different Ta concentrations identified by XRD. The results indicate that phase components of Ti-Ta alloys are dependent on the addition of Ta content. Strong diffraction peaks corresponding to α phase (hexagonal close packed, hcp) can be detected in Ti, while α' phase is identified in Ti-6Ta. When the Ta content increases to 12 wt. %, a small amount of β phase (body centered cubic, bcc) can be detected. Since Ta and β -Ti show a similar atomic radius (~ 0.2 nm) and bcc structure, their peaks share the same location [30]. The peak intensity of β phase increases with the increasing of Ta content from 12 to 25

wt. %.

Characterized by the rapid cooling rate (10^3 - 10^8 K/s), SLM promotes the development of non-equilibrium phases [5], resulting in the formation of metastable α' phase in Ti-Ta alloys. Ti-Ta alloys fabricated by arc-melting exhibited lamellar martensite (α') structure at a Ta content below 20% [17]. During the SLM process, the melting temperature reaches the phase transformation temperature from α to β . The obtained β -Ti is difficult to transforming into α phase due to the high cooling rate in SLM [31]. Meanwhile, the β (Ti, Ta) solid solution can be retained in a metastable state at ambient temperature due to the β stabilization effect of Ta. It is most probable to form a substitution solid solution for alloys with an atomic radius difference of constituent elements below 15 % [32]. Therefore, the β -Ti tends to form a continuous solid solution with Ta due to their same crystal structure (bcc) and small atomic-size difference [30]. Therefore, the amount of β phase rises with the increase of Ta content, accompanying with the decrease of α' phase. It indicates that the Ta content crucially influences phase components of Ti-Ta alloys fabricated by SLM by the formation of solid solution and the restraint of phase transformation.

Fig. 5. XRD patterns of SLM-processed Ti-Ta alloys with different Ta contents.

3.3. Microstructure evolution

The influence of Ta ratio on the microstructure of SLM-produced Ti-Ta alloys is elucidated in Fig. 6. From Fig. 6a to 6c, a typical lath α grain with the length size of $\sim 60\text{ }\mu\text{m}$ can be observed in Ti, while the martensite α' with lath structure can be found in both Ti-6Ta and Ti-12Ta alloys. Particularly, colonies that consist of parallel and finer lath structures form in the Ti-12Ta alloy. The similar characteristics were also obtained in a previous study on casted Ti-Ta alloys, showing a coarse lath structure [17]. The β phase cannot be found in the Ti-6Ta alloy due to its small amount, but the cellular β phase appears in the Ti-12Ta alloy, which is consistent with the XRD results. The microstructure of fabricated Ti-18Ta and Ti-25Ta alloys are different. The acicular martensitic α' and cellular β grains appear with a width of $\sim 1\text{ }\mu\text{m}$ in the Ti-18Ta alloy (Fig. 6d), whereas, the Ti-25Ta alloy exhibits more cellular β grains and less α' grains (Fig. 6e and 6f).

During the solidification in SLM-processed Ti-Ta alloys, the constitutional undercooling leads to the destabilization of the planar solidification front due to the solute redistribution, which facilitates the transformation from a planar to cellular solidification mode [28]. The low diffusion coefficient of Ta in Ti matrix causes the instability of the planar structure and induces the cellular structure. The crystal nucleation rate is greatly increased and the grain size is suppressed simultaneously, resulting in the insufficient growth of secondary dendrite arms [33]. Therefore, microcellular crystals and columnar crystals with a diameter of $1\text{-}10\text{ }\mu\text{m}$ are the main ingredients of microstructure, and more β phase could be obtained. The transition of solidification mode also induces the reduction of dimensions of α' grains. Introducing the β stabilizer such as Ta drops the martensitic start temperature (M_s) and suppresses the phase transformation from β to α' . The starting temperature for solidification changes with the variation of Ta content, which results in different microstructures in

Ti-Ta alloys [28]. Therefore, the amount of β grains increases with the rise of Ta content. The microstructural evolution of SLM-processed Ti-Ta alloys can be described as follows: lath α grain $\rightarrow$ lath α' grain $\rightarrow$ acicular α' grain $\rightarrow$ acicular $\alpha' +$ cellular β grains.

Fig. 6. Microstructure of SLM-processed Ti-Ta alloys with different Ta contents. (a) Ti, (b) Ti-6Ta, (c) Ti-12Ta, (d) Ti-18Ta, (e) and (f) Ti-25Ta.

Fig. 7 shows the element distributions of Ti and Ta on the cross-sectional surface in the Ti-25Ta alloy. The homogeneous distributions of Ti and Ta can be achieved in SLM-processed Ti-Ta alloys, indicating a strong metallurgical bonding [5]. The

sufficient laser energy of SLM improves the diffusion of Ta and Ti [34]. During the SLM process, the laser beam melts the powder to produce a liquid melt pool. A temperature gradient induced by the rapid solidification exists in the melt pool and causes a surface tension gradient that is referred to as Marangoni flow. The convection of molten accelerates the diffusion of Ta and Ti. It indicates that no micro-segregation of element occurs in Ti-Ta alloys fabricated by SLM [35], which is beneficial to improving mechanical properties of the alloys.

Fig. 7. The elemental distribution of SLM-processed Ti-25Ta alloy.

3.4. Mechanical properties

The Ta content plays an important role in mechanical properties of Ti-Ta alloys manufactured by SLM. Representative tensile stress-strain curves of Ti-Ta alloys are shown in 错误!未找到引用源。 . The ultimate tensile strength, yield strength, Young's modulus and microhardness of SLM-processed Ti-Ta alloys with different Ta contents are summarized in Table 1. As Ta addition ranges from 0 to 25 wt. %, the improvement of the yield strength from 560 to 1029 MPa and tensile strength from 641 to 1186 MPa can be observed, respectively. The improvement of 85% in ultimate tensile strength and 83% in yield strength is attributed to o the grain refinement strengthening and solid solution strengthening. As discussed in Section 3.3, the grains of Ti-Ta alloys evolve

from coarsened lath α (60 μm in length) to cellular β (1 μm in width) with the increase of Ta content. According to Hall-Petch theory, the strength of polycrystalline materials increases with a decrease of grain size [36]. The incorporation of Ta in Ti matrix also increases the strength by the formation of the β (Ti, Ta) solid solution [20]. On the other hand, the Young's modulus of Ti-Ta alloys decreases from 115 to 89 GPa with the increase of Ta content, which is much higher than that of trabeculae bones (0.05-3 GPa) and cortical bones (10-25 GPa) [37-39]. The addition of Ta increases the amount of β phase that shows the lowest Young's modulus in titanium alloys [40]. Therefore, the more β phase results in the lowest Young's modulus in the Ti-25Ta alloy. Further investigations can be conducted on the design and manufacture of Ti-Ta porous structures to avoid the stress shielding that caused by the mismatch of the modulus. The microhardness of Ti-Ta alloys decreases from 0 to 6 wt. % and then increase from from 6 to 25 wt. %. The decline is ascribed to the lower relative density in the Ti-6Ta alloy, and the rising results from the solid solution strengthening and the grain refinement strengthening.

Fig. 8 Stress-strain curves of SLM-processed CP-Ti and Ti-Ta alloys.

Compared to the SLM-processed Ti-50Ta alloy studied by Sing et al. [5], the SLM-processed Ti-25Ta alloy in this work shows the superior yield strength, ultimate tensile strength and microhardness. It assumes that more Ta addition is not always better for the improvement on mechanical properties of Ti-Ta alloys. The microstructure of fine α phase precipitates within the β matrix at a low Ta content could contribute to the mechanical strength. Other studies also illustrated that the strength of Ti-Ta alloys sharply decreased with a high content of Ta (> 30 wt. %) [20]. On the other hand, the Ti-Ta alloys fabricated by SLM achieve superior mechanical properties than those prepared by arc melting. The SLM-processed Ti-25Ta alloy shows the 32.36 % higher yield strength than the casted Ti-25Ta alloy, as shown in Table 1. It is attributed to the ultrafast cooling rate in SLM, which leads to the microstructure refinement and homogeneous element distribution.

Table 1 Mechanical properties of Ti-Ta alloys with different Ta contents manufactured by SLM.

Alloy	Ultimate tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Microhardness (HV)	Ref.
Ti	641 ± 10	560 ± 13	115 ± 5	257 ± 7	This work
Ti-6Ta	697 ± 2	595 ± 5	108 ± 4	241 ± 3	This work
Ti-12Ta	783 ± 18	650 ± 7	99 ± 6	267 ± 10	This work
Ti-18Ta	808 ± 17	668 ± 20	96 ± 3	296 ± 10	This work
Ti-25Ta	1186 ± 14	1029 ± 8	89 ± 4	353 ± 11	This work
Ti-50Ta	924 ± 9	882 ± 19	75 ± 4	284 ± 11	SLM [5]
Ti-20Ta	550	470	470	-	Arc melting [17]

The tensile fracture morphologies of Ti-Ta alloys with 0, 12 and 25 wt. % Ta contents are presented in Fig. 9. The fractographs of Ti display shallow ductile dimples and cleavage facets (Fig. 8a and 8b). The Ti-12Ta alloy shows a mixture of ductile and brittle fracture (Fig. 8c and 8d). However, the Ti-25Ta alloy exhibits a higher amount of deep dimples and cleavage facets in a ductile manner (Fig. 8e and 8f). The fine dimple size of 1-3 μm is similar the β subgrain size, which is determined by the initiation site that nucleated at the grain boundaries [41].

Fig. 9. Fracture morphologies of Ti-Ta alloys with different Ta contents. (a) and (b) Ti, (c) and (d) Ti-12Ta, (e) and (f) Ti-25Ta.

3.5 Corrosion properties

The Ta ratio has a critical effect on corrosion properties of SLM-processed Ti-Ta alloys. Fig. 10 describes the typical potentiodynamic curves of Ti-Ta alloys with different Ta contents in the Ringer's solution. All the specimens reach their stable passive current densities with the increase of potential. In the first stage upon anodic

polarization, the current density increases as the potential increases. The corrosion parameters obtained from the curves are listed in Table 2. It reveals that E_{corr} and I_{corr} of Ti-Ta alloys range from -14.84 to 17.8 mV and from 9.22×10^{-2} to $4.34 \times 10^{-2} \mu\text{A}/\text{cm}^2$ with different Ta contents, respectively. In the second stage, Ti-Ta alloys show stable passive behaviors that indicate the formation of protective passive films. In the third stage, oscillations of current density appear due to the nucleation and repassivation of pitting in the films. The lowest passive current density and highest corrosion potential in the Ti-25Ta alloy indicate its best corrosion resistance compared to the alloys with other Ta ratios.

Fig. 10. Potentiodynamic polarization curves of SLM-processed Ti-Ta alloys with different Ta contents in Ringer's solution.

Table 2 Corrosion parameters of SLM-processed Ti-Ta alloys in the Ringer's solution. E_{corr} and I_{corr} represent corrosion potential and corrosion current density, respectively.

Alloy	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (10^{-4} mm/year)
Ti	-14.84	9.22×10^{-2}	3.69
Ti-6Ta	-11.67	7.34×10^{-2}	2.92
Ti-12Ta	-6.54	6.58×10^{-2}	2.62

Ti-18Ta	-2.3	5.23×10^{-2}	2.08
Ti-25Ta	17.8	4.34×10^{-2}	1.72

The corrosion properties of Ti-Ta alloys are determined by phase structures produced in SLM. The *in-situ* alloying of Ti and Ta promotes the formation of β phase in the Ti matrix. It was proved that the oxide film of Ti alloy on the β phase was more stable than that on the α phase [42]. Furthermore, the element distributions of Ti and Ta can affect the corrosion resistance of Ti-Ta alloys. The homogeneous distribution avoids galvanic interaction and forms stable oxide layer to resist the corrosion. Therefore, Ti-Ta alloys exhibit the lower corrosion current densities and rate as well as higher corrosion potentials than Ti counterparts, which is ascribed to the more β phase and homogeneous element distribution to facilitate the formation of oxide films.

Fig. 11 presents the surface morphologies of Ti-Ta alloys with different Ta contents after potentiodynamic polarisation experiments. The wide and deep pits appear on the Ti surface and few pits can be found on the surfaces of Ti-12Ta and Ti-25Ta alloys. Pitting corrosion often attacked the surface of Ti-based alloy in chloride solutions [43]. The Cl^- can intensify the anodic dissolution of TiO_2 passivating film. An increase of metal chloride at the metal substrate/oxide film interface induced oxide film rupture [43]. Ta addition was reported to be immune to the attack of Cl^- in Hank's solution whose components and content were similar to body blood plasma [44]. It demonstrates the superior corrosion resistance of Ti-Ta alloys than Ti.

Fig. 11. Surface morphologies of Ti-Ta alloys after polarization testing. (a) Ti, (b) Ti-12Ta, and (c) Ti-25Ta.

The composition of formed passive films on SLM-processed Ti-Ta alloys with different Ta contents was further investigated through XPS, as presented in Fig. 12. The wide scanning spectrum identifies the existence of Ti, Ta, and O elements. The C 1s peak derives from the contaminant carbon, and the O 1s spectrum consisted of peaks results from oxide and OH^- . The narrow scanning spectrums of Ti 2p and O 1s of Ti-Ta alloys show a different shape to that of Ti, indicating that the Ta crucially influences the valence state of Ti and O elements.

Fig. 12. XPS spectra on the surfaces of SLM-processed Ti-Ta alloys with different Ta ratios after polarization testing.

The deconvolution of a narrow scanning spectrum of Ti 2p, Ta 4f and O 1s of the Ti-25Ta alloy is displayed in Fig. 13. The Ti 2p spectrum can be assigned into three peaks corresponding to TiO_2 (Ti^{4+}), Ti_2O_3 (Ti^{3+}) and TiO (Ti^{2+}), respectively. Previous work illustrated that TiO_2 films could provide good protection for Ti against corrosion in the sodium chloride solution [45]. Similar productions of sub-oxides TiO and Ti_2O_3 were also found in the study of Okazaki et al. [46]. The two peaks of Ta locate at about 26.4 and 28.4 eV and can be decomposed to Ta 4f_{7/2} and Ta 4f_{5/2}, respectively, which validates the formation of Ta_2O_5 in the passive film. On the other hand, the peak of O element can be assigned into the primary peak of 530.4 eV corresponding to O^{2-} ions

and the minor peak of 530.9 eV corresponding to hydroxyl groups (OH^-). The hydroxyl groups are effective to form the hydroxylated metallic ion that can repair oxide film integrity to improve its resistance to chloride ions. In addition, the OH^- in Ti-Ta alloys indicates a superior protective quality of hydrated metal hydroxylated oxide in the passive film [47]. Therefore, the Ti-25Ta alloy with reduced pitting initiations exhibits superior corrosion resistance than other tested Ti-Ta alloys, due to the more Ta_2O_5 , the prevention of Cl^- ions intrude into the passive film, and the improvement on the structural integrity of the passive film.

Fig. 13. XPS deconvoluted spectra of SLM-processed Ti-25Ta alloy for Ti 2p, Ta 4f and O 1s.

In this study, the enhanced corrosion resistance of Ti-Ta alloys in the aggressive body fluids is ascribed to the formation of stable and inert Ta₂O₅/TiO₂ passive films [48]. The incorporation of Ta cations can improve the resistance of alloys in the chloride, which results from the stability of Ta₂O₅ oxide film. Therefore, the increase of Ta content results in the rise in Ta₂O₅ amount. The improvement on the mechanical properties and corrosion resistance endows SLM-processed Ti-Ta alloys the promising candidates for biomedical applications.

4. Conclusions

In this work, Ti-Ta alloys were *in-situ* fabricated by SLM with enhanced mechanical and corrosion properties. The Ta ratio plays a critical role in phase components, microstructure evolution, mechanical and corrosion properties of SLM-processed Ti-Ta alloys. The main results are summarized as follows:

- (1) The phase identification of SLM-processed Ti-Ta alloys reveals the existence of β (Ti, Ta) solid solution phase, except for the alloy with a small amount of 6 wt. % Ta. The increase of Ta content results in the gradual suppression of the martensitic transformation and the formation of β (Ti, Ta) solid solution.
- (2) The Ta element is homogeneously distributed in SLM-processed Ti-Ta alloys. With the increase of Ta content, the microstructure evolution of the Ti-Ta alloys is illustrated as lath α grain $\rightarrow$ lath α' grain $\rightarrow$ acicular α' grain $\rightarrow$ acicular α' + cellular β grains. The grain size also decreases due to the increase of heterogeneous nucleation sites.
- (3) As Ta addition ranges from 0 to 25 wt. %, there is an improvement on the tensile strength from 641 to 1186 MPa, microhardness from 257 to 353 HV, which results from

a combined effect of grain refinement strengthening and solid solution strengthening. Whereas, the Young's modulus decreases from 115 to 89 GPa due to the increasing content of β phase.

(4) The incorporation of Ta enhances the corrosion resistance of SLM-processed Ti-Ta alloys by the formation of stable $\text{Ta}_2\text{O}_5/\text{TiO}_2$ passive films. The Ti-25Ta alloy with reduced pitting initiations exhibits superior resistance to pitting corrosion than alloys with other Ta ratios, due to the more Ta_2O_5 , the prevention of Cl^- ions intrude into the passive film, and the improvement on the structural integrity of the passive film.

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