High hardness in the biocompatible intermetallic compound β-Ti₃Au

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The search for new hard materials is often challenging, but strongly motivated by the vast application potential such materials hold. Ti₃Au exhibits high hardness values (about four times those of pure Ti and most steel alloys), reduced coefficient of friction and wear rates, and biocompatibility, all of which are optimal traits for orthopedic, dental, and prosthetic applications. In addition, the ability of this compound to adhere to ceramic parts can reduce both the weight and the cost of medical components. The fourfold increase in the hardness of Ti₃Au compared to other Ti–Au alloys and compounds can be attributed to the elevated valence electron density, the reduced bond length, and the pseudogap formation. Understanding the origin of hardness in this intermetallic compound provides an avenue toward designing superior biocompatible, hard materials.

INTRODUCTION

In addition to numerous applications in the industrial, automotive, and aerospace fields, Ti has been widely used for implant devices that replace patients’ hard tissues (1, 2). A number of in vivo and in vitro experiments with various grades of Ti concluded that commercially pure Ti is a highly biocompatible material due to the spontaneous buildup of an inert and stable oxide layer (1, 3). Additional properties that make Ti suitable for biomedical applications include its high strength-to-weight ratio (4, 5) and low ion formation levels in aqueous environments (1). Moreover, Ti is one of a few materials capable of osseointegration—the mechanical retention of the implant by the host bone tissue—which stabilizes the implant without any soft tissue layers between the two (6). These properties enable the wide use of Ti for devices, such as artificial knee and hip joints, screws and shunts for fracture fixation, bone plates, pacemakers, and cardiac valve prostheses (7, 8). Not surprisingly, the dental applications of Ti are just as common, including implants and their components, such as inlays, crowns, overdentures, and bridges (1, 9–12).

However, pure Ti is not strong enough for a number of medical devices (13, 14), thus necessitating the development of superior alloys (15–19). Although hardness can be improved by alloying Ti with another element (1), care must be taken to preserve biocompatibility. Previously, a twofold increase in hardness has been achieved by alloying Ti with Cu or Ag (19–22). The use of an alloying element with the same valence as Cu and Ag, but with higher mass density, should result in a higher valence electron density (VED), which would likely lead to higher bond strength and, consequently, enhanced hardness (23, 24). This finding suggests that Au is a suitable alloying candidate to increase the hardness in Ti binary alloys, given its nearly twofold density increase over Cu or Ag (19–22). The current wide use of Au-based implant devices (25–28) is testament to its biocompatibility and corrosion resistance (10).

Biomedical applications of both Ti-rich and Au-rich alloys have been previously explored in detail (19, 25, 29, 30). Although hardness values showed modest increase in both these regimes of the Ti–Au solution [Fig. 1, open circles, reproduced from previous studies (25, 29, 30)], the hardness was comparable to that of Ti–Ag and Ti–Cu alloys (19–22). Here, we present evidence that the hardness varies nonmonotonously in the Ti–Au alloys, and a drastic increase is registered at an intermediate composition, for the cubic compound β-Ti₃Au (Fig. 1, full circles). Further evidence from wear experiments reveal that this enhanced hardness is associated with a low coefficient of friction (COF). Experimental observations and theoretical calculations point to three main factors that contribute to the high hardness in β-Ti₃Au: the cubic structure with short Ti–Au bonds, the high VED, and a pseudogap evident in the electronic density of states (DOS).

RESULTS AND DISCUSSION

Hardness measurements of the Tiₓ–Auₓ alloys reveal a nonmonotonous change with x (Fig. 1, circles), with hardness values in the composition range 0.22 ≤ x ≤ 0.35, which are about three to four times higher than the hardness value of pure Ti. The maximum hardness of ~800 HV (Vickers hardness) is reached for x = 0.25, for which the cubic compound Ti₃Au forms, in two distinct phases, α and β, with the latter stabilized by the presence of small amounts of carbon, nitrogen, or oxygen (31). This maximum hardness value exceeds that of most biocompatible materials [and even the maximum hardness value of some structural materials, such as pearlitic steels (32, 33)] and is similar to that of both drawn pearlite and high-carbon martensitic steels (34). Although other metallic alloys and compounds, such as WC, BN, and high-carbon steels show higher hardness values (35–41), they are often not desirable for medical applications because of their high toxicity (42, 43). However, both Ti and Au are biocompatible and have high resistance to in vivo corrosion, suggesting that the resulting alloys would be suitable for biomedical applications (1, 3, 10). Not surprisingly, biocompatibility and corrosion resistance have been confirmed in the Tiₓ–Auₓ alloys for x ≤ 0.40 (Fig. 1, open circles) (44). Here, relative cell viability was examined, as described in Methods. Remarkably, the relative cell viability values 98.7% (for x = 0.25) and 95.9% (for x = 0.50) were found to be much higher than 33.8% in the case of pure Ti. The exceptional biocompatibility of these Tiₓ–Auₓ alloys makes them particularly well suited for a variety of medical applications. To compare the mechanical properties of the
Ti$_{1-x}$Au alloys with materials typically used for medical applications, we added a hardness-versus-mass density diagram (45) in Fig. 1 (bottom axis). Although Ti$_{0.75}$Au$_{0.25}$ (or Ti$_3$Au) displays high hardness, its mass density is comparable to that of other commonly used implant materials [Fig. 1, squares (37, 46)]. Moreover, among intermetallic compounds (47–54), Ti$_3$Au has significantly enhanced hardness while preserving its biocompatibility. The only other intermetallic compound with a similar hardness value is Ti$_3$Ir, the biocompatible properties of which remain unknown.

Among the Ti–Au binary compounds, Ti$_3$Au is the only cubic one, which is consistent with high mechanical stability and, therefore, high hardness. A three-dimensional bonding network (similar to that in cubic compounds) is deemed one of the most important parameters enhancing hardness (55, 56). This correlation between the crystal structure and hardness is evident from several known Ti-based compounds: Cubic Ti$_3$Au and Ti$_3$Ir (14-fold coordinated Ti) are the hardest, whereas cubic Ti$_3$Sn (12-fold coordinated Ti) and hexagonal Ti$_3$Al exhibit hardness values comparable to that of pure Ti (Fig. 1, circles). Notably, Ti$_3$Au forms in two cubic crystal structures: α-Ti$_3$Au (Pm$ar{3}$m, Cu$_3$Au type; Fig. 2A) and β-Ti$_3$Au (Pm$ar{3}$n, Cr$_3$Si type; Fig. 2B). β-Ti$_3$Au is expected to have higher hardness, considering the Ti coordination (14) and its Ti–Au bond length $d_{\text{Ti–Au}} = 2.84$ Å (57) being shorter than that of the α-Ti$_3$Au phase [$d_{\text{Ti–Au}} = 2.93$ Å (31)].

A full theoretical understanding of hardness remains challenging because of the inherently complex relationship between elasticity and toughness that defines hardness (58). In alloys, in particular, hardness mostly depends on the underlying crystal structure, atomic bonding, and microstructure (23), making the structural analysis of paramount importance (59, 60). Powder x-ray diffraction (XRD) analysis (Fig. 2C) reveals that Ti$_{0.75}$Au$_{0.25}$ consists of a majority phase β-Ti$_3$Au (Pm$ar{3}$n; Fig. 2B) (57) along with minute amounts of α-Ti$_3$Au (Pm$ar{3}$m; Fig. 2A) (less than 0.6%) (57) and α-Ti (less than 4%). The majority phase β-Ti$_3$Au has a lattice constant $a = 5.8$ Å, whereas the minority phase α-Ti$_3$Au has a smaller lattice constant $a = 4.1$ Å (31). Because the formation energy of a Burgers vector (a vector denoting the magnitude and direction of the lattice distortion resulting from a dislocation) is proportional to the unit cell parameter, the compound with the larger unit cell parameter β-Ti$_3$Au is expected to have a higher hardness. Furthermore, the two phases differ profoundly in the atomic environment types (AETs) of Au and Ti. In the α-Ti$_3$Au phase (Fig. 2A), both Ti and Au are 12-fold coordinated with a cuboctahedron AET; Au is surrounded by 12 Ti atoms, whereas Ti is 14-fold coordinated with a 14-vertex Frank-Kasper polyhedron local environment of Ti (right inset). (C) XRD pattern was fitted with the β-Ti$_3$Au phase (blue vertical symbols). Small inclusions of α-Ti$_3$Au and α-Ti are marked by asterisks. arb. units, arbitrary units. (D and E) HRTEM (high-resolution transmission electron microscopy) images of the Ti$_{0.75}$Au$_{0.25}$ sample, taken for the [111] and [100] orientations, respectively. (F and G) SAD (selected area diffraction) images of the [111] and [012] orientations, respectively.
AETs of Au and Ti introduce higher energy barriers for any dislocation movement; that is, atoms cannot easily slide and break as well as reform bonds, resulting in increased hardness. One may argue further that the presence of small amounts of minority phases α-Ti₃Au and α-Ti may favorably interact with β-Ti₃Au to further inhibit dislocation formation and dislocation motion, thus increasing the hardness and toughness of the majority phase β-Ti₃Au.

To investigate the microstructure of the Ti₀.₇₅Au₀.₂₅ sample and its consistency with the x-ray analysis, HRTEM and SAD were performed for different crystallographic orientations. The HRTEM images along [111] (Fig. 2D) and [100] (Fig. 2E), together with the SAD images for the [111] (Fig. 2F) and [102] (Fig. 2G) orientations, are shown in Fig. 2 (F and G) and reveal the atomic arrangement in both real space (HRTEM) and reciprocal space (SAD) in β-Ti₃Au. Similar TEM and XRD analyses were performed on several other Ti₁−ₓAuₓ alloys, with the results summarized in Table 1. For all compositions, the main crystallographic phase is confirmed by both XRD and TEM data.

In addition to the crystal structure, two other factors point to the consistency with the x-ray analysis, HRTEM and SAD data performed for different crystallographic orientations. The HRTEM images along [111] (Fig. 2D) and [100] (Fig. 2E), together with the SAD images for the [111] (Fig. 2F) and [102] (Fig. 2G) orientations, are shown in Fig. 2 (F and G) and reveal the atomic arrangement in both real space (HRTEM) and reciprocal space (SAD) in β-Ti₃Au. Similar TEM and XRD analyses were performed on several other Ti₁−ₓAuₓ alloys, with the results summarized in Table 1. For all compositions, the main crystallographic phase is confirmed by both XRD and TEM data.

Another possible origin of the high hardness of β-Ti₃Au is the reduction in the DOS at the Fermi level E_F, which has been referred to as a pseudogap (62, 63). It has been suggested that the pseudogap formation stabilizes the phase and, consequently, improves the hardness (63). Typically, to significantly affect the crystallographic phase, the pseudogap must have a width W of 0.5 to 1.5 eV and a relative height ratio H/H₀ greater than 0.5, where H and H₀ represent the DOS at the top and bottom of the pseudogap, respectively (63). β-Ti₃Au, Tiₐ₄, and β-Ti₃Au all exhibit pseudogap-like features around the Fermi level (E = 0 in Fig. 3). The pseudogap of β-Ti₃Au is the most pronounced of all the studied Ti–Au compounds (Fig. 3, inset), with W ≈ 1 eV and H/H₀ ≈ 4, a result that reinforces the experimental observation of the highest hardness in β-Ti₃Au.

Together with hardness, the lifetime of a material has to be considered in determining a material’s applicability toward medical components. The lifetime of a component in vivo is determined partially by its component’s wear rate. In particular, knee and hip replacements currently last approximately a decade, making additional component replacements necessary (45). A comparison of the time-dependent COF in Ti₁−ₓAuₓ (x = 0, 0.25, 0.30, and 0.50) alloys is shown in Fig. 4A. The reference sample is Ti (blue, x = 0), with an average COF close to 0.35, which persists for about 700 s. The three Ti₁−ₓAuₓ alloys, however, show
The mechanical properties of the intermetallic compound β-Ti$_3$Au suggest that this material is well suited for medical applications where Ti is already used, with some examples including replacement parts and components (both permanent and temporary), dental prosthetics, and implants. The fourfold increase in hardness, as compared with pure Ti, renders β-Ti$_3$Au as the hardest known biocompatible intermetallic compound. The wear properties of β-Ti$_3$Au indicate that this compound has a COF that is four times less than that of Ti, resulting in the reduction of the wear volume by 70%, which will ensure longer component lifetime and less debris accumulation. Moreover, the ability to adhere to a ceramic surface will result in reducing both the cost and the weight of these components.

The high hardness in β-Ti$_3$Au can be attributed to three main factors: (i) the cubic crystal structure with inherently short Ti–Au bonds and high (14) Ti atomic coordination, (ii) the high VED, and (iii) the pseudogap formation. Between the two cubic Ti$_3$Au compounds, the Ti–Au bond length is smaller for the β phase ($d_{\text{Ti–Au}} = 2.84478 \, \text{Å}$) compared to diamond-SiC (solid).

Fig. 4. Wear analysis of Ti$_{1-x}$Au$_x$ alloys against a diamond-SiC disc. (A) COF as a function of time for $x = 0, 0.25, 0.30,$ and 0.50. Inset: An alumina container showing that Ti$_{1-x}$Au$_x$ adheres to this ceramic component. (B) Wear volumes of Ti$_{1-x}$Au$_x$ (dashed) compared to diamond-SiC (solid).

Fig. 5. SEM images of pin and disc wear tests. (A, C, E, and G) Ti reference ingot (A), Ti$_{1-x}$Au$_x$ pins for (C) $x = 0.25$, (E) $x = 0.30$, and (G) $x = 0.50$. (B, D, F, and H) Corresponding wear tracks on the diamond-SiC disc. Red rectangles (right panels) identify the regions of contact between the disc and the pin. For the (E) and (F) pair, there is little wear on both surfaces, indicating the wear resistance of the Ti$_{0.75}$Au$_{0.25}$ sample.

A COF < 0.15 after an initial running-in period of up to 300 s. This indicates that the lifetime of current Ti-based medical implants could be increased by the use of β-Ti$_3$Au ($x = 0.25$) in equivalent components. An added benefit of the Ti$_{1-x}$Au$_x$ alloys is that, when melted, they adhere to the walls of Al$_2$O$_3$ containers (Fig. 4A, inset), a valuable property that can be exploited to reduce both the weight and the cost of medical components by using the Ti$_{1-x}$Au$_x$ alloys as coating for ceramic parts. Moreover, the melting temperatures of the hardest intermetallic Ti$_{1-x}$Au$_x$ alloys (64) are lower than that of Ti, which would allow for the preparation of components via casting, thus eliminating machining cost (20). However, a quantitative assessment of the bonding strength or the diffusivity of the two materials is beyond the scope of this work and is left to a future study.

The wear volumes of the Ti$_{1-x}$Au$_x$ alloys are shown in Fig. 4B, indicating that the wear in these alloys is reduced compared to that in pure Ti (blue, $x = 0$). These results demonstrate that the addition of Au is an effective route to reducing the friction of Ti. To identify the wear modes, scanning electron microscopy (SEM) analysis was conducted, and the results are shown in Fig. 5, with the wear images of the Ti$_{1-x}$Au$_x$ pins (left panels) compared to those of the diamond-SiC disc (right panels). The bright and groove-like features correspond to abrasion from diamond grits, whereas the darker spots indicate adhesion wear. The Ti$_{1-x}$Au$_x$ alloys have some areas that seem to be worn less, corresponding to regions with elevated hardness. These features are most pronounced in the Ti$_{0.75}$Au$_{0.25}$ sample, consistent with its lower wear rates. The wear modes and volumes of the Ti$_{1-x}$Au$_x$ alloys are given in Table 1.

CONCLUSIONS

The mechanical properties of the intermetallic compound β-Ti$_3$Au suggest that this material is well suited for medical applications where Ti is already used, with some examples including replacement parts and components (both permanent and temporary), dental prosthetics, and implants. The fourfold increase in hardness, as compared with pure Ti, renders β-Ti$_3$Au as the hardest known biocompatible intermetallic compound. The wear properties of β-Ti$_3$Au indicate that this compound has a COF that is four times less than that of Ti, resulting in the reduction of the wear volume by 70%, which will ensure longer component lifetime and less debris accumulation. Moreover, the ability to adhere to a ceramic surface will result in reducing both the cost and the weight of these components.

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compared to the α phase \(d_{Ti-Au} = 2.93237 \) Å. Together with the more complex crystallographic environments of both Ti and Au in β-Ti3Au, this inhibits dislocations and results in high hardness in this particular compound. Understanding the factors that influence the hardness of β-Ti3Au provides insights for improving the existing biocompatible alloys and designing new biocompatible materials with superior mechanical properties.

**METHODS**

Alloys of Ti1–xAu, were prepared by arc melting Ti (Cerac, 99.99%) and Au (Cerac, 99.99%) in stoichiometric ratios, with mass losses of no more than 0.3%. To ensure homogeneity, the samples were remelted several times. Given that Ti alloys are frequently heat-treated to improve both hardness and ductility, annealing studies were carried out for the Ti–Au system. However, the use of different annealing cycles, similar to those used for other Ti-based alloys (65), resulted in minimal changes in the hardness compared to the as-cast samples. This might be caused by variation in microstructure homogeneity, which can mask the true annealing effects. The hardness of the arc-melted samples made it virtually impossible to grind these samples, which rendered powder XRD experiments difficult. Therefore, XRD data were collected at room temperature, using a four-circle Huber diffractometer with a Rigaku rotating anode source producing CuKα radiation.

HV was measured in a Tukon 2100 microhardness tester, equipped with a Vickers diamond pyramid indenter. The microhardness tests were performed on a polished sample surface of about 3 mm in diameter. Multiple tests were conducted for all samples to maintain repeatability, using a 300-g load, with a duration of 10 s.

Tribological experiments were conducted using a pin-on-disc tribometer (CST Instruments) with a total of 40,000 cycles. The diamond-SiC disc was selected for its durability. The ingot samples of Ti1–xAu (x = 0.25, 0.3, and 0.50) were used as a pin, with a Ti ingot used as a reference. An example of the Ti0.75Au0.25 sample used for wear tests is shown in the inset of Fig. 4A. To simulate wear during walking, a linear reciprocal motion was used with a sliding speed of 3.15 cm s–1 and an applied load of 2 N. The sliding distance of wear tests was set at 4 mm per stroke, with a total of 40,000 cycles. A synthetic body fluid was used as the test medium. The total wear is presented as volume loss. Details regarding the wear of the diamond-SiC disc have been previously reported (66–68).

The MTS assay was used to assess the cytotoxicity of the samples. For the study, 293T cells were cultured in Dulbecco’s modified Eagle’s medium supplemented with 10% fetal bovine serum, penicillin, and streptomycin. Five thousand cells were seeded in a 24-well plate along with the samples. The cells with the samples were incubated at 37°C. After 3 days of incubation, 150 µl per well of MTS reagent was added. It was further incubated for an hour and then the optical density was measured using a microplate reader. The sample of pure titanium had very poor cytocompatibility. The cells were observed to be strained and rounded, whereas the alloys did not show any significant effects.

Samples for HRTEM analysis were prepared via grinding and ion milling. The HRTEM image of the x = 0.25 sample was performed using a JEOL 2100 field emission gun transmission electron microscope. The microstructures of the x = 0.33 and x = 0.50 samples were investigated by a probe aberration–corrected JEOL JEM-ARM200Cf at 200 kV.

Band-structure calculations were performed using the full-potential linearized augmented plane-wave method implemented in the WIEN2k package (69, 70). The Perdew-Burke-Ernzerhof generalized gradient approximation was used as the exchange correlation potential, and a 10 x 10 x 10 grid was used to sample the k-points in the Brillouin zone.

**REFERENCES AND NOTES**

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