Average oxidation state of Ti-Cu alloys comprised of lower temperature α-Ti(Cu) and Ti_2Cu phases

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Abstract. It is known from literature that high oxidation state results in high oxygen-to-metal coverage which results in a stable protective metal-oxide layer. The metal-oxide layer that forms is a protective layer against corrosion. Current study uses the theoretical valence electron count (VEC) or electron per atom ratio (*e/a*) to determine average oxidation states of α-Ti(Cu) phase below eutectoid point and intermetallic Ti_2Cu phase. This was done in order to study the effect of α-Ti(Cu) and Ti_2Cu on average oxidation state of binary Ti-Cu alloys with various copper content. Using the theoretically determined oxidation states, it was possible to calculate average oxidation state of Ti-Cu alloys comprised of α-Ti(Cu) + Ti_2Cu phases based on the volume fraction ratio. Oxidation state increased when Ti_2Cu ratio increased.

1 Introduction

In medical applications that require high corrosion resistance and tribological performance, titanium (Ti) and its alloys exhibit good corrosion resistance, but poor tribological performance which leads to poor corrosion resistance [1]. Poor tribological performance refers to a situation where materials come into contact with each other and experience excessive friction, wear, or other undesirable behaviours during relative motion. This situation can lead to decreased component lifespan, and even system failure. Tribological factors such as high friction and wear, can negatively impact corrosion resistance. This is because when a material experiences high friction and wear, it can disrupt the protective surface layers that normally prevent corrosion, leading to accelerated degradation in corrosive environments. Consequently, the continuous frictional movements in a corrosive medium result in tribo-corrosion. In implants, the friction can be aggravated by the loosening of the implant from the bone or its attachment. This loosening of the implant is due to an undesirable phenomenon called stress shielding which is caused by the discrepancy between the Young's modulus of a human bone and that of an implant [2-5]. Alloying Ti with suitable elements enables scientists and engineers to alter a metallic implant material towards desired properties by controlling the amounts of phases present in an alloy [1]. Excellent corrosion resistance, biocompatibility and low melting temperature has been attained using Cu as an alloying element in Ti metals [6-9]. Different Cu contents were found to have an effect in the improvement of alloy mechanical properties, which were attributed to the different phases observed using X-ray diffractometer (XRD) analysis [1, 10].

The presence of copper (Cu) in small amounts is not only biocompatible but exhibits antibacterial properties which are beneficial in implant transplants [11, 12]. At room temperature binary titanium-copper (Ti-Cu) alloys cannot retain the β-Ti phase despite cooling by quenching, they are commonly comprised of alpha-titanium (α-Ti) and intermetallic Ti_2Cu phases resulting from a eutectoid reaction (Equation 1).

$$\beta\ Ti\ (5.4\ at.\%\ Cu) \rightarrow \alpha\ Ti\ (1.6\ at.\%\ Cu) + Ti_2Cu \qquad (1)$$

Low temperature binary Ti-Cu alloys with a minute Cu content have a matrix of the α-Ti phase, but when the Cu concentration is beyond 5 weight percent (wt.%), the Ti_2Cu precipitates in the grain boundaries of the α-Ti phase. Takada et al. discovered that the Ti-Cu alloys consisting of α-Ti(Cu) and Ti_2Cu phases have high corrosion resistance necessary for dental applications [1, 10]. However, the underlying mechanism which forms basis for observed high corrosion resistance is not well-understood. As a result, studies to reveal the mechanism behind this increase in corrosion resistance are required. In addition to increased corrosion resistance, the Ti_2Cu phase is thought to have a critical role in the antibacterial behaviour of Ti-Cu alloys. On the other hand, the heat treatments such as ageing and annealing of mechanical milled Ti-Cu are reported to increase the corrosion resistance and mechanical properties by size distribution of Ti_2Cu precipitates [11, 12]. It is therefore evident that copper plays a major role in the development and design of new biocompatible and corrosion resistant Ti alloys. Thus, the current study uses the valence electron count (VEC) also known as *e/a* ratio theoretical method to establish the underlying mechanism behind the increase in the oxidation state, and therefore an improvement in the corrosion performance of the Ti-Cu alloys containing higher amounts of Cu, consisting of α-Ti(Cu) + Ti_2Cu phases upon cooling.

2 Methodology

The microstructures of the Ti-xCu alloys containing different compositions of copper below and at eutectoid point are depicted in Figure 1.

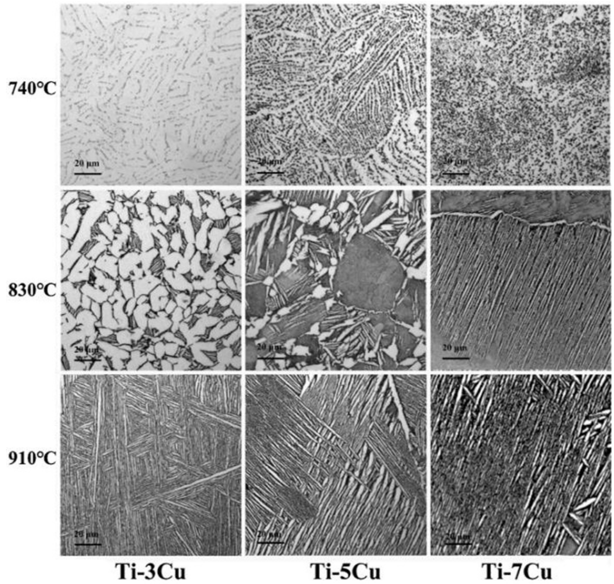

Fig. 1. Microstructures of heat-treated Ti-xCu alloys with different Cu content [13].

Using the theoretical valence electron count (VEC) or *e/a* ratio method [14] in Equation 2, it was possible to calculate the average oxidation states (AOS) of the α-Ti(Cu) solid solution alloys below the eutectoid point following Equation 3 below.

$$VEC_{\alpha\mathrm{Ti(Cu)}} = d_{\alpha Ti(Cu)} + s_{\alpha Ti(Cu)} = [(100 - x)d_{Ti} + xd_{Cu}] + [(100 - x)s_{Ti} + xs_{Cu}] \quad (2)$$

$$\begin{aligned} AOS_{\alpha Ti(Cu)} &= (unpaired\ electrons)d_{\alpha Ti(Cu)} + s_{\alpha Ti(Cu)} \quad (3) \\ &= (0.128+) + (1.984+) \\ &= 2.112+ \end{aligned}$$

where the d_{Ti}, d_{Cu}, s_{Ti}, and s_{Cu} are the number of valence electrons in the outer *d*- and *s*-orbitals of pure constituent elements, Ti and Cu, respectively, whereas *x* represents the atomic composition of Cu. It therefore follows that $d_{\alpha Ti(Cu)}$ is the number of valence *d*-electrons, while $s_{\alpha Ti(Cu)}$ is the number of valence *s*-electrons for the alloy. For example, using Equation 2 above, the value of $d_{\alpha Ti(Cu)}$ for α-Ti(Cu) solid solution at 1.6 at.% Cu is equal to 2.128. Thus, since the *d*-orbital electron filling in α-Ti(Cu) phase follows the method described by Phasha et al. [14], as shown in Table 1, the *d*-contribution of the average oxidation state (AOS) equation is given by the number of unpaired *d*-electrons, which is equal to 0.128 whereas the *s*-contribution remains the same as in Equation 2. As a result, the AOS of α-Ti(Cu) solid solution at 1.6 at.% Cu calculated using Equation 3 is equal to 2.112+.

Table 1. The *d*-orbital filling of αTi(Cu) at 1.6 at.% Cu.

t_{2g} *d*-orbital	d_{xy}	d_{xz}	d_{yz}
	↑↓	↑ (0.128)	

On the other hand, the average oxidation state of the Ti_2Cu intermetallic phase is determined using Equation 4

$$AOS_{Ti_2Cu} = \frac{2 * OS_{Ti} + OS_{Cu}}{n_T} = \frac{(2 * 4 +) + (1+)}{3} = 3 +, \quad (4)$$

where OS_{Ti} and OS_{Cu} are the most stable oxidation states of elemental Ti (4+) and Cu (1+), respectively, and n_T is the total number of atoms in the intermetallic compound. From the above determined oxidation states, the average oxidation state (AOS) of binary Ti-Cu alloys consisting of α-Ti(Cu) + Ti_2Cu phases at different volume fraction ratios were calculated using Equation 5 below, with α-Ti(Cu) having maximum solid solubility of 1.6 atomic percent (at.%) Cu.

$$AOS_{Ti-Cu} = (1 - x)OS_{\alpha Ti(Cu)} + (x)OS_{Ti_2Cu} \quad (5)$$

where x is the volume fraction of Ti_2Cu phase, $OS_{\alpha Ti(Cu)}$ oxidation state of α-Ti(Cu) at 1.6 at.%, and OS_{Ti_2Cu} oxidation state of Ti_2Cu phase.

3 Results and discussion

In order to study the oxidation state and therefore corrosion resistance of Ti-Cu alloys, the VEC theoretical method sometimes referred to as *e/a* ratio was used to calculate the oxidation states of the binary α-Ti(Cu) solid solution alloys with Cu composition ranging from 1-5 at.% below the eutectoid point. The calculated average oxidation state results are depicted in Figure 2, where the oxidation states of the α-Ti(Cu) alloys increase linearly with an increase in the Cu content.

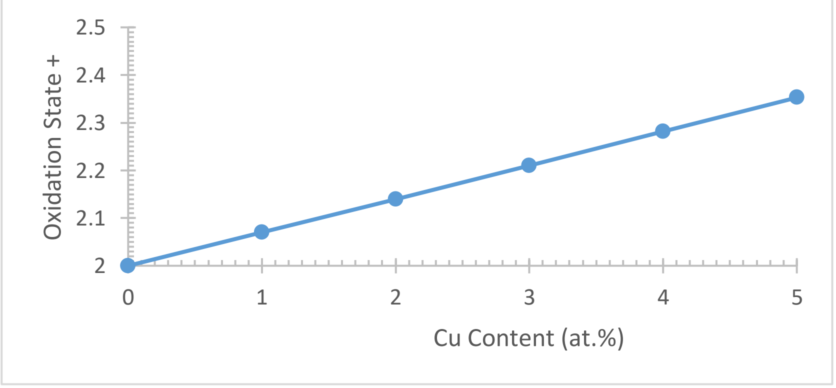

Fig. 2. Theoretical oxidation states of binary α-Ti(Cu) solid solutions below eutectoid point.

It has been experimentally shown that the binary Ti-Cu alloys up to maximum solubility Cu content of about 1.6 at.% consist of α-Ti(Cu) phase in their matrix, but when the Cu composition increases beyond the 3.8 at.% (5 wt.%) the Ti_2Cu phase precipitates at the grain boundaries of α-Ti(Cu) phase [1]. Even though the small Cu amount soluble in α-Ti(Cu) phase does improve corrosion resistance performance of α-Ti, this increase is minimal. This minimal increase can be attributed to a small increase in average oxidation state from 2.0+ to ~2.15+ as depicted in Figure 2. It is only upon precipitation of Ti_2Cu phase observed by researchers when the Cu content exceeds 3.8 at.% that the corrosion resistance increases significantly [10]. In order to determine the mechanism behind increase in the corrosion performance of Ti-Cu alloys comprised of α-Ti(Cu) and Ti_2Cu phases, the average oxidation state for Ti_2Cu phase was calculated according to Equation 4. Since the average oxidation states of individual phases in binary Ti-Cu alloys with Cu composition up to 10 wt.% have been determined using Equations 3 and 4, it is now possible to theoretically determine for the first time the AOS of Ti-Cu alloys containing various volume fractions of the constituent phases (α-Ti(Cu), Ti_2Cu) using Equation 5. The calculated results are depicted in Figure 3. The graph in Figure 3 starts where the α-Ti(Cu) with 1.6 at.% Cu content has a volume fraction (VF) of 100% and that of Ti_2Cu is equal to 0%. The average oxidation state of the binary Ti-Cu alloys increases linearly with an increase in the volume fraction of Ti_2Cu phase. This is owed to the fact that the AOS of Ti_2Cu (3+) is much higher than that of α-Ti(Cu) phase (2.15+). It thus follows that the experimentally observed significant increase in corrosion resistance of Ti-Cu alloys upon increasing Cu content [10, 15] is correlated to an increase in the volume fraction of Ti_2Cu precipitation phase having higher average oxidation state. As a result, the current calculated results based on our proposed theoretical method are able to explain the mechanism behind Takada et al., Kikuchi et al., Takahashi, Wang et al, Lui et al. experimental observations on the α-Ti and Ti_2Cu phases that form at and near eutectoid reaction of titanium rich binary Ti-Cu alloys that were found to enhance corrosion resistance, biomedical and mechanical properties necessary for dental applications [7, 10, 13, 15, 16]. Shao et al. further showed that as the copper content of Ti-Cu alloys increases the volume fraction of Ti_2Cu phase also increases [17], their observation is depicted in Figure 4. The volume fraction of Ti_2Cu precipitate was determined with the scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). It was observed that the volume fraction of Ti_2Cu is enhanced when Cu content is increased. The Ti_2Cu volume fractions of 2.37 %, 5.20 %, 24.96 %, 34.55 %, and 39.24 % were discovered in the Ti-2Cu, Ti-7Cu, Ti-12Cu, Ti-17Cu and Ti-22Cu respectively [17].

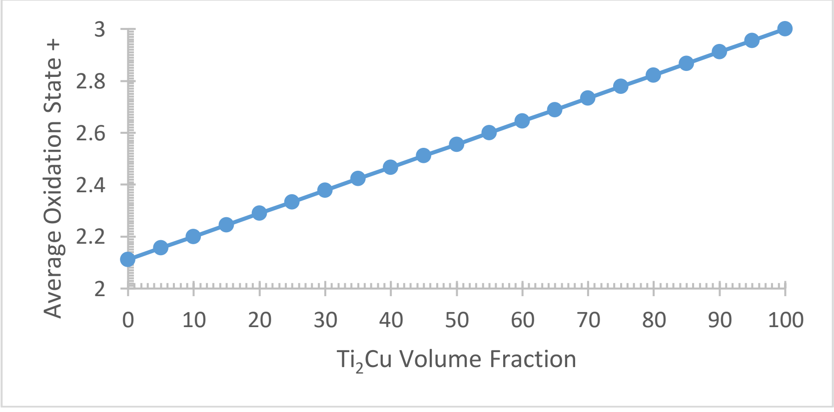

Fig. 3. The average oxidation states of Ti-Cu alloy at different volume fractions of Ti_2Cu precipitate.

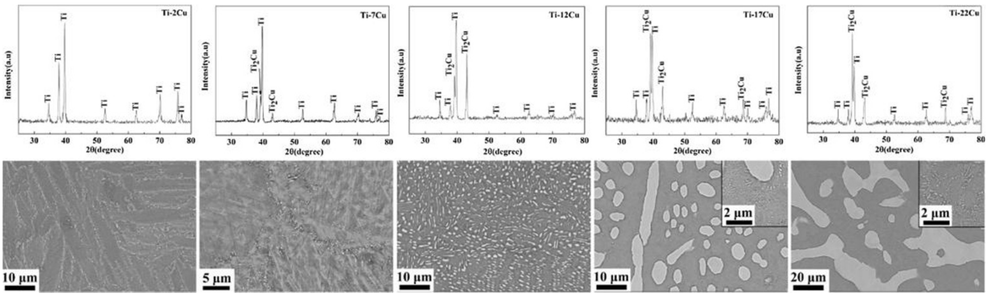

Fig. 4. The x-ray diffraction (XRD) patterns and SEM micrographs of Ti-xCu (x = 2, 7, 12, 17 and 22 wt.%) alloys, showing Ti_2Cu and a certain amount of eutectoid structure.

4 Conclusion

The average oxidation state (AOS) of the binary Ti-Cu alloys increases linearly with an increase in the volume fraction of Ti_2Cu phase. This is owed to the fact that the AOS of Ti_2Cu (3+) is much higher than that of α-Ti(Cu) phase (2.15+). Established theoretical trend correlates with experimentally observed corrosion resistance pattern. Therefore, from the current results, it can be concluded that the significant increase in the corrosion resistance of binary TiCu alloys as Cu content increases, is mainly attributed to an increase in the volume fraction of Ti_2Cu phase precipitating along the grain boundaries of the α-Ti(Cu) phase. Thus, current calculated results based on our proposed theoretical method are able to explain for the first time the mechanism behind Takada et al., Kikuchi et al., Takahashi, Wang et al, Lui et al. and Shao et al. experimental observation where they observed that Ti-Cu alloys with α-Ti(Cu) and Ti_2Cu have high corrosion resistance necessary for dental applications, rendering the method viable for use in similar corrosion resistance studies [7, 10, 13, 15-17].

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Data availability: Data supporting the findings of this study can be made available by the corresponding authors upon reasonable request, subject to MINTEK's confidentiality policy.

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