

1       **The effect of Cu content on corrosion, wear and tribocorrosion**  
2       **resistance of Ti-Mo-Cu alloy for load-bearing bone implants**

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13       **Abstract**

14       In this study, the effects of Cu content on wear, corrosion, and tribocorrosion resistance  
15       of Ti-10Mo-xCu alloy were investigated. **Results revealed that hardness of Ti-10Mo-xCu**  
16       **alloy increased from 355.1±15.2 HV to 390.8±17.6 HV by increasing Cu content from 0%**  
17       **to 5%, much higher than CP Ti (106.6±15.1 HV) and comparable to Ti64 (389.7±13.9**  
18       **HV).** With a higher Cu content, wear and tribocorrosion **resistance** of Ti-10Mo-xCu  
19       alloys were enhanced, and corrosion resistance showed an initial increase with a  
20       subsequent decrease. Wear mechanisms under pure mechanical wear and tribocorrosion  
21       conditions of Ti-10Mo-xCu alloys were a combination of delamination, abrasion and  
22       adhesion wear.

23       **Keywords**

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24 Ti-10Mo-xCu alloys, wear, corrosion, tribocorrosion, bone implants

## 25 **1. Introduction**

26 Over one million knee and hip replacements surgeries take place every year  
27 worldwide due to an aging population and injuries to the bone tissue and joint from trauma  
28 and sports accidents [1, 2]. Thus, there exists an increasing demand for load-bearing bone  
29 implants. Ti-based alloys, owing to their high strength, low elastic modulus, excellent  
30 corrosion resistance, and biocompatibility have received growing interests [3-6].  
31 However, currently widely used Ti-based materials, such as commercially pure titanium  
32 (CP Ti) and Ti-6Al-4V (Ti64) alloys, still have some limitations. Firstly, the elastic  
33 modulus of CP Ti (~110 GPa) and Ti64 (~120 GPa) are substantially higher than human  
34 bones (e.g. 0.01-3 GPa for trabecular bone and 3-30 GPa for cortical bone) [7]. This  
35 elastic modulus mismatch could cause a stress shielding effect, which leads to bone  
36 resorption around the implants and ultimately the failure of implantation. Secondly, CP  
37 Ti has relatively low strength and wear resistance, which may greatly shorten the  
38 implant's service life. **Thirdly, Ti64 alloy may have some negative health concerns in**  
39 **regards to its long-term implantation, such as mental disorder, hypomnesia, and**  
40 **Alzheimer's disease, because of the release of aluminum (Al) or vanadium (V) ions [8].**  
41 Lastly, bacterial infections could still occur even if surgeries are carried out under strict  
42 aseptic conditions, which could lead to revisions, resulting in extra pain and cost to  
43 patients and healthcare providers [9, 10]. Therefore, new-generation Ti alloys with higher  
44 strength, excellent biocompatibility, lower elastic modulus, and the antibacterial property  
45 are of urgent need. **We recently developed a new Ti-Mo-Cu alloy that 1-5 wt% Cu was**  
46 **added in Ti-10Mo alloys due to the excessive Cu will deteriorate the ductility and also**  
47 **may result in cytotoxicity [11], and the effects of Cu content on the tensile properties,**  
48 **cytocompatibility, and bacterial inhibitory ability of Ti-10Mo alloys were investigated.**  
49 **The results indicated that this kind of alloys has promising mechanical properties,**

50 **cytocompatibility, and antibacterial property.**

51 For load-bearing bone implants, corrosion, wear, and the interaction of mechanical  
52 loading and chemical/electrochemical reactions, or so-called tribocorrosion are also  
53 important properties. It is well known that Ti-based alloys are surrounded by body fluids  
54 containing a variety of complex electrolytes (e.g. proteins and chloride ion) when it is  
55 implanted into the human body [12, 13], which leads to corrosion. In addition, there are  
56 also relative motions, such as sliding and fretting, between the implant and bone.  
57 Sometimes, these two phenomena can occur simultaneously [14, 15]. Under  
58 tribocorrosion conditions, the deterioration of the materials is exacerbated, and the  
59 material loss is often higher than the sum of the material loss by corrosion or wear alone,  
60 because of the synergistic effect between pure mechanical wear and electrochemical  
61 corrosion [16, 17]. Additionally, metal ion release can also be accelerated, and more  
62 debris can be generated under the tribocorrosion conditions, which may induce  
63 cytotoxicity [18-21]. **Therefore, it is crucial to investigate the corrosion, wear, and**  
64 **tribocorrosion properties of Ti-Mo-Cu alloy, which have been rarely reported in the**  
65 **literature.**

66 The objectives of this study were to investigate the effect of Cu content on the wear,  
67 corrosion, and tribocorrosion properties of Ti-10Mo-xCu alloy, and to clarify the  
68 mechanisms of interactions between pure mechanical wear and corrosion of Ti-10Mo-  
69 xCu alloy, so as to provide basic guidance for its practical application as load-bearing  
70 bone implants.

## 71 **2. Materials and methods**

### 72 *2.1 Materials and specimen's preparation*

73 Ti-10Mo-xCu (x=0,1,3,5) alloys were fabricated by powder metallurgy (PM) using

74 commercial Ti, Mo, and Cu powders (purity  $\geq$  99.9%). The fabrication process was as  
75 follows: (1) the Ti powders were coated by polyethylene glycol (PEG) to decrease the  
76 oxygen content to enhance the mechanical properties. The coated process of Ti powders  
77 by PEG is as follows: 1 g PEG was added into 50 mL dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and  
78 magnetically stirred for 1 h until complete dissolution. Then 100 g HDH Ti powder was  
79 added into the PEG-dichloromethane solution at room temperature and stirred it for 0.5  
80 h. The entire process was carried out in an Ar protective glove box. Afterward, the mixed  
81 solution was taken out and heated at 50 °C in a fume hood for complete evaporation of  
82 the dichloromethane. After being dried in a vacuum oven, the PEG-coated Ti powder was  
83 obtained; (2) the coated Ti powders were mixed with Cu and Mo powders in a nominal  
84 composition of Ti-10Mo-xCu ( $x=0,1,3,5$ ) in a blender for 6h with the rotation speed of  
85 100 rpm/min. (3) the mixed powders were compressed into a cylindrical compact by cold  
86 isostatic compaction at 200 MPa; (4) the cylindrical compacts were sintered at different  
87 temperatures ranging from 1360 °C to 1400 °C under argon (Ar) atmosphere in a tube  
88 furnace. The detailed information on the particle size of the powders and sintering  
89 processes were described elsewhere [22, 23].

## 90 *2.2 Tribocorrosion and pure mechanical wear testing*

91 The tribocorrosion test of Ti-10Mo-xCu alloy was performed by a ball-on-plate  
92 tribometer (UMT- II ) by reciprocating slide integrated with an electrochemical  
93 workstation in phosphate-buffered saline (PBS) solution at  $37 \pm 0.5$  °C. The  
94 electrochemical workstation consisted of a working electrode (specimens), a reference  
95 electrode (saturated calomel electrode, SCE), and a counter electrode (platinum grid). The  
96 components of the PBS solution were NaCl 8 g/L, KCl 0.2 g/L,  $\text{KH}_2\text{PO}_4$  0.2 g/L,  
97  $\text{Na}_2\text{HPO}_4$  1.15 g/L, and the pH was 7.2. The volume of electrolytes was 100 mL.  
98 Specimens were cut into rectangular plates ( $20 \times 6 \times 2$  mm<sup>3</sup>) by electrical discharge

99 machining (EDM) and embedded in epoxy resin. The exposed areas were 120 mm<sup>2</sup>. The  
100 specimens were ground with SiC abrasive paper to 2000 grit and then polished to the  
101 mirror surface. Finally, the samples were ultrasonic cleaned with absolute ethyl alcohol  
102 and dried in a vacuum desiccator at room temperature. As-cast CP Ti and Ti64 alloy were  
103 tested simultaneously as references. The slip frequency was 1 Hz, and the stroke lengths  
104 were 15 mm. The applied load was 1.5 N, which led to a Hertzian contact pressure of  
105 343-349 MPa for all alloys. The counter material was ZrO<sub>2</sub> ball, and the diameter was 10  
106 mm. Also, to eliminate electrochemical corrosion, the tribocorrosion measurement was  
107 also performed under an applied potential of -0.8 V (vs. SCE), namely pure mechanical  
108 wear. The coefficient of friction (COF) and open circuit potential (OCP) values before,  
109 during, and after sliding were continuously recorded. Before sliding, the potential of each  
110 specimen was stabled by immersing the specimens into the solution for 2h. After the  
111 potential was stabled, the sliding began for 1h. Afterward, the OCP values were recorded  
112 for another 0.5h continuously. For tribocorrosion and pure mechanical wear tests, 5  
113 experiments were repeated to verify the reproducibility.

### 114 2.3 Electrochemical corrosion testing

115 Different electrochemical measurements were performed in a conventional three-  
116 electrode system according to the ASTM G59-97 standard [24] in PBS solution at 37 ±  
117 0.5 °C. The size and preparation process of tested specimens were the same as the  
118 tribocorrosion tests. Prior to the potentiodynamic polarization (PD) measurements,  
119 samples were stabilised in the PBS solution for 2h. After that PD curves with (dynamic  
120 corrosion) and without (static corrosion) sliding was measured. The scan rate was 0.5  
121 mV/s while the scan scale was -0.3-2 V vs OCP. The corrosion potential ( $E_{\text{corr}}$ ) and the  
122 passive current density ( $i_p$ , determined at 0.5 V) were obtained from PD curves. For the  
123 electrochemical test, 5 experiments were repeated to verify the reproducibility.

124 *2.4 Characterisation*

125 A Dmax-RB X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu target ( $\lambda =$   
126 0.15406 nm) was used to analyse the phase constituents of the alloys. The Vickers micro-  
127 hardness was tested using a Buehler Micromet 2100 tester with a 0.5 N load based on the  
128 ASTM E384-11 standard [25]. Ten points were tested for each sample and the average  
129 value was obtained.

130 After tribocorrosion and pure mechanical wear tests, the samples were ultrasonically  
131 cleaned in ethyl alcohol absolute for 10 mins and dried in a vacuum desiccator at room  
132 temperature. Scanning electron microscope (SEM, JSM-6480LV, Japan) equipped with  
133 an energy dispersive X-ray spectrometry (EDS) was used to analyse the surface  
134 topography and chemical composition of the alloys. The three-dimensional (3D)  
135 topographies of all specimens were observed using the white light interference  
136 microscope (Contour GTK, Bruker), and the wear volume was obtained.

137 *2.5 Calculation*

138 Repassivation rate for a certain period was calculated by the formula (1) [26], as  
139 follows:

140 
$$\Delta E = K_1 \times \log t + K_2 \quad (1)$$

141 where  $t$  is a certain time after interrupting sliding, which is usually 300 s;  $\Delta E$  is the  
142 potential variation during the time of  $t$ , V;  $K_1$  is a value that represented the repassivation  
143 rate;  $K_2$  is the constant, which is determined by the solution, and 0.1 for PBS.

144 The total material loss rate ( $W$ , mm/y) and the pure mechanical wear rate ( $W_0$ ,  
145 mm/y), namely the tribocorrosion and pure mechanical wear testing, were calculated by  
146 the following equation (2) according to ASTM G119-09 [27]:

147 
$$Wear \cdot rate = \frac{\Delta m}{S \times \rho \times t} \times 24 \left( \frac{h}{d} \right) \times 365 \left( \frac{d}{y} \right) \quad (2)$$

148 where,  $\Delta m$  is the wear loss, obtained indirectly from the laser scanning confocal

149 microscopy,  $g$ ;  $S$  is the area of worn surface,  $\text{mm}^2$ ;  $\rho$  is specimen density,  $\text{g/cm}^3$ ;  $t$  is test  
150 time, h.

### 151 **3. Results and discussion**

#### 152 *3.1 Phase constituents and Vickers micro-hardness*

153 XRD is used to analyse the phase constituents of Ti-10Mo-xCu using CP Ti, and  
154 Ti64 alloy as control samples. In Fig. 1(a), Ti-10Mo and Ti-10Mo-1Cu alloys were  
155 characterized by  $\alpha$  and  $\beta$  phases, while Ti-10Mo-3Cu and Ti-10Mo-5Cu showed a small  
156 amount of  $\text{Ti}_2\text{Cu}$  co-existing with  $\alpha$  and  $\beta$  phases. In addition, the content of  $\text{Ti}_2\text{Cu}$   
157 increased with an increase in Cu content, which was in agreement with the previous result  
158 [28]. Furthermore, as the Cu content increased, the intensity of the  $\beta$  phase became  
159 gradually higher, indicating that more  $\beta$  phases had been generated. **This result can be**  
160 **explained by the well-known stabilizing effect of Cu towards the  $\beta$  phase.** For the CP Ti  
161 and Ti64 alloy, they consisted of  $\alpha$  phase and  $\alpha+\beta$  phases, respectively.

162 Fig.1(b) presents the Vickers micro-hardness values of Ti-10Mo-xCu with different  
163 Cu content, alongside with CP Ti, and Ti64 alloy. It can be seen that the micro-hardness  
164 of Ti-10Mo-xCu alloys increased from  $355.1\pm 15.2$  HV to  $390.8\pm 17.6$  HV when the Cu  
165 content increased from 0 to 5 wt.%, which are much higher than that of the CP Ti  
166 ( $106.6\pm 15.1$  HV) and comparable to the Ti64 alloy ( $389.7\pm 13.9$  HV). This is mainly  
167 caused by solid strengthening by Mo and Cu elements [29, 30]. In addition, the  $\text{Ti}_2\text{Cu}$   
168 phase, which is a hard brittle intermetallic, also can improve the strength of the Ti-Mo-  
169 Cu alloys [31]. As a result, the Ti-10Mo-5Cu alloy exhibits the highest hardness of 390.8  
170 HV.

#### 171 *3.2 Wear behaviour*

##### 172 *3.2.1 COF*



173 The COF values of Ti-10Mo-xCu alloys, alongside with CP Ti, and Ti64 alloy under  
174 pure mechanical wear and tribocorrosion conditions are shown in Fig. 2. It can be  
175 observed that the COF values exhibited a relatively steady-state with local fluctuations  
176 under pure mechanical wear and tribocorrosion conditions. The COF of Ti-10Mo-xCu  
177 alloys decreased with the Cu content, due to the formation of Ti-Cu intermetallic  
178 compounds, e.g. Ti<sub>2</sub>Cu in the present study [32]. Comparing with Fig. 2(a) and (b), it can  
179 be seen that the COF of all alloys under the tribocorrosion condition were higher than  
180 those under pure mechanical wear condition. Under the tribocorrosion condition, there is  
181 an interaction between wear and corrosion, which will result in stronger friction. This  
182 friction can lead to higher COF values. This is agreed with Zhang's study, who  
183 demonstrated that during tribocorrosion the COF of the nickel-aluminium bronze (NAB)  
184 was higher compared with that observed without corrosion [33]. The Ti-10Mo-5Cu alloy  
185 presented the lowest average COF under pure mechanical wear ( $0.48\pm 0.02$ ) and  
186 tribocorrosion conditions ( $0.58\pm 0.03$ ), much lower than those of the Ti64 alloy  
187 ( $0.51\pm 0.04$  and  $0.62\pm 0.03$ , respectively) and CP Ti ( $0.75\pm 0.07$  and  $0.95\pm 0.09$ ,  
188 respectively).

### 189 3.2.2 The morphologies of wear tracks

190 The white light interference microscope was used to analyse the 3D morphologies  
191 of the wear tracks after pure mechanical wear and tribocorrosion tests (Fig. 3). It can be  
192 seen that the surface of all samples exhibited similar morphologies, namely, all samples  
193 had obvious furrows and severe plastic deformation. In addition, it can be found that the  
194 wear tracks of Ti-10Mo-xCu alloys became shallower and narrower with an increasing  
195 Cu content due to the increase of hardness. The Ti-10Mo-5Cu alloy exhibits the smallest  
196 width of  $0.454\pm 0.05$  mm and  $0.821\pm 0.04$  mm under pure mechanical wear and  
197 tribocorrosion conditions, respectively, smaller than those of the CP Ti significantly

198 (0.514±0.03 mm and 1.17±0.09 mm) and comparable to those of the Ti64 alloy  
199 (0.458±0.06 mm and 0.829±0.05 mm).

### 200 3.2.3 Wear rate

201 Fig. 4 shows the wear rates under pure mechanical wear and tribocorrosion  
202 conditions calculated by equations (1) and (3). The wear rate of Ti-10Mo-xCu alloys  
203 decreased gradually with the increasing Cu content, and the Ti-10Mo-5Cu alloy exhibited  
204 the lowest wear rate of 8.25033±0.11 mm/y and 4.234±0.06 mm/y under tribocorrosion  
205 and pure mechanical wear tests, respectively, lower than those of the CP Ti  
206 (20.56984±0.09 mm/y and 11.49±0.08 mm/y) and comparable to those of the Ti64 alloy  
207 (8.54568±0.04 mm/y and 4.5625±0.03 mm/y). Furthermore, it can be found that the  
208 alloys exhibit higher wear rates under the tribocorrosion than those values under pure  
209 mechanical wear conditions. This was mainly because the passive film formed on the  
210 surface was loose and coarse under tribocorrosion, which can be easily peeled off [34].

### 211 3.2.4 Wear track surface analysis and wear mechanisms

212 In order to further characterise the wear mechanisms, the surfaces of the wear tracks  
213 on all alloys after pure mechanical wear and tribocorrosion tests were examined using  
214 SEM. In Fig. 5, parallel grooves to the sliding direction indicated that the occurrence of  
215 abrasive wear [35]. Meanwhile, there were some laminar tearing on the wear track due to  
216 the delamination of the alloys caused by rubbing against the ZrO<sub>2</sub> ball, suggesting that  
217 the delamination wear also existed [36]. In this study, the ZrO<sub>2</sub> ball was used as counter  
218 material, which has a higher hardness (~700 HV) than all the specimens (100-400 HV).  
219 During the sliding motion, the harder ZrO<sub>2</sub> ball can be embedded into the softer alloys  
220 under the applied load, resulting in abrasive wear and provoking an increase in wear rate  
221 [21, 37]. Additionally, two kinds of zones, namely dark and grey zone, can be observed  
222 from the back-scattered electron and secondary electron (BSE-SE) images. To identify

223 these two zones, an EDS analysis was carried out. Taking Ti-10Mo-5Cu alloy as an  
224 example (Fig. 5(d)), the EDS results indicated that the grey zone (Z1) consisted of Ti,  
225 Mo, and Cu elements only, while the dark zone (Z2) possessed much higher O content,  
226 suggesting the existence of oxides of  $\text{TiO}_2$ ,  $\text{MoO}_3$ , and  $\text{CuO}_2$ . As a result of squeezing and  
227 scraping between the alloys surface and the counter material, some oxidised wear debris  
228 were generated under sliding. The oxidised debris accumulated gradually with the  
229 continued sliding, and finally adhered to the surface, indicating that the occurrence of  
230 adhesion wear. Similar results were observed for the CP Ti and Ti64 alloy, i.e. oxides  
231 such as  $\text{TiO}_2$  and  $\text{TiO}_2\text{-Al}_2\text{O}_3$  are presented in the dark area (Fig. 5(e) Z3 and (f) Z4). The  
232 results under tribocorrosion conditions (Fig. 5(g)-(l)) were similar to those under pure  
233 mechanical wear. Therefore, it is reasonable to assume that the wear mechanisms for all  
234 the alloys under both conditions were a combination of delamination, abrasion, and  
235 adhesion wear.

### 236 3.3 Electrochemical analyses

#### 237 3.3.1 Open circuit potential

238 Fig. 6 shows the OCP of Ti-10Mo-xCu, CP Ti, and Ti64 alloy before the static  
239 corrosion test in PBS solution at  $37 \pm 0.5$  °C. It can be observed that all the alloys showed  
240 a similar tendency where the  $E_{\text{ocp}}$  moved towards more positive values with the extended  
241 immersion time until they became quasi-stationary. The  $E_{\text{ocp}}$  values of all the Ti-10Mo-  
242 xCu were more positive than that of CP Ti and Ti64 alloy, meaning that the addition of  
243 Cu has decreased the tendency of corrosion. Among them, the Ti-10Mo-3Cu exhibits the  
244 most positive potential ( $-0.084 \pm 0.02$  V vs. SCE), indicating that a more passive surface  
245 may have formed on this alloy.

246 Fig. 7 presents the OCP values for Ti-10Mo-xCu, alongside with the CP Ti and Ti64  
247 alloy before, during, and after sliding in PBS solution at  $37 \pm 0.5$  °C. Similar to the OCP

248 values before the static corrosion test, the values before sliding increased gradually, and  
249 finally reached a quasi-stationary state after some time. With the start of sliding, the OCP  
250 shifted abruptly towards more negative values. After that, it increased within several  
251 seconds and then fluctuated within small amplitudes around a value before the sliding  
252 stopped. In general, the OCP is a mixed potential of active areas and passive unworn areas  
253 and is affected by the ratio of these two areas [38, 39]. It should be noted that the surface  
254 of all the samples formed stable oxide films before sliding. When sliding started the  
255 formed mixed oxide films were damaged by the mechanical attack at the contact region  
256 [40, 41], leading to a sharp decrease in the OCP. However, when the de-passivation and  
257 passivation rates reached a dynamic equilibrium, the OCP values became relatively stable.  
258 The OCP value of Ti-10Mo-xCu alloys increased initially and then decreases during  
259 sliding with increasing Cu, which suggested that the corrosion tendency decreased at first  
260 and then increased. The Ti-10Mo-3Cu alloy demonstrated the noblest OCP ( $-0.41 \pm 0.03$   
261 V vs. SCE), higher than that of CP Ti ( $-0.66 \pm 0.05$  V vs. SCE) and Ti64 alloy ( $-0.51 \pm 0.04$   
262 V vs. SCE). This result indicated that the Ti-10Mo-3Cu also were least likely to be  
263 corroded under the tribocorrosion condition. After the sliding stopped, the OCP values  
264 remarkably increased and gradually recovered to the original values, indicating the re-  
265 passivation of the worn surface [42].

266 Similar to the results during sliding, the OCP values of Ti-10Mo-xCu alloys after  
267 sliding increased firstly and subsequently decreased with increasing Cu. The Ti-10Mo-  
268 3Cu alloy exhibited the highest potential of  $-0.03 \pm 0.01$  V vs. SCE compared with the CP  
269 Ti ( $-0.221 \pm 0.04$  V vs. SCE) and Ti64 alloy ( $-0.158 \pm 0.03$  V vs. SCE). The  $K_1$  value that  
270 represented repassivation ability was calculated based on the formula (1), as shown in  
271 Fig. 8. It was observed that with the increase of Cu content, the value of  $K_1$  of Ti-10Mo-  
272 xCu alloys increased gradually, and it showed the maximum value of  $0.121 \pm 0.003$  when

273 adding 5% Cu content. While continuing to rise Cu content, the value of  $K_1$  decreased  
274 slightly to  $0.112\pm 0.002$ . In comparison with the  $K_1$  value of pure Ti ( $0.068\pm 0.003$ ) and  
275 Ti-6Al-4V ( $0.109\pm 0.002$ ),  $K_1$  of Ti-10Mo-3Cu alloy was greater indicating that the alloy  
276 had the highest re-passivation capability after sliding.

### 277 3.3.2 Potentiodynamic polarisation

278 Fig. 9 shows the PD curves of Ti-10Mo-xCu, alongside with CP Ti and Ti64 alloy  
279 under static corrosion and tribocorrosion conditions. No significant difference was found  
280 for the cathodic branches for all the alloys, indicating that a similar cathodic reaction  
281 occurred on the surface of Ti-10Mo-xCu, CP Ti, and Ti64 alloy. The anodic branches  
282 under both static corrosion and tribocorrosion conditions exhibited similar curves,  
283 characterised by three regions. Taking the Ti-10Mo-3Cu alloy under static corrosion as  
284 an example (Fig. 9a), in the first region, the current density increases with the scanning  
285 potential until it reached the second region. In the second region, the current density  
286 remained almost constant with the increase in the scanning potential, owing to the  
287 passivation of the surface. In the third region, the current density began to increase again  
288 with the increasing scanning potential due to the destruction of the formed oxide films by  
289 overpotential.

290 Table 1 lists the  $E_{\text{corr}}$  and  $i_p$ . It is obvious that under both static corrosion and  
291 tribocorrosion conditions, the  $i_p$  of Ti-10Mo-xCu alloy was lower than that of CP Ti and  
292 Ti64 alloy. With increasing in Cu content, the  $i_p$  of Ti-10Mo-xCu alloys decreased  
293 initially and then increased. Among them, the Ti-10Mo-3Cu exhibited the lowest  $i_p$  of  
294  $0.195\pm 0.02 \times 10^{-6} \text{ A/cm}^2$  and  $0.93\pm 0.05 \times 10^{-5} \text{ A/cm}^2$ , respectively. In theory, with more  
295 Cu, the corrosion resistance of Ti-10Mo-xCu alloy enhances due to more  $\beta$  and  $\text{Ti}_2\text{Cu}$   
296 intermetallic phases are generated [43, 44]. However, the corrosion resistance of Ti-  
297 10Mo-5Cu took on a downward trend instead. This is mainly because although  $\text{Ti}_2\text{Cu}$  can

298 improve the corrosion resistance, it can also form galvanic cells with the  $\alpha$  or  $\beta$  phase,  
299 which could reduce the corrosion resistance [45]. Compared with Ti-10Mo-3Cu alloy,  
300 there were more  $Ti_2Cu$  phases formed in Ti-10Mo-5Cu alloy, which can result in more  
301 galvanic cells formed in the Ti-10Mo-5Cu alloy. So, the corrosion resistance of Ti-10-  
302 3Cu was higher than the Ti-10Mo-5Cu alloy.

303 Additionally, it can be observed that the passive current density under the  
304 tribocorrosion conditions was generally higher than that under static corrosion conditions,  
305 indicating that mechanical wear can accelerate the corrosion process. As mentioned  
306 before, under the tribocorrosion conditions, the exfoliation of oxide films caused by  
307 sliding could expose the fresh-metal to the corrosive medium, thereby accelerating the  
308 corrosion process. In addition, galvanic corrosion occurring between the passivated areas  
309 (cathode) and the surrounding de-passivated areas (anode) under tribocorrosion  
310 conditions can also lead to an accelerated corrosion rate [46].

#### 311 4. Conclusions

312 Ti-10Mo-xCu alloy was fabricated from a PM route in this study. The effects of Cu  
313 content on pure mechanical wear, electrochemical corrosion, and tribocorrosion of Ti-  
314 10Mo-xCu alloys were fully investigated. The main conclusions can be summarised as  
315 follows:

- 316 (1) The Vickers micro-hardness of Ti-10Mo-xCu increases with the Cu content, and the  
317 Ti-10Mo-5Cu alloy exhibits the highest hardness of  $390.8 \pm 17.6$  HV due to the solid  
318 strengthening by Mo and Cu elements.
- 319 (2) The passive current density of Ti-10Mo-xCu alloys decreases initially and  
320 subsequently increases with an increase in Cu content under both static corrosion and  
321 tribocorrosion conditions. The Ti-10Mo-3Cu alloy exhibits the lowest passive

322 current density of  $0.195 \pm 0.02 \times 10^{-6}$  A/cm<sup>2</sup> and  $0.93 \pm 0.05 \times 10^{-5}$  A/cm<sup>2</sup>, respectively.  
323 (3) The Ti-10Mo-5Cu alloy exhibits the lowest wear rate of  $4.234 \pm 0.06$  mm/y and  
324  $8.25033 \pm 0.11$  mm/y under pure mechanical wear and tribocorrosion conditions  
325 respectively.  
326 (4) A synergy interaction between wear and corrosion accelerated the materials loss  
327 greatly. The wear mechanisms for all the Ti-10Mo-xCu alloys are a combination of  
328 delamination, abrasion and adhesion wear.

329

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339

### 340 **Data Availability**

341 The data that support the findings of this study are available from the corresponding  
342 authors on reasonable request.

343

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472

## Figure and table captions

473 **Fig. 1** XRD patterns (a) and Vickers micro-hardness (b) of Ti-10Mo-xCu alloys with  
474 different Cu content, alongside with the CP Ti, and Ti64 alloy for comparison

475 **Fig. 2** The COF of Ti-10Mo-xCu, alongside with CP Ti and Ti64 alloy in PBS solution  
476 at  $37 \pm 0.5$  °C under (a) pure mechanical wear and (b) tribocorrosion

477 **Fig. 3** 3D surface morphologies recorded on Ti-10Mo-xCu, CP Ti, and Ti64 alloy after  
478 pure mechanical wear (a-f) and tribocorrosion (g-l) tests: (a) and (g) Ti-10Mo; (b) and (h)  
479 Ti-10Mo-1Cu; (c) and (i) Ti-10Mo-3Cu; (d) and (j) Ti-10Mo-5Cu; (e) and (k) CP Ti; (f)  
480 and (l) Ti64

481 **Fig. 5** SEM and EDS analysis of Ti-10Mo-xCu alloys, alongside with the CP Ti, and Ti64  
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484 Ti; (f) and (l) Ti64

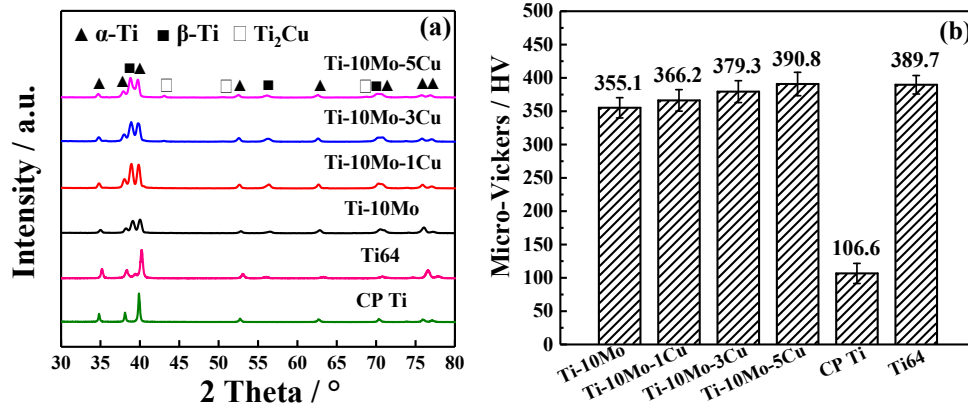
485 **Fig. 6** OCP vs. time curves for Ti-10Mo-xCu, alongside with the CP Ti and Ti64 alloy  
486 before static corrosion test in PBS solution at  $37 \pm 0.5$  °C

487 **Fig. 7** OCP vs. time curves for the Ti-10Mo-xCu, alongside with the CP-Ti and Ti64 alloy  
488 before, during, and after sliding in PBS solution at  $37 \pm 0.5$  °C

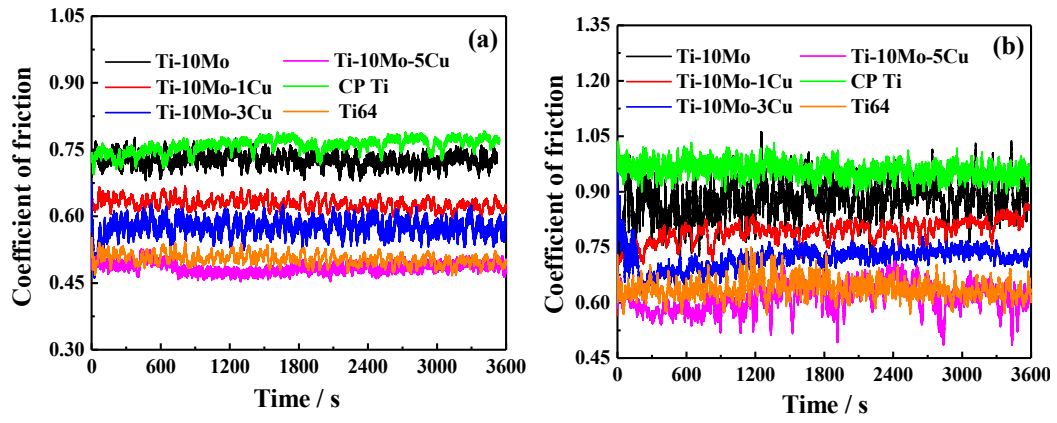
489 **Fig. 8** Repassivation rate of Ti-10Mo alloys with different Cu contents, CP-Ti alloy, and  
490 Ti64 alloy

491 **Fig. 9** The potentiodynamic polarisation curves of Ti-10Mo-xCu, alongside with the CP  
492 Ti, and Ti64 alloy under (a) static corrosion and (b) tribocorrosion conditions

493 **Table 1** Obtained corrosion parameters from the PD curves of Ti-10Mo-xCu, alongside  
494 with the CP Ti, and Ti64 alloy under static corrosion and tribocorrosion conditions

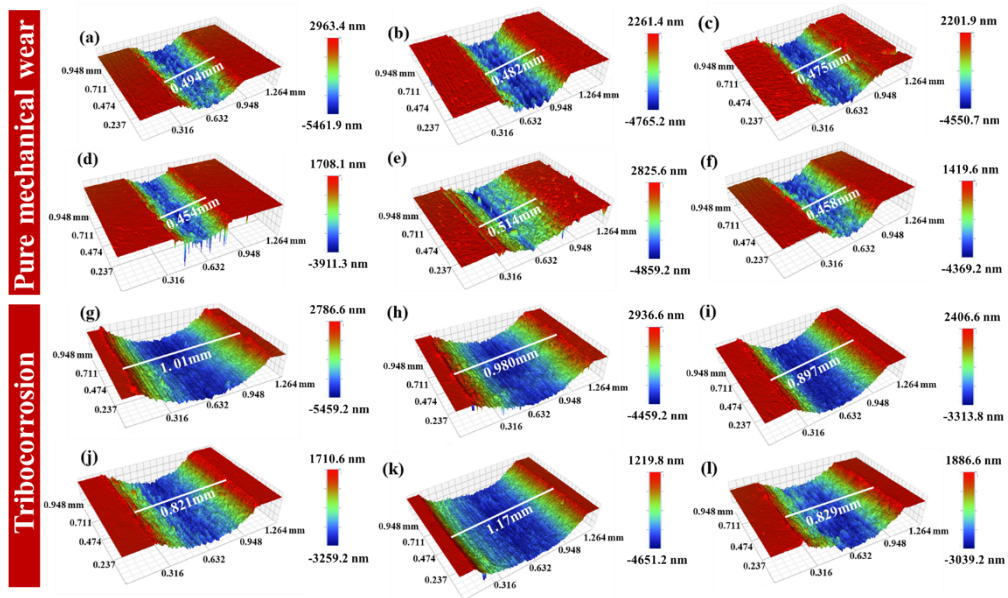


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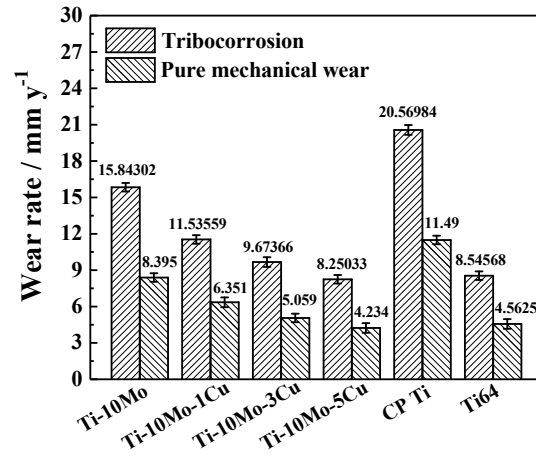


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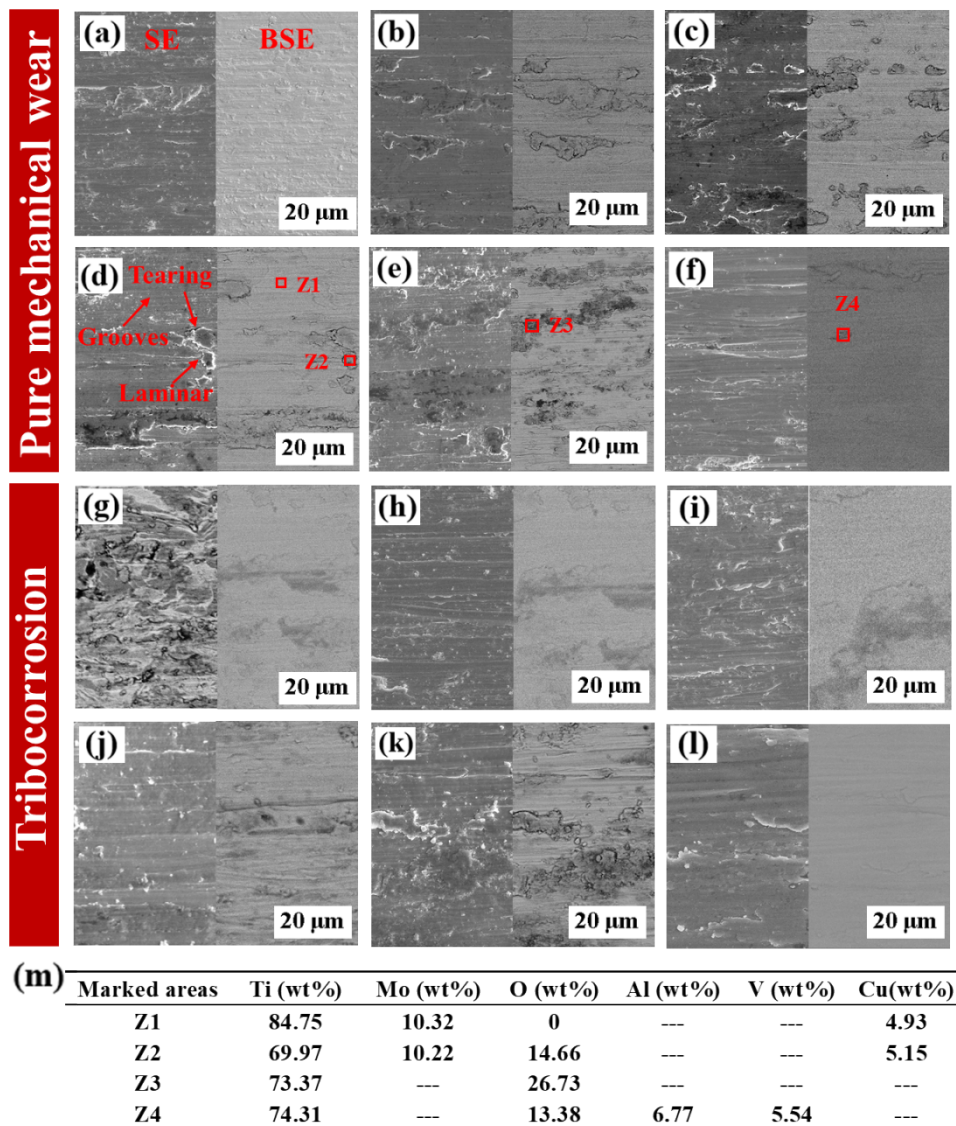




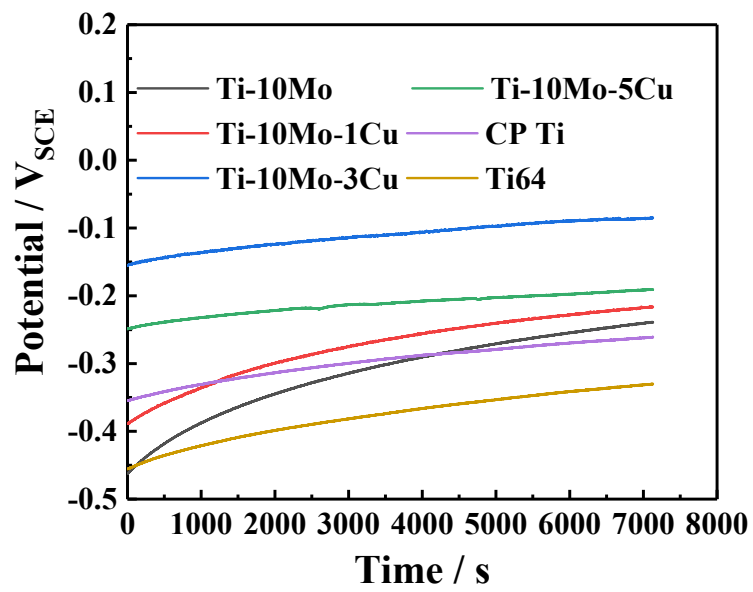
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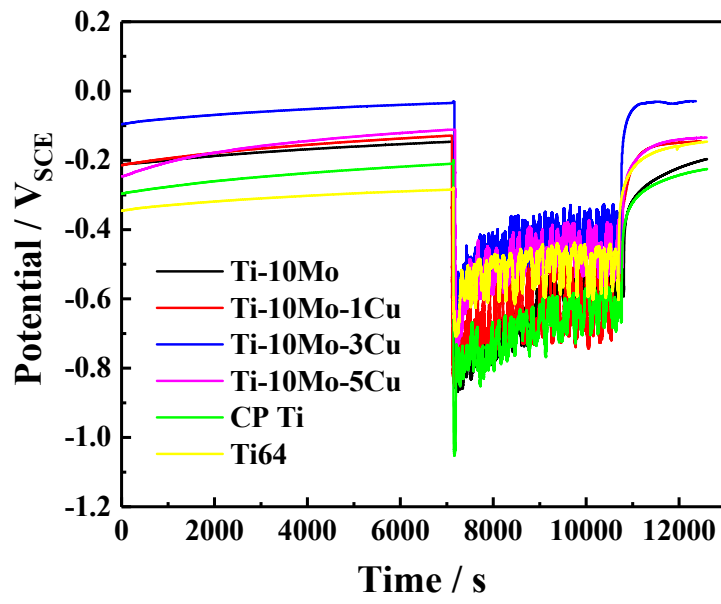
**Fig. 4** Wear rate of Ti-10Mo-xCu, CP-Ti, and Ti64 under pure mechanical wear and tribocorrosion test conditions



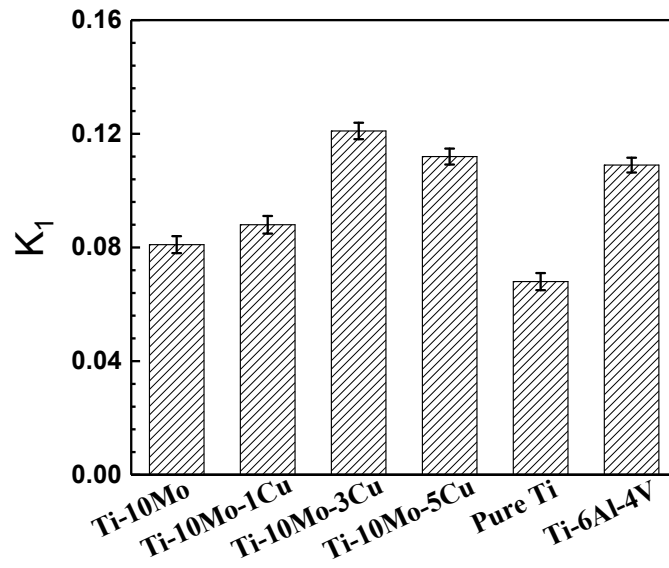
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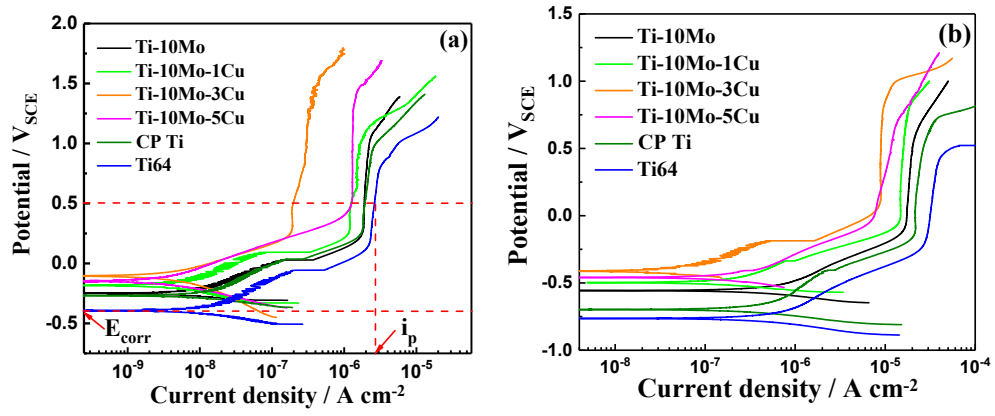
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**Fig. 8** Repassivation rate of Ti-10Mo alloys with different Cu contents, CP-Ti alloy and Ti64 alloy



**Fig. 9** The potentiodynamic polarisation curves of Ti-10Mo-xCu, alongside with the CP Ti, and Ti64 alloy under (a) static corrosion and (b) tribocorrosion conditions





**Table 1** Obtained corrosion parameters from the PD curves of Ti-10Mo-xCu, alongside with the CP Ti, and Ti64 alloy under static corrosion and tribocorrosion conditions

Alloy	Static corrosion		Tribocorrosion	
	$E_{\text{corr}}$ (V)	$i_p \times 10^{-6}$ (A/cm <sup>2</sup> )	$E_{\text{corr}}$ (V)	$i_p \times 10^{-5}$ (A/cm <sup>2</sup> )
Ti-10Mo	-0.249±0.05	1.89±0.05	-0.556±0.09	2.02±0.06
Ti-10Mo-1Cu	-0.185±0.02	1.27±0.06	-0.491±0.11	1.61±0.04
Ti-10Mo-3Cu	-0.106±0.01	0.195±0.02	-0.408±0.12	0.93±0.05
Ti-10Mo-5Cu	-0.154±0.02	1.25± 0.04	-0.455±0.08	1.15±0.08
CP Ti	-0.279±0.06	1.94± 0.06	-0.701±0.19	2.75±0.12
Ti64	-0.395±0.08	2.67± 0.07	-0.766±0.22	5.29±0.15

### **Conflict of interest**

The authors declare that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Author Statement**

Xin Lu: Conceptualization, Data curation, Formal analysis, Writing - original draft, Writing - review & editing, Supervision, Project administration; Dawei Zhang: Investigation, Writing - review & editing; Wei Xu: Conceptualization, Data curation, Formal analysis, Writing - original draft, Writing - review & editing; Aihua Yu: Data curation, Formal analysis, Investigation; Jiazhen Zhang: Investigation, Writing - review & editing; Maryam Tamaddon: Investigation, Writing - review & editing; Jianliang Zhang: Investigation, Writing - review & editing; XuanHui Qu: Formal analysis, Investigation; Chaozong Liu: Formal analysis, Investigation; Bo Su: Investigation, Writing - review & editing.