

## EFFECT OF COLD ROLLING ON ELECTROCHEMICAL IMPEDANCE BEHAVIOR OF NEW $\beta$ -TYPE Ti-6Mo-6V-5Cr-3Sn-2.5Zr ALLOY

In this study, the corrosion properties of Ti-6Mo-6V-5Cr-3Sn-2.5Zr alloy were investigated as a function of the cold rolling ratio and annealing temperature. The annealing treatment was carried out at temperature of 680°C, 730°C, and 780°C. The highest corrosion potential observed in the specimen with a 10% rolling ratio was 179 mV, which was more positive than that of the non-rolled specimen ( $-0.214 V_{SSC}$ ). The lowest corrosion current density ( $1.30 \times 10^{-8} A/cm^2$ ) was observed in the non-rolled specimen which suggested that the integrity of its passive oxide layer was superior to that of the cold-rolled specimens. Time-dependent EIS evaluation revealed that the consistency of the passive oxide layer was highly affected by the subjected rolling ratio over time.

*Keywords:* Beta-titanium alloy, Electrochemical impedance spectroscopy, Potentiodynamic polarization

### 1. Introduction

Titanium and its alloys are widely used in biomedical applications because of the formation of a passive film, composed mainly of amorphous titanium dioxide ( $TiO_2$ ) on their surface, which has high corrosion resistance and biocompatibility [1,2]. Titanium alloys are designed by alloying quantities of  $\alpha$ - and  $\beta$ -stabilizing elements; hence, the fractions of the  $\alpha$  and  $\beta$  phases are determined by the alloying elements [3].

Ti-6Al-4V alloy is the most commonly used alloy. The alloying element of aluminum (Al) has precipitation and solid solution hardening effects in  $\beta$ -titanium alloys. The high-strength titanium alloys such as Ti-4.5Fe-6.8Mo-1.5Al (TIMETAL LCB) [4], and Ti-3Al-8V-6Cr-4Mo-4Zr (Beta-C) [5] also possess Al elements that increase the strength. However, aluminum can cause cytotoxic effects or neurological disorders. Hence, titanium alloys without Al elements have been recently developed [6]. The alloy performance is strongly affected by the composition and microstructure. The microstructure of titanium alloys can be controlled by thermomechanical treatment [7]. The high strength of an alloy related to a small grain size but has a detrimental effect on its ductility [8]. Also, the grain size, including texture orientation, can be varied with plastic working. Therefore, a proper combination of heat and mechanical treatment is required to accomplish the strength-ductility trade-off [9].

In this study, the effects of cold rolling and annealing on the corrosion properties of the Ti-6Mo-6V-5Cr-3Sn-2.5Zr alloy were investigated.

### 2. Experimental

Newly developed  $\beta$ -type Ti-6Mo-6V-5Cr-3Sn-2.5Zr (wt%) alloy was fabricated by a vacuum arc re-melting (VAR, ACE VACUUM, AVA-1500, Korea) process. Commercially pure titanium chips (ASTM CP Grade II), 99.8 wt% pure Mo bars, 99.9 wt% pure V sheets, 99.9 wt% pure Cr chips, 99.9 wt% pure Sn balls and 99.9 wt% pure Zr sheets were melted in a water-cooled copper hearth, using a tungsten electrode arc furnace. The as-cast specimens were then homogenized at a temperature of 850°C for 4 h, subjected to solution treatment at 780°C for 30 min, and quenched with water. The solution-treated specimens were then subjected to uniaxial cold rolling with rolling ratios of 10%, 30%, and 50%. Following cold rolling, all the specimens were subjected to heat treatment at 680, 730, and 780°C for 10 and 30 min to evaluate the corrosion properties after cold rolling.

The electrochemical test was conducted in a flat cell containing 300 ml TAS simulated body fluid (TAS-SBF) solution at pH 7.41 and a temperature of  $37 \pm 1^\circ C$  using a PARSTAT 2273 potentiostat/galvanostat (Princeton Applied Research). A three-electrode cell was used for potentiodynamic polarization tests, where the reference electrode was a silver-silver chloride electrode (SSC), the counter electrode was made of platinum plate, and the specimen was the working electrode. All experiments were carried out at a constant scan rate of 0.25 mV/s, initiated at  $-250$  mV below the open-circuit potential.

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### 3. Results and discussion

Fig. 1 shows the potentiodynamic polarization curves of the Ti-6Mo-6V-5Cr-3Sn-2.5Zr alloy as a function of the rolling ratio. In general,  $E_{\text{corr}}$  represents the corrosion potential and  $i_{\text{corr}}$  represents the current density. A low  $i_{\text{corr}}$  indicates a more stable passive film and less corrosion. There was no significant pattern to the potential shifts following the cold rolling. Furthermore, the highest corrosion potential shifting was only around 179 mV at a 10% rolling ratio and toward the positive zone, which indicates that this specimen was thermodynamically more stable than the other specimens. It was also found that the formation of a passive layer on all the specimens occurred at a slow rate, as signified by the polarization graph. The lowest current density ( $1.3 \times 10^{-8} \text{ A/cm}^2$ ) was observed in the non-rolled specimen, while the specimen with a 10% rolling ratio showed the highest corrosion current density of  $1.86 \times 10^{-7} \text{ A/cm}^2$ . The high current density of the cold-rolled specimens could be due to the residual stress residing along the grain boundaries, which are known to be the preferable corrosion sites. Further increasing the rolling ratio up to 50% gradually reduced the corrosion current density to  $1.34 \times 10^{-8} \text{ A/cm}^2$ , which was slightly higher than that of the non-rolled specimen. The corrosion current density gradually decreased as the rolling ratio increased [10]. At a higher potential, the passive oxide layer which formed on the surface of the cold-rolled alloys became less stable and gradually disintegrated. It was clearly visible at the 50% rolling ratio that the disintegra-

tion rate of the oxide layer was faster than those at lower rolling ratios. The integrity of the passive oxide layer on the non-rolled specimen seemed to be superior to that of the cold-rolled specimens. In comparison with those of the available cardiovascular stent materials such as 316L stainless steel and L605 (Co-Cr) alloy, the corrosion resistance of the currently studied Ti alloy appeared to be superior [11].

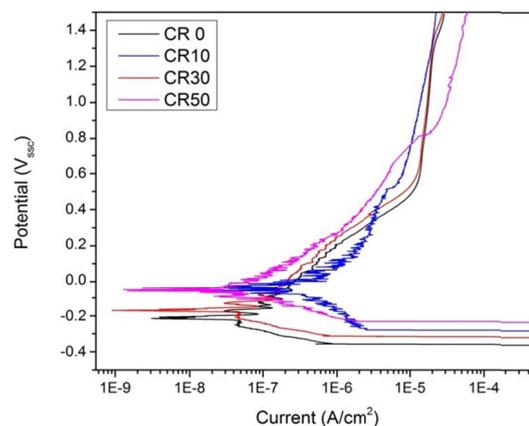


Fig. 1. Potentiodynamic polarization curves as a function of cold rolling ratios of 10%, 30%, and 50%

Fig. 2 displays the potentiodynamic polarization curves of the cold-rolled specimens with rolling ratios of (a) 10%, (b) 30%, and (c) 50% followed by heat treatment at various tem-

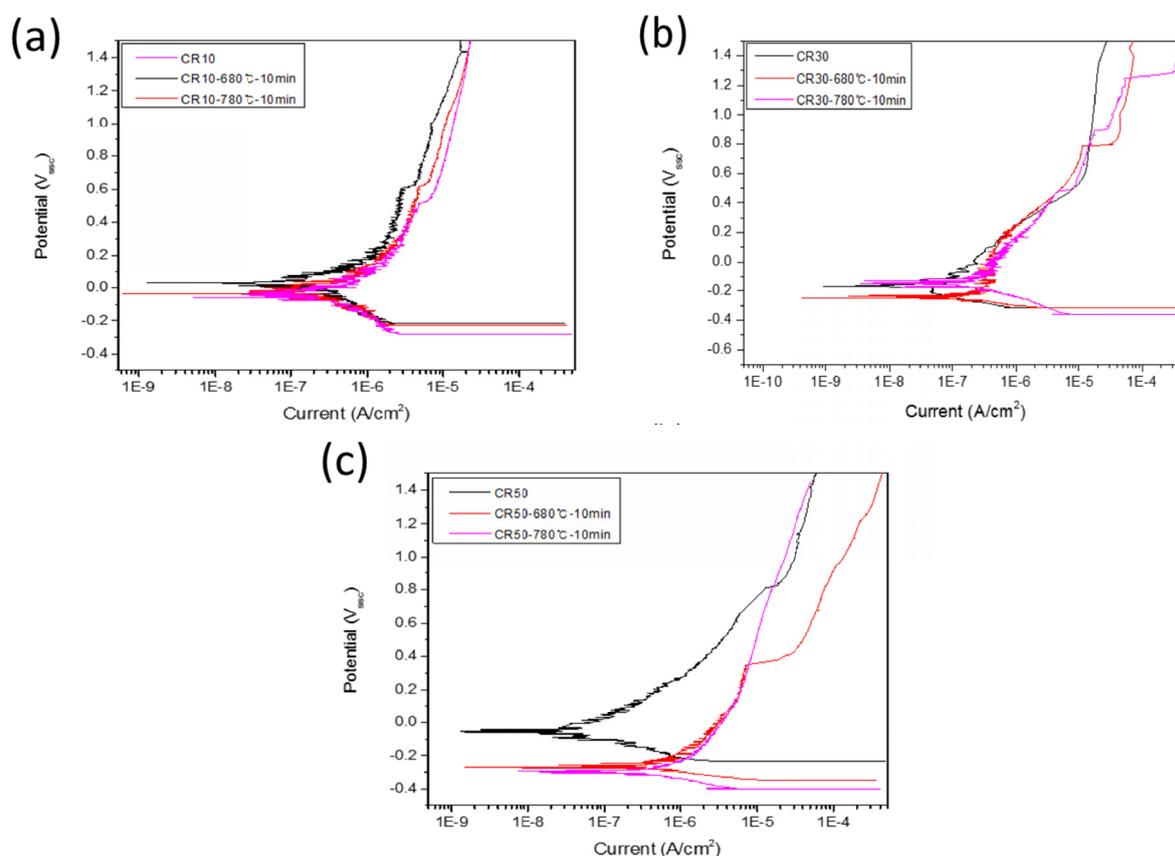


Fig. 2. Potentiodynamic polarization curves of cold-rolled specimens with rolling ratios of (a) 10%, (b) 30%, and (c) 50% followed by heat treatment at various temperatures for 10 min

peratures for 10 min. The heat treatment temperature was set below or above the  $\beta$ -transus temperature of  $690^{\circ}\text{C}$ . It could be observed that there was a slight change in the corrosion potential toward the positive zone upon heat treatment below the  $\beta$ -transus temperature, at  $680^{\circ}\text{C}$  and for 10 min. However, heat treatment above the  $\beta$ -transus temperature, at  $780^{\circ}\text{C}$ , for 10 min simply shifted it back toward the negative zone. On the other hand, heat treatment at  $680^{\circ}\text{C}$  slightly lowered the overall corrosion current density. This could be due to the abundant formation of the  $\alpha$  phase in the microstructure, which did not transform when the heat treatment temperature was below the  $\beta$ -transus temperature. Increasing the heat treatment temperature to  $780^{\circ}\text{C}$  slightly increased the corrosion current density to a value close to that of the non-heat-treated specimen ( $1.8 \times 10^{-7} \text{ A/cm}^2$ ). The formation of the mixed  $\alpha$  and small amount of  $\beta$  phase, observed after the heat treatment at  $780^{\circ}\text{C}$ , appeared to be the reason for this corrosion behavior. In contrast to the specimens with a 10% rolling ratio, those with a 30% rolling ratio showed significant improvement in the corrosion current density (by 1 magnitude) among the specimens heat-treated at  $680^{\circ}\text{C}$  for 10 min. A finer  $\alpha$  phase microstructure seems to play an important role in improving the corrosion resistance. However, the oxide passive layer formed on the surface appeared to be less protective in specimens with a rolling ratio beyond 30%. The lowering of the breakdown potential value of the specimen heat-treated at  $680^{\circ}\text{C}$  for 10 min was an indication of the low integrity of its passive layer. Corresponding to that of a 30% rolling ratio, a 50% rolling ratio resulted in an improvement in the corrosion resist-

ance. Although the corrosion potentials tend to shift toward the negative zone, the overall current density decreased by one order of magnitude. An improvement in corrosion current density was observed in the specimen heat-treated at  $680^{\circ}\text{C}$  for 10 min. This suggested that the presence of the martensite ( $\alpha''$ ) phase formed after quenching played an important role in the corrosion current density improvement. In addition, the superior corrosion characteristics after heat treatment at  $680^{\circ}\text{C}$  were due to the finer grain size observed after heat treatment at this low temperature [11].

Fig. 3 displays the potentiodynamic polarization curves of the cold-rolled specimens with rolling ratios of (a) 10%, (b) 30%, and (c) 50% followed by heat treatment at various temperatures for 30 min. It appears that a longer holding time of up to 30 min could not significantly improve the corrosion performance of the studied alloy as the lowest current density observed was with the specimen heat-treated at  $680^{\circ}\text{C}$  with a 10% rolling ratio. At a higher rolling ratio, increasing the holding time to 30 min appeared to be sufficient in improving the integrity because the breakdown potential increased. However, the severe damage of the grains following cold rolling increased the susceptibility to pitting corrosion even after 30 min of heat treatment. The previous study [6] also suggested that after annealing, which was performed at a temperature of  $680^{\circ}\text{C}$  following cold rolling, a small fraction of the  $\alpha$  phase was observed. These results suggested that the  $\alpha$  phase influenced the overall corrosion characteristics of the studied alloy.

Fig. 4 displays the Nyquist plots of Ti-6Mo-6V-5Cr-3Sn-2.5Zr as a function of the immersion time at cold rolling ratios

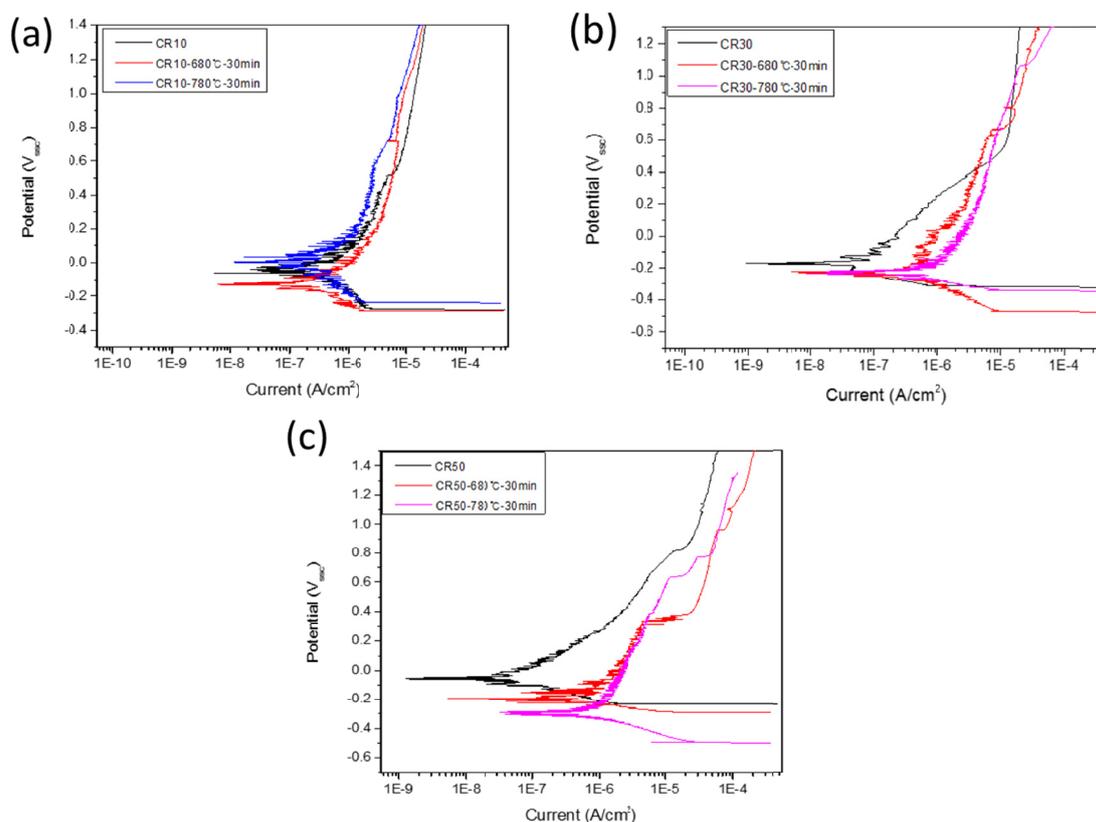


Fig. 3. Potentiodynamic polarization curves of cold-rolled specimens with rolling ratios of (a) 10%, (b) 30%, and (c) 50% followed by heat treatment at various temperatures for 30 min

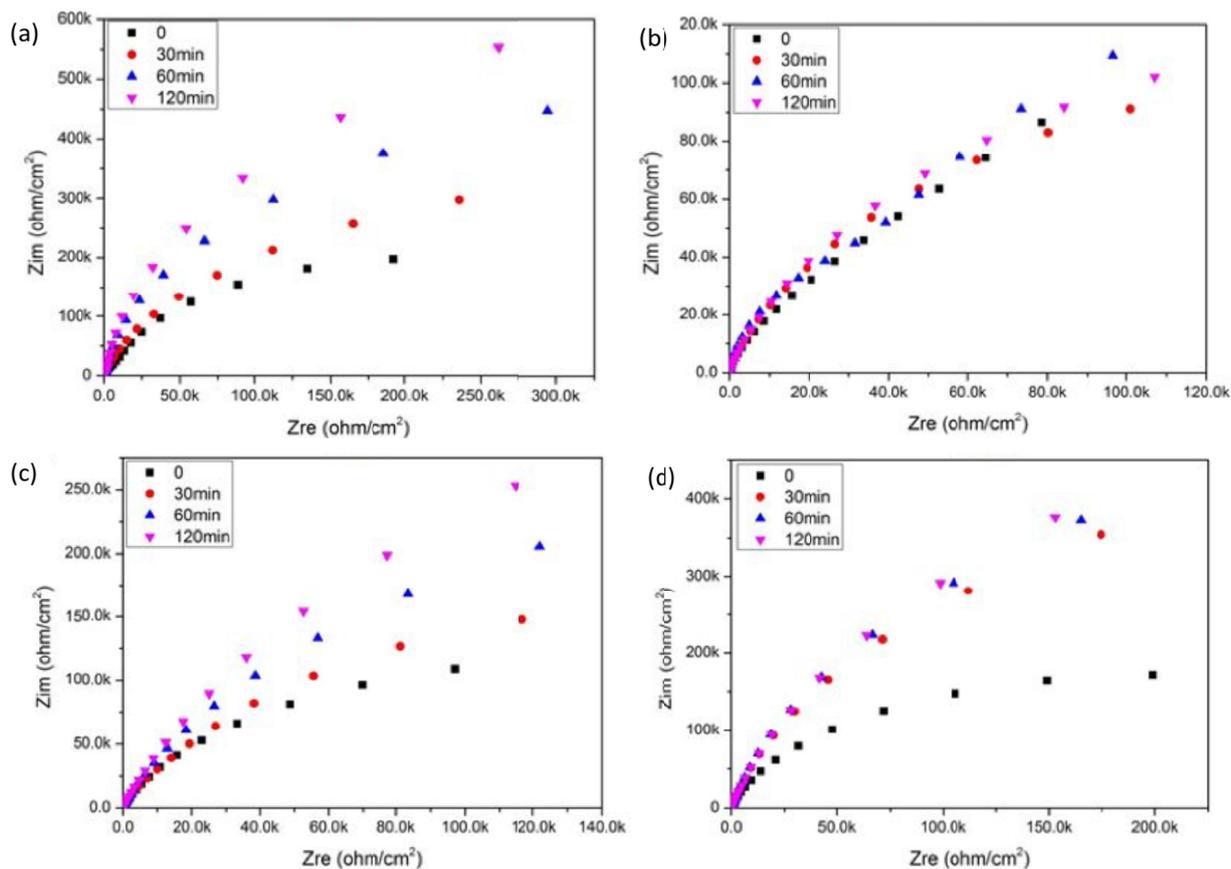


Fig. 4. Nyquist plots of Ti-6Mo-6V-5Cr-3Sn-2.5Zr as a function of immersion time at cold rolling ratios of (a) 0%, (b) 10%, (c) 30%, and (d) 50%

of (a) 0%, (b) 10%, (c) 30%, and (d) 50%. The value of the semicircle represents the magnitude of the corrosion resistance, i.e., as the semicircle widens, the ion elution decreases and the corrosion resistance increases. As shown in Fig. 4(a), as the immersion time increased, the size of the semicircle also increased. This indicated that the passive film of the specimen was stable. Fig. 4(b) shows that the size of the semicircle at 60 min was greater than that at 120 min. This meant that the passive film of the specimen was unstable. When the immersion time increased in Fig. 4(c) and (d), the size of the semicircle also increased. The magnitude of corrosion resistance was largest in the non-rolled specimen and smallest in the specimen with a 10% rolling ratio. This behavior was similar to that in the previous polarization experiment.

#### 4. Conclusions

The corrosion resistance of the specimens annealed at 680°C after cold rolling were superior due to the small grain sizes of the specimens and the presence of the  $\alpha$  phase. The current density value in the non-rolled specimen was  $1.30 \times 10^{-8} \text{ A/cm}^2$ , and the corrosion resistance of the currently studied Ti alloy appeared to be superior compared to the available cardiovascular stent materials such as 316L stainless steel and L605 (Co-Cr) alloy.

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