Micro-electrochemical evaluation of \( \alpha \)- or \( \beta \)-type titanium alloys

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Abstract. In order to evaluate electrochemical stabilities of \( \alpha \), \( \beta \) phases, the micro-electrode techniques was employed to test the micropolarization behavior of \( \alpha \)-type pure Ti and \( \beta \)-type Ti15Mo alloys. The comparison between macropolarization and micropolarization curves demonstrates that the \( \alpha \)-type pure Ti alloy tends to exhibit the uniform corrosion, on the other hand, the pitting corrosion is the main form for the \( \beta \)-type Ti15Mo alloys. The \( \alpha \) grains with different orientations shows similar polarization behavior, but the polarization behavior of those \( \beta \) grains are strongly affected by their crystalline orientations, particularly the worse electrochemical stabilities of \( \beta \) grains with (200)-dominance. The corrosion potential and corrosion current density of \( \alpha \)-type pure Ti is lower than \( \beta \)-type Ti15Mo alloys. The \( \alpha \) grains have better electrochemical stabilities in comparison to \( \beta \) grains, which indicate that the \( \alpha + \beta \) dual-phase Ti-6Al-4V ELI alloys is highly possible to suffer from the preferential dissolution of \( \beta \) grains in free immersion condition and/or polarized states. Finally, by combining the SEM, EDS and polarization curves of dual-phase Ti-6Al-4V ELI alloys, it is concluded that \( \beta \) phases are corroded prior to \( \alpha \) phases.

1. Introduction
Titanium alloys are widely used in the aerospace, marine engineering, biomedical and other fields because of their good properties such as good fatigue and corrosion resistance, high strength to weight ratio, non-magnetic and good biocompatibility\([1-5]\). Titanium alloys are generally classified into three types according to their different microstructures, \( \alpha \)-type, \( \beta \)-type, and \( \alpha + \beta \) titanium alloys\([6]\). Currently, the most widely used are \( \alpha \)-type and \( \alpha + \beta \) titanium alloys. With the extensive applications of titanium alloys in the ship industries and marine engineering, it is especially necessary to investigate the corrosion behavior of titanium alloys. Characteristic differences of \( \alpha \) and \( \beta \) phases in dual-phase titanium alloys can result in the different corrosion behavior of \( \alpha \)- and/or \( \beta \)-phase in the corrosive mediums, such as corrosion forms, corrosion morphology and even the corrosion mechanisms. In special corrosion conditions, \( \alpha \) or \( \beta \) phases are preferentially corroded and become vulnerable regions of corrosion, resulting in the failures of titanium alloys in the form of stress cracking corrosion. Therefore, evaluation of the electrochemical properties of the \( \alpha \) and \( \beta \) phases is important for understanding the corrosion mechanisms of titanium alloys. The macropolarization behavior of dual-phase titanium alloys has been widely evaluated by the conventional polarization measurements to reflect the integrated effects of all coexisting phases in the matrixx before. The capillary microelectrode methods have been developed to investigate the corrosion behavior of inclusions\([7-9]\) and the intermetallic phases last decades\([10,11]\). However, the evaluation of the individual \( \alpha \) phases and \( \beta \) phases in the electrochemical stabilities has not been conducted before.
In order to study the different electrochemical properties of \( \alpha \) and \( \beta \) phases, \( \alpha \)-type pure Ti, \( \beta \)-type Ti15Mo alloys and dual-phase Ti-6Al-4V ELI alloys were studied by traditional macro-polarization electrochemical methods and micro-area masking corrosion testing techniques. The X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), optical microscopy (OM) and micro-electrochemical experiments were employed to judge which has a better electrochemical stability between \( \alpha \) and \( \beta \) phases of the titanium alloys. Through the above studies, micro-electrochemical evaluation of \( \alpha \), \( \beta \) phases of titanium alloys can be achieved.

2. Experimental procedure

Two model alloys, \( \alpha \)-type pure Ti and \( \beta \)-type Ti15Mo alloys, were prepared by using a water-cooled cold copper crucible suspension melting furnace, and the samples of Ti-6Al-4V ELI alloy with basket-woven microstructure were purchased from Baotai Co. Ltd. Both \( \alpha \)-type pure Ti and \( \beta \)-type Ti15Mo alloys were used in their as-forged states, because the phase size of the alloys was several hundredth micrometers so that the micro-polarization behavior of two alloys can be easily studied by using the micro-area masking corrosion testing techniques. The specimens were polished successively to 2000 grits with SiC papers and 1 \( \mu \)m \( \text{Al}_2\text{O}_3 \) pastes. The as-forged alloys were directly used for electrochemical evaluation because the \( \alpha \) or \( \beta \) grains are able to expose to the testing solutions by using the organic sealing chemical agents under the help of optical microscopes. Before the electrochemical and surface analysis tests, the samples were ultrasonically cleaned in ethanol and pure water. The etching solution of HF:HNO\(_3\):H\(_2\)O (volume ratio is set as 1:2:7) is used to prepare the metallographic samples. Electrochemical testing of two alloys were performed in the self-made electrochemical cells equipped with a reference electrode of \( \Phi 0.1 \) mm Ag wires with AgCl coatings and a counter electrode of \( \Phi 0.1 \) mm Pt wires. The test areas were masked by using the insoluble organic agents purchased from Wako Sendai Co. Ltd. Micro-area masking corrosion testing techniques[9] were used to perform the micro-polarization measurements on the exposed areas marked with aid of XRD analysis and optical microscope. The polarization curves were collected in 0.1mol/L NaCl solution by an electrochemical workstation (Corrtest, CS350) with a scan rate of 1 mV/s. The metallographic structure and microstructure of two alloys were observed by using an optical microscope (OM, ZEISS, AxioObserver.A1m) and a scanning electron microscope (JEOL, FEI Quanta 200). The chemical compositions of the samples were determined using an energy dispersive X-ray spectroscopy (EDS, JEOL, FEI Quanta 200). Identification of the grain orientations and the crystalline states of the model alloys at the corresponding exposed areas were conducted by an X-ray diffractometer (XRD, Rigaku, Geigerflex) and an optical microscope (OM, ZEISS, AxioObserver.A1m).

3. Results

3.1. Micro-polarization behavior of \( \alpha \) phases in \( \alpha \)-type pure Ti

The metallographic photos of as-forged \( \alpha \)-type pure Ti are shown in Fig 1. It can be seen that the metallographic structure of \( \alpha \)-Ti consists of \( \alpha \) phases with a size of several hundredth micrometers. The masked micro-regions with rectangular areas of about 100 \( \mu \)m×100 \( \mu \)m are marked in Fig 1. The \( \alpha \)-type pure Ti has close-packed hexagonal structure. The XRD patterns of \( \alpha \)-Ti macro-region and six micro-regions are shown in Fig 2. It can be clearly seen that the XRD patterns in macro-regions are typical and those in the micro-regions are different in the crystalline orientations. The diffraction peaks at 20 of 35°, 38°, 40°, 53°, 63°, 70°, 76° and 77° were assigned to (100), (002), (101), (102), (110), (103), (112) and (201), which are corresponded to the diffraction patterns of \( \alpha \) phases. Figure 3 shows the polarization curves of the macro-region and the corresponding micro-regions marked in Fig 1. The curve fluctuates around -0.1, 0, 0.05 and 0.1 V in the polarization curve of the macro-region which is considered to be due to the high dissolution of less stable \( \alpha \) phases with different orientations such as (101) dominant grains in Region 2 and 4. The grains with a preferential dominance of (002) in Region 1, 3, 5 and 6 have relatively large passive current densities, indicating their higher electrochemical
activities. The vulnerable parts of corrosion protective films on α-type pure Ti surface are damaged instantaneously while being pitted, and the corrosion protective films were repaired rapidly. It can be seen from the corresponding polarization curves that both corrosion potential and corrosion current density are larger than those in macro-region. It can be concluded that the corrosion potential and pitting potential of α-Ti are about -0.42 and 0.11 V, respectively. The corrosion current density of macro-region is about 2.65×10⁶ A/cm² and the other six micro-regions are about 8.07×10⁶ A/cm². The electrochemical properties of the macro-region and the other six micro-regions are not much different.

Fig. 1 OM micrograph of α-type pure Ti in macro-region.

Fig. 2 XRD patterns of α-type pure Ti in macroscopic and different regions marked in Fig.1.

Fig. 3 Polarization curves of α-type pure Ti in macroscopic and different micro-regions.

Fig. 4 shows the SEM morphology of α-type pure Ti in macroscopic and different grains before and after micro-electrochemical tests. There are almost no pits on the surface of the remaining micro-region in Fig. 4a. SEM images of the α-type pure Ti without masking shows the uniform corrosion without localized corrosion in the whole macro-region. The dissolution tended to be uniform. In other regions, such as the corrosion morphology in Region 3-5 in Fig. 4, the corrosion were considered to be uniform. But the corrosion morphology in Fig. 4b, several small pits can be observed which are considered to be from the some small intermetallic particles distributed from the interstitial inclusions. Therefore, the corrosion for α-type pure Ti is concluded to be uniform and the effect of the grain boundaries is able to be neglected.
3.2. Micro-polarization behavior of β-type Ti15Mo alloys

The metallographic structure of as-forged β-type Ti15Mo alloy is shown in Fig 5. The grains of β-type Ti15Mo alloys are several hundredth micrometers in size. The selected micro-regions on different grains are marked in Fig. 5. The β-type Ti15Mo has body-centered cubic structure. XRD patterns on the macro-region and six micro-regions are shown in Fig 6. Compared with complex orientations in the XRD patterns of α-type pure Ti, there are three orientations in the crystal planes of β-Ti(Mo) grains, which are (110), (200), (211) corresponding to the diffraction peaks at 2θ of 39°, 56° and 71°, respectively. In Region 1, the XRD pattern in Fig. 6 shows the dominant distribution of (200) and (110) orientations of the crystal planes. The (211) and (110) orientations of the crystal planes are prevailed in Region 5. The XRD patterns in other micro-regions are similar with that of macro-regions. The macropolarization curves of macro-region and the micropolarization curves of six micro-regions of the β-type Ti15Mo alloys are shown in Fig. 7. It can be seen that the corrosion potential in the macro-region and the other six micro-regions is between about -0.26 V. The corrosion potential of the macro-region is about -0.23 V, and its corrosion current density is smaller than those at the other six micro-regions. The breakdown potential of the native passive films, so-called pitting potential, was 0.13 V. Compared with the polarization curves of α-type pure Ti, the passivation potential range of β-type Ti15Mo alloy is narrow. The micropolarization curves in the β grains can be divided into two groups: Group I from Region 1-3 and Group II from Region 4-6. It can be seen from the XRD pattern of Region 1 that the peak intensity of the (200) crystal plane is significantly higher than that of the macroscopic region. The pitting potential is confirmed to be -0.15 V, comparable to those in Region 2 and 3. The corresponding micro-polarization curve continuously fluctuates between -0.15 and 0.13 V. This is due to the repeated process of pitting corrosion destroying the protective film on the surface of the regions and the rapid self-healing of the protective films, which results in the increase of pit depths and corrosion area. As shown in Fig. 8b, a plurality of corrosion pits are joined together to form a large one. In addition, the micropolarization curves of Regions 2 and 3 are very similar to that of Region 1, and the corrosion behavior is considered to be similar. The corrosion potential is about -0.29 V, and the corrosion current density is significantly larger than that of the macro-region. The polarization curves of Group II for Region 4, 5 and 6 show that the corrosion potential is about -0.24 V, close to that of macro-region, and the corrosion current density is also larger than macro-region. Thus, the corrosion potential of β-Ti(Mo) phases is slightly positive than that of α-Ti phases, which is ascribed to integrated enhancement of the corrosion resistance of passive films consisting of MoO₃[12-14]. The corrosion current density of macro-region is about 6.59×10⁻⁶ A/cm² and the other six micro-regions are about 3.94×10⁻⁴ A/cm². However, the corrosion current density of micro-regions is about two orders of magnitude larger than that of the α-Ti phases. On the basis of the micropolarization curves of Group I and Group II, the distribution of (110) and (200) orientations played an important role of the shift of the pitting potential. The more the grains with higher distribution of (110) and (200) orientations, the worse corrosion resistance is regarded to be.
3.3. Integrated macro-polarization behavior of dual-phase Ti-6Al-4V ELI alloys

Figure 9a is a SEM image of $\alpha$+$\beta$ dual-phase Ti-6Al-4V ELI alloys after etching in the above metallographic solution. The black area in the image corresponds to $\alpha$ phase, and $\beta$ phases in the flaky white area are distributed in Ti-6Al-4V ELI alloys with the basket-weave microstructure. After corrosion, Ti-6Al-4V ELI alloys structure has been difficult to see with basket-weave structure, because phase structure has been corroded in large quantities. However, the distribution tendency of the stabilizing Al element for $\alpha$ phase and V element for $\beta$ phase is considered to be the similar. EDS
spectra of Zone A and Zone B in Fig. 9b exhibited that the elemental composition of Zone A is 94.38% of Ti, 4.65% of Al and 0.97% of V, and these of Zone B is 88.27% of Ti, 3.20% of Al, and 8.53% of V. The largest difference in the elemental composition between Zone A and B is the V content, and the V content in Zone A is significantly less than the percentage of Zone B. It can be seen that the major phases are α-Ti, and the white β phases have been dissolved preferentially. As shown in the polarization curve in Fig. 9c, there is a small increase of the current densities at 0.07-0.12V, which might be due to the preferential dissolution of the β phases in Ti-6Al-4V ELI alloys. On the other hand, there are many etched grain boundaries and the black regions in the metallographic images in Fig. 5, which is regarded to result from the fast corrosion of the β phases. These facts prove that the β phases in Ti-6Al-4V ELI alloys have higher electrochemical activities and is corroded prior to coexisting α phases[15]. The macropolarization behavior of single-crystal titanium alloys might be better for understanding the corrosion mechanism, although the experiments are difficult to conduct so far.

Fig. 9 Scanning electron microscope (SEM) images of α+β dual-phase Ti-6Al-4V ELI alloys (a), EDS spectra corresponding to Zone A and B (b), and Macropolarization curves of Ti-6Al-4V ELI alloys in macro-region (c).

4. Summary
On basis of the crystalline and orientation analysis by XRD, observation of the corrosion morphology and the micropolarization behavior of the two α-type pure Ti and β-type Ti15Mo alloys and two-phase Ti-6Al-4V ELI alloys, the orientations of the crystalline planes and the distribution of the intermetallic phases can affect the micropolarization behavior. The corrosion of α-Ti phase in α-type pure Ti tends to take place uniformly, but that of β-phase in β-type Ti15Mo alloys is more localized. The corrosion rate of α phases in the 0.1 mol/L NaCl solution is significantly lower than that of β phases. For the two-phase titanium alloys, β phases are corroded prior to α phases due to the less electrochemical stabilities of β-phases.

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