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Effects of Heat Treatment on the Mechanical Property and Corrosion Behavior of PT-7M Titanium Alloy

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ABSTRACT

The effects of heat treatment on the mechanical property and corrosion behavior of PT-7M titanium alloy have been evaluated. The alloy was heat-treated in the temperature range of 500 to 1000℃ for 1 hr, and water quenched. Tensile test results indicated that there was little effect of the α heat-treatment (from 500 to 900℃) on the strength and ductility of this alloy whilst there was a considerable reduction of the strength and ductility in the alloy heat-treated at the β-Ti phase region (1000℃). The hardness test results revealed that there was little effect of the α heat-treatment on the hardness values whilst the β heat-treatment induced a significant increase of the hardness values in this alloy. It would be mainly attributed to the microstructure change by the β heat-treatment. Corrosion test results at 360℃ in an ammonia aqueous solution of a pH 9.98 showed that the α heat-treatment of this alloy induced a significant reduction of corrosion resistance. It would be mainly responsible for the enlargement of precipitate size.

1. INTRODUCTION

Titanium and its alloys are increasingly being used in conditions where a high corrosion resistance is required, because of its excellent corrosion resistance due to the high stability and protective character of the titanium oxide. Moreover, its good mechanical properties along with density ratio make these materials very attractive for applications in which reduced weight is an important consideration. These attractive properties of titanium make it possible to use in

marine and certain chemical industry equipments [1-8].

Meanwhile, SMART (System-integrated Modular Advanced ReacTor) has been recently developed for the electricity generation and seawater desalination; it is a small-sized advanced integral PWR (Pressurized Water Reactor). However, there is little identification about the effects of heat treatment on the mechanical property and corrosion behavior of PT-7M titanium alloy, which is considered as a material for steam generator U-tube in SMART. It is expected that the mechanical property of PT-7M alloy would be possibly dependent on the heat-treatment temperature in the α- and β-Ti regions. In addition, the heat-treatment in the temperature range of α-Ti region would affect on the corrosion behavior of this alloy.

In this study, the effects of heat-treatment on the mechanical property and corrosion resistance of PT-7M titanium alloy have been evaluated. The evaluation of mechanical properties of this alloy was performed by the tensile and hardness tests at room temperature, and that of corrosion behavior of this alloy was also carried out at 360℃ in the ammonia aqueous solution of a pH 9.98 using a recirculating loop system.

PT-7M: CAS Registry number 66082-54-0 (American Chemical Society).

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2. EXPERIMENTAL PROCEDURE

The chemical composition of PT-7M titanium alloy examined in this study is analyzed and given in Table 1. The as-received alloy tubes (6 mm outer dia.× 4 mm inner dia.) were subjected to heat treatment in the temperature range of 500 to 1000℃ for 1 hr, respectively, and then water quenched. The Vickers hardness test was carried out. Room temperature tensile tests were also performed at a constant crosshead speed of 0.127 mm/s. The corrosion behavior was evaluated at 360℃ in the ammonia aqueous solution adjusted to a pH 9.8 under a pressure of 2680 psi for 116 days using a recirculating loop system.

The microstructures of the as-received and heat-treated alloys were examined using an optical microscopy (OM) and a transmision electron microscope (TEM). The fractured surfaces of the tensile tested alloys were examined using a scanning electron microscope (SEM). The chemical structures and morphologies of oxides formed in this alloy were also examined using a X-ray diffraction (XRD) and a SEM.

3. RESULTS AND DICUSSION

3.1 Microstructure

Fig. 1 shows the cross-sectional microstructures of as-received and heat-treated PT-7M titanium alloy tubes at 800, 900 and 1000℃ for 1 hr. The as-received alloy revealed an average grain size of 10 μm. By the heat treatment, there was a considerable enlargement of the grain size in this alloy. In particular, the alloys heat-treated alloys above 900℃ showed recrystallization structures. This implies that the final heat-treatment temperature after a final pilgering stage in the manufacturing procedures of this alloy would be in the temperature of 800 to 900℃. The heat-treated alloy at 1000℃ for 1 hr showed the mixture of a hexagonal close-packed (hcp) α and the body centered-cubic (bcc) β phases including a significant grain growth. This observation implies that the heat-treatment at 1000℃ for 1 hr was not sufficient to complete transformation from the α phase to β one. In addition, this result reflects that the α-β transition temperature of this alloy would be in the temperature of 900 to 1000℃. In the case of pure titanium alloy, the α-β transition temperature is about 882℃. It is thus considered that the α-β transition temperature of PT-7M titanium alloy is somewhat higher than that of pure titanium alloy.

Fig. 2 shows a bright field TEM image of the longitudinal section of as-received PT-7M titanium alloy tube. The as-received PT-7M titanium alloy having the α structure (hcp, a = 0.2950 nm, c = 0.4686, c/a = 1.59) showed a fully recrystallization structure with an average grain size of about 20 μm. This means that the final annealing temperature after the final pilgering temperature in the manufacturing procedures of this alloy was less than the temperature of α-β transition in Ti-2.25Al-2.24Zr ternary alloy system examined in this study.

Fig. 3 shows TEM/EDS studies for the matrix and precipitation of as-received PT-7M titanium alloy. It is observed that PT-7M alloy mainly contains the Al-rich precipitate with a size of about 50 nm. The chemical composition of the precipitate was determined to be (wt.%) 92.35Ti, 3.11Al, 4.36Zr, and 0.18Fe, whereas that of the matrix was analyzed to be (wt.%) 93.96Ti, 2.24Al, 3.87Zr, and 0.09Fe. The crystal structure of precipitate was identified as a face-centered cubic (fcc, a = 0.3942 nm) with a chemical formulation of $Al_3 Ti_{0.75} Fe_{0.25}$. The Zr would be possibly substituted with Ti, because they have the same crystal structures of an hcp. This imply that the chemical formulation of precipitation would be again written as $Al_3 (Ti, Zr)_{0.75} Fe_{0.25}$. The mechanism that PT-7M titanium alloy contains Al-rich precipitation could be explained in terms of the crystal structures of the main alloy components. Whereas Ti and Zr have an hcp crystal structures and become the main components of the hcp α matrix, Al, which has a fcc structure, would tend to destabilize the hcp α matrix and then become main components to form

a precipitate.

Fig. 4 shows a bright field TEM image of PT-7M titanium alloy heat-treated at 800℃ for 1 hr. It is observed that there was an enlargement in the precipitate size from approximately 50 nm in as-received alloy (Fig. 3a) to approximately 200 nm in the heat-treated one. This observation means that the heat-treatment induced the enlargement of the size of the precipitates in PT-7M titanium alloy up to 800℃ in the present study.

3.2 Effect of heat-treatment on the mechanical property

Fig. 5 shows the effect of heat-treatment on the tensile properties of PT-7M titanium alloy. It is observed that there was little variation of the values of yield strength, ultimate tensile strength and elongation up to the heat-treatment temperature of 800℃. The heat-treatment of the alloy induced the enlargement of grain and precipitates sizes as shown in Figs. 1, 3 and 4. It is thus considered that the enlargement of grain size compensated the precipitation hardening as a result of the enlargement of precipitate size, giving the similar tensile properties. However, it is observed that the heat-treatment above 900℃ significantly affected on the tensile properties of titanium alloy examined in the present study. The heat-treatment at 900℃ induced a considerable reduction of the values of the strengths. However, there was little effect on the value of elongation. It would be mainly attributed to the grain growth and the enhanced recrystallization structure, respectively (Fig. 1). The tensile test results for the alloy heat-treated at 1000℃ showed that there was a significant reduction of the values of strengths and elongation. It would be mainly responsible for the formation of the β phase including the enlarged grain size.

Fig. 6 shows SEM micrographs of the fractured surfaces of the tensile tested PT-7M titanium alloys. It is observed that there are two distinct fracture modes: transgranular ductile failure (Fig. 6 (a)~(f)) and the mixture of ductile and cleavage modes (Fig. 6 (g)). As can be seen in Fig. 6 (a)~(f), it is observed that large voids, illustrating the ductile failure, are apparent on the fracture surfaces of the as-received titanium alloy as well as this alloy heat-treated in the temperature range of 500 to 900℃. The large voids are originally intergranular cracks formed by grain boundary sliding at an early stage of deformation. As deformation proceeds, the original grain boundary crack is distorted into an elongated void, until final failure occurs by necking between the voids. These results mean that there is little effect on the heat-treatment below 900℃, which is regarded as the α-Ti region of PT-7M alloy. In contrast, the alloy having the mixture microstructure of the α + β phases showed the mixture of ductile and cleavage failure modes as

shown in Fig. 6 (g), reflecting a brittle property of the β phase in the presence of stress. It is considered that the β-Ti phase promoted a cleavage failure mode, giving the cleavage fracture mode.

Fig. 7. shows the effect of heat-treatment on the Vickers hardness of PT-7M titanium alloy. It can be seen that there was a slight reduction of the hardness values by the heat-treatment of PT-7M titanium alloy in the temperature range of 500 to 900℃. These results would be possibly explained in terms of the microstructure change associated with the grain size and precipitates. Usually, the heat-treatment induces the enlargement of the grain and precipitates sizes, if it is below a solution heat-treatment temperature of the precipitates. These results indicate that the effect of the enlarged grain size on the hardness dominated the precipitation hardening as a result of the enlarged precipitation size. It is thus considered that the enlarged grain size by the heat treatment would be mainly responsible for a slight reduction of hardness value of the as-received PT-7M titanium alloy. However, there was a significant increase in the Vickers hardness value by the β heat-treatment. It would be mainly attributed to the partial formation of β phase shown in Fig. 1(d), because the β phase has a brittle property. This tendency coincides well with the tensile test results which indicate that the presence of the β phase has a significant influence on the ductility in PT-7M titanium alloy shown in Fig. (5).

3.3 Effect of α heat-treatment on the corrosion behavior

Fig. 8 shows the effect α heat-treatment on the corrosion behavior of PT-7M titanium alloy at 360℃ in the ammonia aqueous solution of a pH 9.98. It can be seen that the heat-treatment of as-received PT-7M titanium alloy accelerated the corrosion rate, and the corrosion rate of the alloys heat-treated in the temperature range of 500 to 800℃ increased with increasing the heat-treatment temperature. The final weight gains of PT-7M titanium alloys heat-treated at 500, 600, 700 and 800℃ appeared to be 2.9, 3.1, 3.4 and 4.3 mg/dm^2, respectively, whilst that of as-received one revealed to be 2.2 mg/dm^2. This result indicates that the enlargement of the grain and precipitate sizes by the heat-treatment of titanium alloy considerably attribute to the oxidation reaction of the metal with oxygen, accelerating the corrosion of the alloy in an ammonia aqueous solution.

Fig. 9 shows an X-ray diffraction pattern of PT-7M titanium alloy corroded at 360℃ in the ammonia water chemistry of a pH 9.98 for 116 days. It is observed that the oxides formed on the surface of PT-7M titanium alloy mainly composed of two phases: rutile phase (tetragonal, a = 0.4594 nm, c = 0.2959 nm, c/a = 0.64) and anatase phase (tetragonal, a = 0.3786 nm, c =

0.9517 nm, c/a = 2.51). Anatase is formed in the pressure below 195,750 psi at 360℃ (if the pressure is over than 195,750 psi at 360℃, anatase phase transforms to TiO_2-II) [9]. The rutile is the stable phase at all temperatures and ambient pressure. In the present study, the oxides on the surface of PT-7M titanium alloy formed at 360℃ under a pressure of 2,680 psi. This implies that two phases, the anatase and rutile, are stable oxides, and the rutile is a product transformed from the anatase phase.

Fig. 10 shows SEM micrographs of oxide surfaces at the metal-oxide interface of PT-7M titanium alloys corroded in the ammonia aqueous solution of a pH 9.98 having an equal weight gain of approximately 2 mg/dm^2. The morphologies of oxide surface at the metal-oxide interface of the as-received alloy appeared to be a uniform thin oxide layer with a large number of the protruded round oxide. However, it is observed that the size of the protruded oxides increased with increasing the heat-treatment temperature before the corrosion test.

Fig. 11 shows SEM micrographs and EDS results of oxide surfaces at the metal-oxide interfaces formed in the heat-treated PT-7M titanium alloy at 800℃ before corrosion test. It is observed that the oxide grown in the ammonia aqueous solution for 30 days revealed a small size of the protruded round oxides in the uniform oxide layer. The SEM micrograph of the oxide surface at the metal-oxide interface of the alloy corroded for 96 days exhibited that the protruded oxides grew as the corrosion proceeds. In addition, the oxide morphologies can be divided into three district regions: uniform oxide layer, protruding oxides and considerably protruded oxide. The EDS results for three regions indicated that the considerably protruded oxide region contained a large amount of aluminum content. In addition, no effect of enlarged grain size on the corrosion is observed, because most growth of the oxide is in the matrix. These results indirectly reflect that the corrosion of PT-7M titanium alloy is intimately correlated with the precipitate size. It is thus considered that the accelerated corrosion rate of the alloys by the heat-treatment, especially at 800℃, before corrosion test would be attributed to the enlarged precipitate size.

4. CONCLUSIONS

The effects of heat treatment on the mechanical property and corrosion behavior of PT-7M titanium alloy have been determined in the present study. The α heat-treatment of PT-7M titanium alloy in the temperature range of induced little effect on the Vickers hardness as well as the tensile property. These results indicate that the enlargement of grain size compensated the precipitation hardening as a result of the heat-treatment. The heat-treatment of PT-7M titanium alloy at 1000 ºC induced a significant increase in the Vickers hardness values and a considerable

reduction in the tensile properties. It would be mainly attributed to the formation of the bcc β phase having a brittle property. The precipitation with a chemical formulation of $Al_3(Ti, Zr)_{0.75}Fe_{0.25}$ has a significant effect on the corrosion behavior of PT-7M titanium alloy, since the enlarged precipitates promote the oxide growth in an uniform oxide layer.

ACKNOWLEDGEMENTS

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Table 1. Chemical composition of PT-7M titanium alloy (wt.%)

Ti	Al	Zr	V	Fe	Co	S	C	O	N	H
95.24	2.25	2.24	0.06	0.05	0.14	0.0001	0.0090	0.0050	0.0004	0.0051

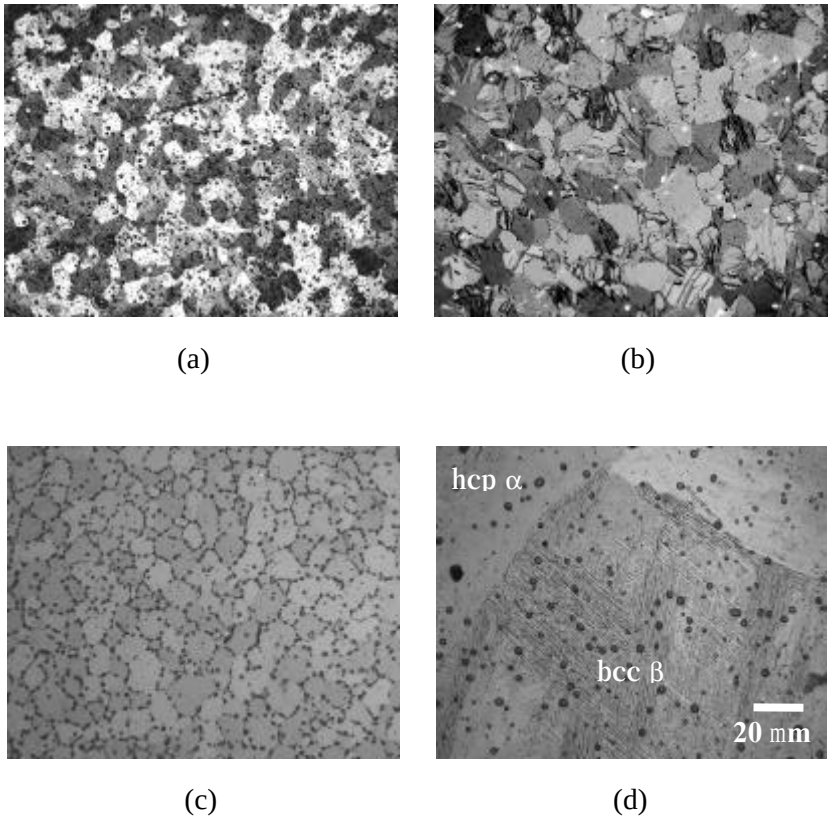


Fig. 1. Cross-sectional microstructures of as-received and heat treated PT-7M titanium alloy tubes: (a) as-received, and heat-treated at (b) 800, (c) 900, (d) 1000℃ for 1 hr.

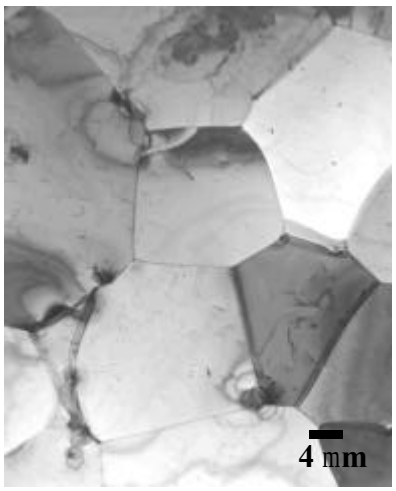


Fig. 2. Microstructure of the longitudinal section of as-received PT-7M titanium alloy tube.

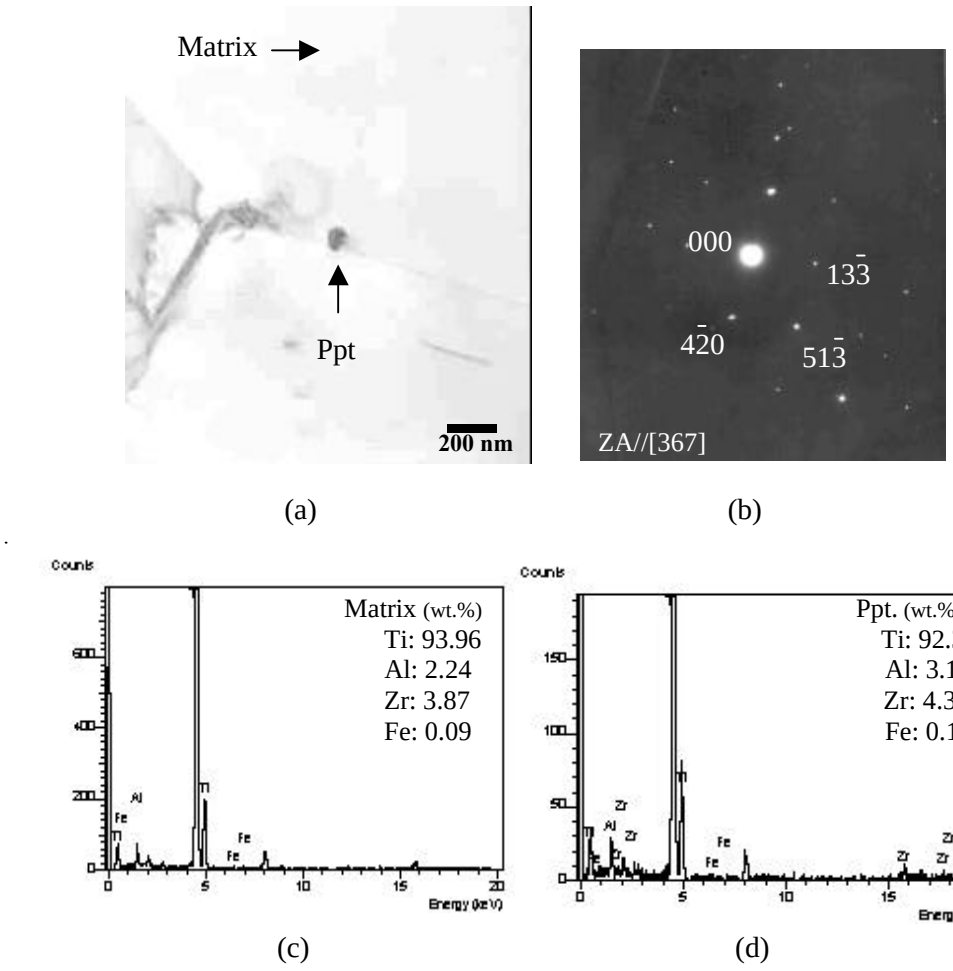


Fig. 3. TEM/EDS results of matrix and precipitation in PT-7M titianium alloy: (a) bright-field image, (b) selected area diffraction pattern from precipitation allowed in (a), (c) spectrum from matrix, and (d) spectrum from precipitation.

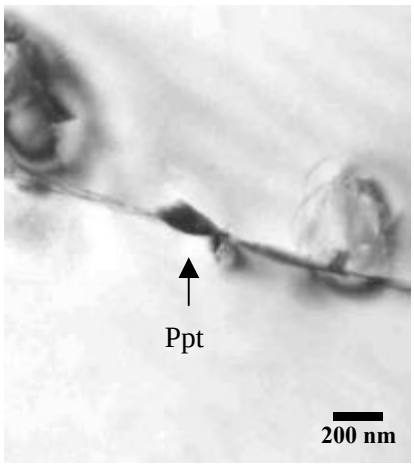


Fig. 4. Bright field TEM image of PT-7M titianium alloy heat-treated at 800℃ for 1 hr: Note that the precipitation size is much larger than that allowed in Fig. 3(a).

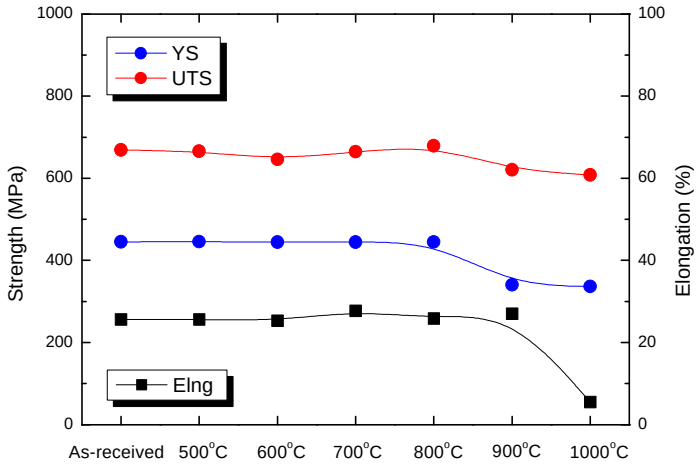
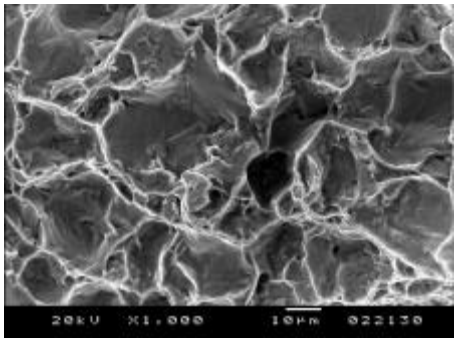
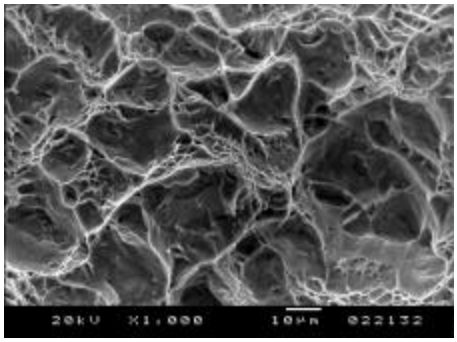


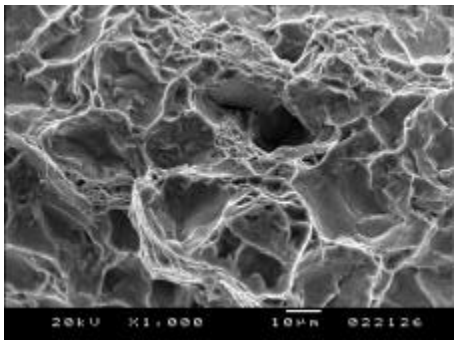
Fig. 5. Effect of heat-treatment on the tensile property of PT-7M titanium alloys.



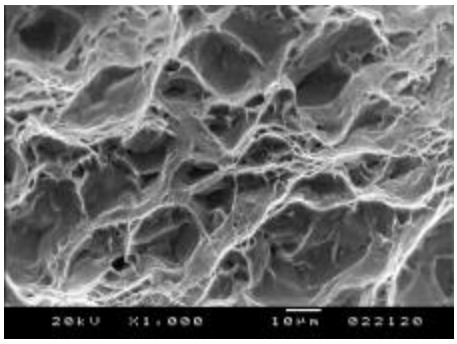
(a)



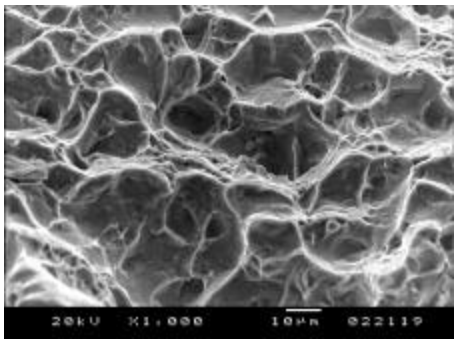
(b)



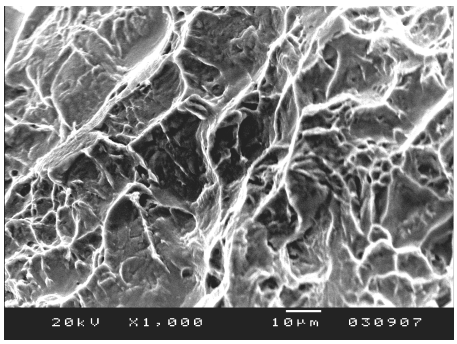
(c)



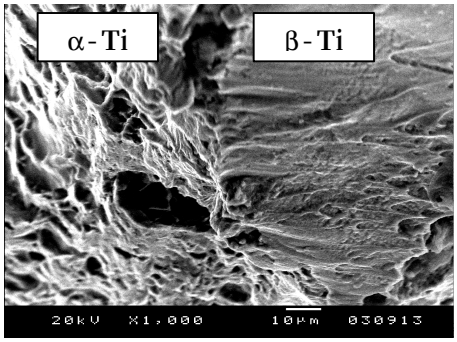
(d)



(e)



(f)



(g)

Fig. 6. Fracture surfaces of as-received and heat-treated PT-7M titanium alloys: (a) as-received, (b) 500 (c) 600 (d) 700 (e) 800 (f) 900 and (g) 1000℃ for 1 hr.

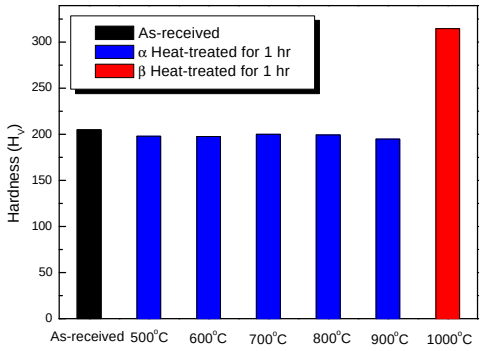


Fig. 7. Effect of heat-treatment on the hardness of PT-7M titanium alloy.

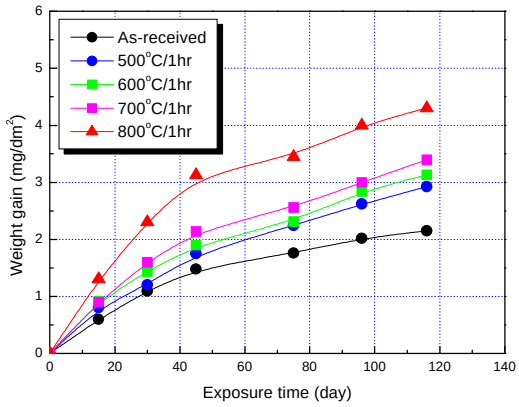


Fig. 8. Effect of α heat-treatment on the corrosion behavior of PT-7M titanium alloy at 360℃ in the ammonia aqueous solution of a pH 9.98.

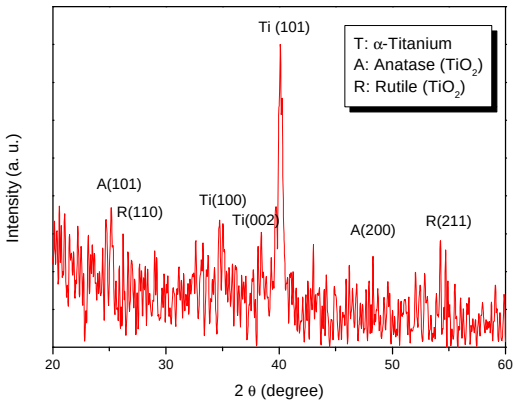


Fig. 9. X-ray diffraction pattern of PT-7M titanium alloy corroded at 360℃ in the ammonia water chemistry of a pH 9.98 for 116 days.

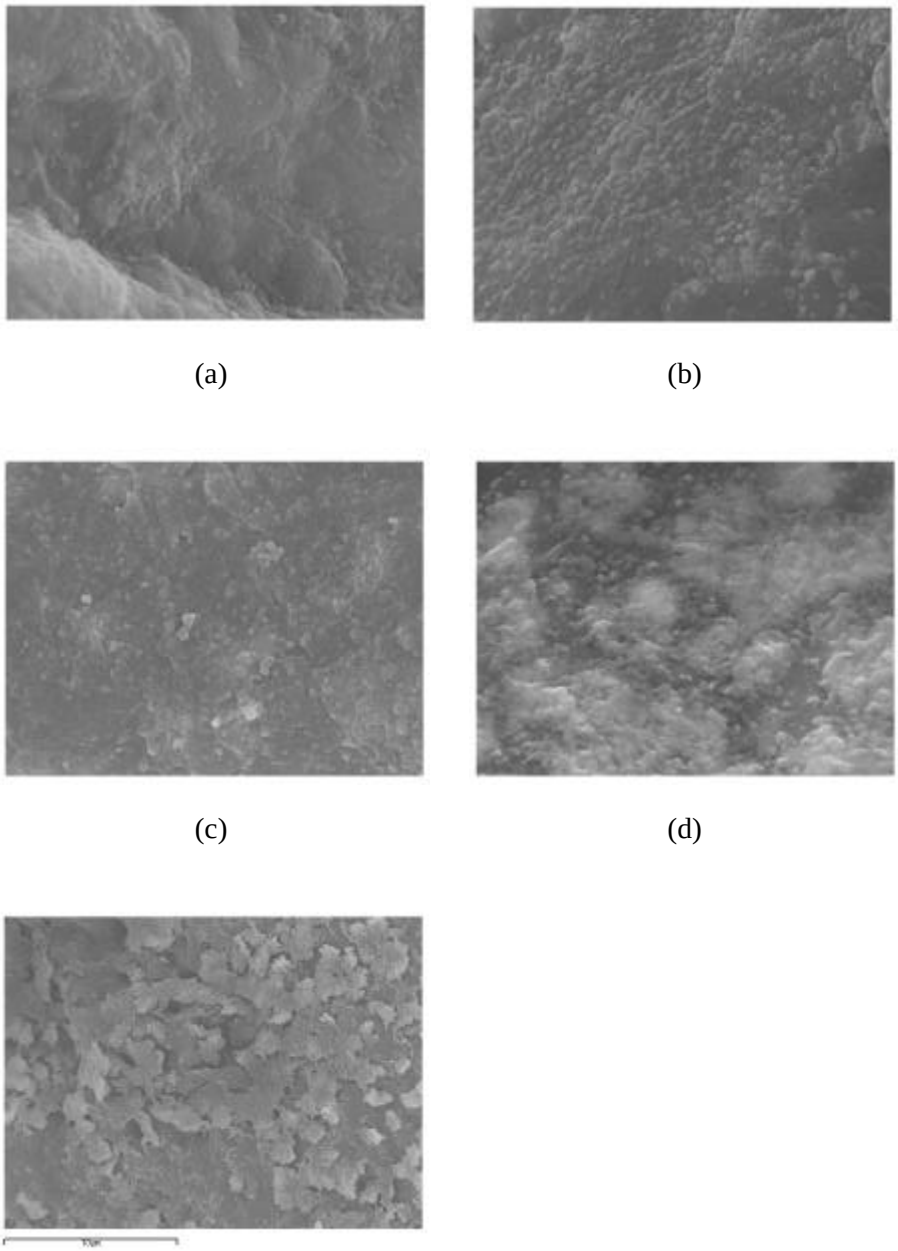
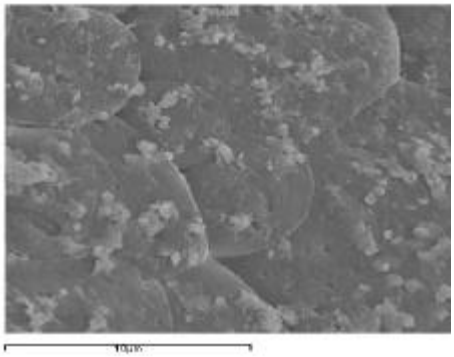
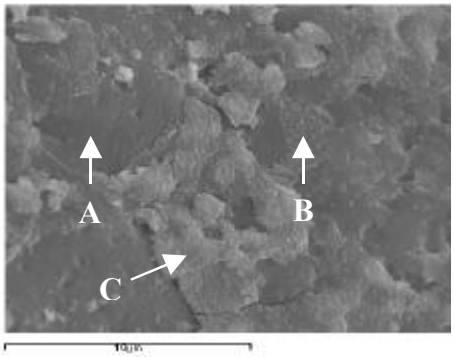


Fig. 10. SEM micrographs of oxide surfaces at the metal-oxide interfaces of PT-7M titanium alloys with equal weight gain of approximately 2 mg/dm^2 grown in an ammonia aqueous solution of a pH 9.98: (a) as-received, and heat-treated at (b) 500 (c) 600 (d) 700 and (e) 800℃ for 1 hr.



(a)



(b)

(wt.%)

	Ti	Al	Zr	Fe	O
A	15.31	0.00	4.12	0.00	80.57
B	20.64	0.86	5.74	0.01	72.77
C	27.85	4.39	3.82	2.18	61.78

(c)

Fig. 11. SEM micrographs and EDS results of oxide surfaces at the metal-oxide interfaces formed in the heat-treated PT-7M titanium alloy at 800℃ before corrosion test: exposure time of (a) 30 and (b) 96 days, and (c) EDS results from oxide allowed in (b).