Ion nitriding of titanium aluminides with 25–53 at.% Al

II: Corrosion properties

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Abstract

The corrosion resistance of ion-nitrided titanium aluminides containing from 25 to 53 at.% Al were investigated by acid immersion tests and electrochemical potentiodynamic tests. The results indicate that all the non ion-nitrided specimens are easily attacked by our acid solutions. The corrosion rate in a 10 vol.% H_2SO_4 solution is larger than that in a 10 vol.% HCl solution. Higher Al contents lead to greater weight losses. The corrosion rate in these solutions can be markedly reduced by the ion-nitriding process. The reduction is greater in 10 vol.% HCl than in 10 vol.% H_2SO_4 . The ion-nitrided layer of titanium aluminides contains TiN and Ti_2AlN . The improved corrosion resistance in 10 vol.% H_2SO_4 and 10 vol.% HCl aqueous solution is attributed to the TiN and Ti_2AlN formed in the ion-nitrided layer. TiN is more corrosion resistant than Ti_2AlN in these acid solutions.

Keywords: Ion nitriding; Titanium aluminides; Immersion test; Corrosion resistance

1. Introduction

Titanium aluminide is a potential structural material for use at elevated temperatures. It has a low density, a high specific strength and a high melting point. However, its inherently low ductility and workability at room temperature restrict its applications in critical applications. Its low surface hardness may restrict its tribological applications, and its poor corrosion characteristics may restrict its applications in chemical environments.

Nitriding techniques are used to increase the surface hardness and to improve the fatigue and wear resistance of metals and alloys [1]. In Part I of this work [2], we found that the surface hardness of titanium aluminides can be significantly improved by the ion-nitriding process. The improvement in surface hardness is attributed to the formation of TiN and Ti_2AlN in the surface layer. In industrial applications, titanium and its alloys are used as corrosion-resistant materials in acid environments. Several investigations on corrosion resistance have been done on nitrided pure titanium and nitrided titanium alloys [3–7]. However, to our knowledge, there are few data on the corrosion characteristics of titanium aluminides [8]. In this study, the effects of aluminium content and ion-nitriding parameters on the corrosion resistance of titanium aluminides in hydrochloric acid

and sulfuric acid aqueous solutions are investigated. The corrosion characteristics of titanium aluminides in these two acid solutions are also discussed.

2. Experimental details

2.1. Specimen preparation

A conventional tungsten arc-melting technique was employed to prepare the titanium aluminides. Four different compositions with 25, 40, 50 and 53 at.% Al, were prepared. Titanium (purity, 99.7%) and aluminium (purity, 99.99%), totaling 100 g, were melted and remelted at least six times in a low pressure argon atmosphere.

Ion nitriding was carried out in an NDK furnace model JIN-6SS-C-SV. In order to reduce sample contamination from the sample support and holder, these two components were made of titanium. After nitriding, specimens were cooled in vacuum. The cooling rate was approximately 20°C s^{-1} at the initial stage, but this rate slowed towards the end of the cooling period. The details of the specimen preparation and the ion-nitriding process have been described in Part I of this study [2].

2.2. Immersion test

All immersion experiments were conducted at 26 ± 1 °C in 10 vol.% H_2SO_4 or 10 vol.% HCl solutions under atmospheric conditions for 5 days. Then, specimens were removed and cleaned in ethyl alcohol using ultrasonic equipment. Thereafter, they were weighed and recorded, and the corrosion rates were calculated.

2.3. Electrochemical potentiodynamic measurement

Both non-ion-nitrided and ion-nitrided specimens were examined by electrochemical potentiodynamic measurements. The experimental set-up, shown in Fig. 1, included a three-electrode system, a Nichia model NP G1001ED potentiogalvanostat, a potential scanner ES-511A and a personal computer. Scans were initiated by lowering the corrosion potential of the specimen to a pre-set value of -1.0 V (vs. the saturated $\text{Ag}|\text{AgCl}$ electrode), and scanned to $+1.0$ V (vs. the saturated $\text{Ag}|\text{AgCl}$ electrode) at a rate of 1 mV s^{-1} ; following this, a scan was run from $+1.0$ to -1.0 V at the same rate to complete a cycle. The experiment was conducted in a 0.5 M HCl solution at room temperature under static and atmospheric conditions. A platinum sheet was used as a counterelectrode. Oxygen was removed from the electrolyte by purging with purified nitrogen. In order to minimize the internal resistance drop in the solution, the reference electrode was positioned as closely as possible to the working electrode.

2.4. Surface analysis and cross-section microanalysis

After the experiments in Section 2.2, the surface of specimens were investigated using a Philips 515 scanning

Fig. 1. Schematic diagram of electrochemical potentiodynamic instruments.

electron microscope with energy-dispersive X-ray analysis facility. The cross-sections of these specimens were examined with a JEOL JXA-8600SX electron probe microanalyzer. X-ray diffraction (XRD) tests were carried out using a Philips PW1710 X-ray diffractor which provided $\text{Cu K}\alpha$ radiation. The power was $40 \text{ kV} \times 30 \text{ mA}$ and the 2θ scanning rate was 3° min^{-1} .

3. Results

3.1. Surface morphologies of ion-nitrided titanium aluminides

Typical surface morphologies of ion-nitrided Ti-25Al specimen (where the composition is in atomic per cent) are illustrated in the scanning electron micrographs in Fig. 2. Surface morphologies of ion-nitrided Ti-40Al, Ti-50Al and Ti-53Al specimens are similar to those shown in Fig. 2 and therefore are not shown here. Ion nitriding at a low temperature (700 °C) and a short time (4 h), can be seen in Fig. 2(a). The surface scratches

Fig. 2. Scanning electron micrographs photographs of surface morphology of Ti-25Al after ion nitriding (a) at 700 °C for 4 h and (b) at 900 °C for 12 h .

Fig. 3. Immersion test results in 10 vol.% HCl or 10 vol.% H₂SO₄ solutions. The ion-nitriding conditions are listed in Table 1.

Table 1
Ion-nitriding conditions of Fig. 3.

Number	Ion-nitriding conditions
1	None
2	700 °C for 4 h, 6 Torr, (N ₂)/(H ₂) = 10
3	800 °C for 4 h, 8 Torr, (N ₂)/(H ₂) = 1
4	900 °C for 4 h, 10 Torr, (N ₂)/(H ₂) = 4
5	None
6	700 °C for 12 h, 8 Torr, (N ₂)/(H ₂) = 4
7	800 °C for 12 h, 10 Torr, (N ₂)/(H ₂) = 10
8	900 °C for 12 h, 6 Torr, (N ₂)/(H ₂) = 1

induced during polishing, before the ion nitriding, can still be observed. These surface scratches disappear after the ion nitriding at a higher temperature (900 °C) and a longer time (12 h) (Fig. 2(b)). The elimination of these surface scratches is thought to be caused by two effects. First, N⁺ atoms sputter the surface and eliminate the scratches. Second, TiN and AlN are deposited on the surface and form a uniform and dense surface layer. The details of the ion-nitriding mechanism in titanium aluminides have been discussed in Part I of this study [2].

After shorter nitriding times and lower nitriding temperatures, the surface color of Ti-25Al appears light yellow. After longer nitriding times and higher nitriding temperatures, the surface color of Ti-25Al is the well-known TiN golden yellow. With increasing aluminium content, the surface color of nitrided titanium aluminides gradually changes from golden yellow to brown.

Fig. 4. Scanning electron micrographs of the surface morphology of non-ion-nitrided titanium aluminides after immersion in 10 vol.% H₂SO₄ aqueous solution for 5 days: (a) Ti-25Al; (b) Ti-40Al; (c) Ti-50Al; (d) Ti-53Al.

(a)

(b)

Fig. 5. Scanning electron micrographs of the surface morphology of the ion-nitrided titanium aluminides after immersion in 10 vol.% H_2SO_4 aqueous solution for 5 days: (a) 700 °C for 12 h; (b) 800 °C for 12 h; (c) selected area from (a).

3.2. Corrosion characteristics of ion-nitrided titanium aluminides

Corrosion data from the immersion test are plotted in Fig. 3 in terms of weight loss vs. ion-nitriding conditions. The data from the non-ion-nitrided specimens (conditions 1 and 5) are also plotted for comparison. In Fig. 3, the symbols in the left half of the diagram are the data points for samples exposed to a 10 vol.% HCl solution and the symbols in the right half of the diagram are for samples exposed to a 10 vol.% H_2SO_4 . The ion-nitriding conditions of Fig. 3 are listed in Table 1. From Fig. 3, one can see that the ion-nitrided titanium aluminides are more corrosion resistant than the non-ion-nitrided samples. At the same time, ion-nitrided titanium aluminides exposed to higher nitriding temperatures or longer nitriding times have better corrosion properties. Surface morphologies after the immersion test for specimens with and without ion nitriding are shown in Figs. 4 and 5. Fig. 4 shows the surface morphologies of non-ion-nitrided titanium aluminides after immersion in a 10 vol.% H_2SO_4 solution for 5 days. Fig. 5(a) shows the surface morphologies of ion-nitrided titanium aluminides treated at 700 °C for 12 h and 8 Torr, with $[\text{N}_2]/[\text{H}_2] = 4$ (condition 6 in Table 1) and immersed in a 10 vol.% H_2SO_4 solution for 5 days. Fig. 5(b) shows the surface morphologies for specimens ion nitrided at 800 °C for 12 h and 10 Torr with $[\text{N}_2]/[\text{H}_2] = 10$ (condition 7 in Table 1) and then immersed in a 10 vol.% H_2SO_4 solution for 5 days. The weight loss corresponding to the specimens in Figs. 5(a) and 5(b) can also be seen in Fig. 3. Fig. 5(c) is a scanning electron micrograph of the corrosion pits in Fig. 5(b) at a higher magnification. From Figs. 3 and 4, one can see that all non-ion-nitrided specimens are easily attacked by 10 vol.% H_2SO_4 and

HCl solutions. At the same time, a higher aluminum content leads to a greater weight loss. For non-ion-nitrided specimens, the corrosion rate in 10 vol.% H_2SO_4 solution is higher than that in 10 vol.% HCl. For the ion-nitrided specimens, the corrosion rate in 10 vol.% H_2SO_4 solution or 10 vol.% HCl solution can be markedly improved by the ion-nitriding process even at low nitriding temperatures and short nitriding times. The improvement in corrosion resistance in 10 vol.% HCl solution after ion nitriding is more evident than in 10 vol.% H_2SO_4 even though the thickness of the nitrided layer of the samples used in 10 vol.% HCl solution is thinner than that used in 10 vol.% H_2SO_4 solution. This is shown in conditions 2–4 and 6–8 of Fig. 3.

3.3. Electrochemical potentiodynamic behavior

A typical potentiodynamic scanning diagram for titanium aluminides treated in a 0.5 M HCl solution with and without ion nitriding at 900 °C for 12 h is shown in Fig. 6. Fig. 6(a), Fig. 6(b) and Fig. 6(c) are for Ti–25Al, Ti–40Al and Ti–53Al respectively. The upper diagram shows the non-ion-nitrided sample, while the lower diagram shows the ion-nitrided sample. The anodic potentiodynamic polarization curve of Fig. 6 is shown in Fig. 7. Values of the corrosion potential ϕ_{corr} and the corrosion current density i_{corr} from Tafel extrapolation are listed in Table 2. From Table 2, one can see that the corrosion potential and the current density of ion-nitrided specimens are much lower than the corresponding values for non-ion-nitrided specimens.

4. Discussion

4.1. Effect of Al content on the corrosion behavior of titanium aluminides without ion nitriding

As mentioned above, increasing the Al content in titanium aluminides results in an increasing corrosion rate. This means that the corrosion resistance of Ti–25Al (single α_2 phase) is superior to that of Ti–53Al (single γ phase) and explains why the α_2 phase is nobler than the γ phase in HCl and H_2SO_4 solutions. The cathodic reaction for non-ion-nitrided Ti–25Al occurs during the reverse scan of the potentiodynamic experiment, as shown by the arrow in Fig. 6(a). This feature also reveals that Ti–25Al forms surface hydrides and reaches a passive state more easily than higher Al content aluminides in HCl aqueous solution. The corroded surface morphologies shown in Figs. 4(a) and 4(d) are consistent with this corrosion behavior. The clearly laminar picture of the corroded Ti–40Al specimen in Fig. 4(b) suggests a difference in the corrosion rates of α_2 -Ti₃Al and γ -TiAl. This means that, for the laminar α_2 -Ti₃Al and γ -TiAl, the corrosion proceeds at different rates across the surface and is faster in areas containing γ -TiAl.

Fig. 6. Potentiodynamic scan for (a) Ti-25Al, (b) Ti-40Al and (c) Ti-53Al in 0.5 M HCl solution. The ion-nitriding conditions are 900 °C for 12 h and 6 Torr with $[N_2]/[H_2]=1$.

(a)

(b)

(c)

Fig. 7. Anodic potentiodynamic polarization curve for (a) Ti-25Al (b) Ti-40Al and (c) Ti-53Al in 0.5 M HCl solution.

Table 2

Corrosion data of the Tafel slope extrapolation calculated from Fig. 7 (0.5 M HCl solution)

Sample	Corrosion potential ϕ_{corr} (V vs. Ag/AgCl)	Corrosion current density i_{corr} (mA cm ⁻²)
Ti-25Al (non ion nitrided)	-0.31	0.0021
Ti-40Al (non ion nitrided)	-0.40	0.0035
Ti-50Al (non ion nitrided)	-0.50	0.0017
Ti-53Al (non ion nitrided)	-0.51	0.0017
5 ^a	-0.08	0.0011
6 ^a	-0.14	0.0028
7 ^a	-0.14	0.0015
8 ^a	-0.15	0.0014

^a Samples 5, 6, 7 and 8 were Ti-25Al, Ti-40Al, Ti-50Al and Ti-53Al respectively ion nitrided at 900 °C for 12 h and 6 torr with $[\text{N}_2]/[\text{H}_2]=1$.

4.2. Effect of the ion-nitriding process on the corrosion behavior of titanium aluminides

As mentioned in Part I of this study, TiN phase forms more easily in Ti-25Al than in Ti-53Al under the same nitriding temperature and time. At lower Al contents, the XRD intensity of TiN phase increases and the TiN layer in the compound layer becomes thicker [2]. At the same time, higher nitriding temperatures, and longer nitriding times cause thicker nitrided layers [9]. It has been described that TiN is more chemically inert and electrically insulating than titanium alloys [3]. We also believe that TiN is more chemically inert than ion-nitrided titanium aluminides. This belief is supported by the results of Fig. 3 in which Ti-25Al is found to have a better corrosion resistance than the other titanium aluminides. Although there is insufficient corrosion data for a comparison of Ti_2AlN and TiN, we postulate that the corrosion resistance of TiN is better than that of Ti_2AlN in H_2SO_4 or HCl solutions. Our reasoning is that higher Al content alloys have more Ti_2AlN in the ion-nitrided layer and correspondingly poorer corrosion resistance in HCl or H_2SO_4 .

4.3. Corrosion characteristics in different solutions

Many corrosion pits are observed after the immersion tests as shown in Fig. 5. These pits are initiated at local defects or inhomogeneities in the nitrided surface. As the test proceeds, the pits grow and combine together. Ultimately, the nitrided layer is pitted and destroyed. If the nitrided layer is destroyed, the layer below the nitriding layer (i.e. the diffusion layer) will corrode rapidly because there is no TiN or Ti_2AlN in the diffusion layer to resist the acid. Such a failure in the nitriding layer is indicated with an arrow shown in Fig. 5(c). This feature is quite similar to features reported

in (Ti, Al)N- or TiN-coated steel exposed to a 0.5 M sulfuric solution [3].

The corrosion current density and the corrosion potential of ion-nitrided titanium aluminides show much lower values than those of non-ion-nitrided specimens, as indicated in Table 1. This is because TiN and Ti₂AlN provide better corrosion resistance than non-ion-nitrided titanium aluminides in the acid solutions.

5. Conclusions

In this study, the corrosion characteristics of titanium aluminides with and without ion nitriding were investigated by immersion tests in 10 vol.% H₂SO₄ and 10 vol.% HCl solutions, and by electrochemical potentiodynamic tests in a 0.5 M HCl solution. The results indicate that all the non-ion-nitrided specimens are easily attacked by these solutions. The corrosion rate in 10 vol.% H₂SO₄ solution is greater than in 10 vol.% HCl. Higher Al levels result in greater weight loss. The corrosion rate in these solutions can be markedly reduced by the ion-nitriding process. The resistance to the 10 vol.% HCl solution shows more improvement than the resistance to the 10 vol.% H₂SO₄ solution. The ion-nitrided layer of titanium aluminides contains TiN and Ti₂AlN. The improved corrosion resistance in

10 vol.% H₂SO₄ or 10 vol.% HCl aqueous solution is attributed to TiN and Ti₂AlN formed in the ion-nitrided layer. TiN is more corrosion resistant than Ti₂AlN in these acid solutions.

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