Reduction and carbonitriding of anodic titanium oxide film by using a mixture of iron and carbon powders

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Titanium plates covered with anodic oxide films with thicknesses of approximately 10 μm were embedded in a mixture of iron, graphite, and alumina powders, and then heated in the temperature range of 1073–1373 K for 3.6 ks in a nitrogen flow. We refer to this heat treatment method as “iron-powder pack (IPP) treatment”, and its ability to reduce the anodic oxide film was examined inclusive of a diffusion phenomenon of carbon and nitrogen into the film. From X-ray diffraction results, the film consisting of rutile and anasovite was gradually converted to titanium nitride with increasing heating temperature. The diffusion of carbon was also confirmed in the film after the IPP treatment. However, such a remarkable change was not achieved by heating without the powder mixture. This indicates that the powder mixture has an important role in reducing and carbonitriding the anodic oxide film. A porous structure in the film formed by anodic oxidation was retained regardless of the heating temperature in the IPP treatment. On the other hand, the peeling of the film from the titanium plate occurred through the IPP treatment at 1373 K. This would be caused by the accumulation of carbon monoxide gas, which was generated by the reduction of the oxide film.

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Key-words : Anodic titanium oxide film, Iron powder, Graphite, Alumina, Nitrogen, Reduction, Carbonitriding

1. Introduction

Titanium and its alloys are used for applications in the automobile, aerospace and chemical industries because they have excellent corrosion resistances and high specific strengths. The major disadvantage of these materials is poor wear resistance. This is one of properties required as mechanical components, and techniques to harden the surface of titanium and its alloys, such as plasma nitriding1) and plasma carburizing,2) have attracted great interest. However, most of them need special equipment and complicated process flows to produce a hardened layer like titanium carbide (TiC) and nitride (TiN) on the titanium surface. Therefore, a simpler and quicker method is still desired.

The authors have found a simplified technique for forming a titanium carbonitride [Ti(C,N)] layer on the titanium surface.3) Specifically, a titanium plate is embedded in a mixture of iron, carbon and alumina (Al₂O₃) powders, and then heat-treated at 1273 K for 3.6 ks in a nitrogen flow. During heating, a hardened layer, which has been identified as Ti(C,N), forms on the titanium surface. It is notable that carbon monoxide (CO) gas is generated during a heating step in the heat treatment.3) This is probably due to a chemical reaction between carbon in the powder mixture and residual oxygen in an electric furnace. Since the CO gas is exhausted with the nitrogen flow from the furnace, oxygen in the furnace should be expelled. Accordingly, the oxygen partial pressure should be low around the titanium plate. It is thought that this contributes to the decomposition of the oxide film on the titanium surface, making it easy for carbon and nitrogen to diffuse into the titanium plate. We refer to such a surface modification technique as “iron-powder pack (IPP) treatment”. This also enables the carburization of stainless steel, which is known to be covered with a stable chromium oxide film.4)

According to a modification mechanism of the IPP treatment, there is a possibility that titanium oxides are decomposed by heating in a nitrogen flow using a mixture of iron, carbon and Al₂O₃ powders. Therefore, we applied this treatment to titanium plates covered with anodic oxide films. Anodizing is an electrochemical oxidation process in an electrolytic solution to increase the thickness of an oxide film on the metal surface. This is industrially used for aluminum and titanium materials to provide aesthetic property and excellent corrosion and wear resistances.

In the present study, the IPP treatment was applied to anodized titanium plates, and its effect on the reduction and the diffusion of carbon and nitrogen is discussed on the basis of the microstructures in the anodic oxide film.

2. Experimental procedures

A commercially pure titanium plate with a purity of 99.5 mass% was used as a substrate. The plate, which had a thickness of 1 mm, was cut into square shapes with dimensions of 10 mm × 10 mm. Anodic oxidation of the titanium plates was carried out in Kumabou Metal Co., Ltd.5) An aqueous solution containing oxalic acid was used as an electrolytic bath, and the titanium plates covered with anodic oxide films with thicknesses of approximately 10 μm were provided in the present study.

IPP treatment was conducted by the following procedure. A 4:6:3 (v/v/v) mixture of iron, graphite and Al₂O₃ powders was put into an Al₂O₃ crucible, and an anodized titanium plate was embedded in the mixture. The volume ratio of these powders was determined on the basis of previous studies.3) A commercially available carbonyl iron powder was selected as an iron powder. It was fine and spherical (particle size, D₉₀ = 3.9–5.2μm), and contained 0.75–0.90 mass% C, 0.65–0.90 mass% N and 0.15–
0.40 mass % O. We are thinking that the iron powder has the effect of enhancing the carbon movement in graphite, like catalyst. The graphite powder was used as a carbon source and an anti-sintering agent, and the Al₂O₃ powder was added to reliably prevent the powder mixture from sintering. The crucible, which was filled with the anodized titanium plate and the powder mixture of approximately 8 ml, was placed in an electric furnace, as shown in Fig. 1. After repeatedly evacuating the furnace using a rotary vacuum pump and refilling it with nitrogen gas a few times, the crucible was heated in the temperature range of 1073–1373 K for 3.6 ks in a nitrogen flow. The nitrogen gas had a purity of >99.99 vol %, and its flow rate was 500 ml/min. The heat treatment in a nitrogen flow without the powder mixture was also performed for comparison. All specimens were allowed to cool in the furnace to room temperature. In some cases, a detector of CO gas was attached to an exhaust port in the electric furnace, and its concentration was monitored during heat treatment.

X-ray diffraction (XRD) measurement, scanning electron microscopic (SEM) observation and analysis by glow discharge optical emission spectrometry (GD-OES) were carried out on the surface of the specimens. Thereafter, the specimens were cut in half to reveal the microstructures. The cross sections were ground with emery paper and then mirror-finished using diamond slurry with a particle size of 0.5 µm. They were examined by using optical microscopy, SEM and electron probe X-ray micro analysis (EPMA). In some cases, a Vickers hardness test was conducted on the cross sections in the specimens. A load of 0.49 N was applied at room temperature for 15 s in the hardness test.

3. Results and discussion

3.1 Surface observation

Anodized titanium plates were provided by Kumabou Metal Co., Ltd. Figure 2(a) shows an SEM image of the titanium surface after anodic oxidation. There were many pores in the anodic oxide film with a thickness of approximately 10 µm. These are thought to be formed by spark discharge during anodizing. An XRD pattern of the surface of the anodized titanium plate is shown in Fig. 2(b). Almost diffraction peaks were identified as rutile (TiO₂), whereas the ones which appear to be anosovite were detected. Anosovite is described as Ti₃O₅ and Ti₂O₃·TiO₂. Saeki et al. have reported its formation in TiO₂ films deposited by electron beam evaporation. As we will describe later, this anodic oxide film contained aluminum. Since an electrolytic bath for anodizing is also applied to aluminum materials in actual operation, aluminum would be dissolved into the electrolytic bath and trapped in the anodic titanium oxide film. Thus, it may influence the formation of anosovite.

Figure 3 shows XRD patterns of the surface of the anodized titanium plate after IPP treatment at 1073, 1173, 1273 and 1373 K. The plates were embedded in a 4:6:3 (v/v/v) mixture of iron, graphite and Al₂O₃ powders, and then heated at each temperature for 3.6 ks in a nitrogen flow. At 1073 K, the obtained pattern was almost consistent with that in Fig. 2(b). Diffraction peaks for TiO₂ and anosovite became small as the heating temperature increased. Accordingly, the peaks for TiN began to be detected, and were clearly seen in Fig. 3(d). In addition, a porous structure in the anodic oxide film, which was shown in Fig. 2(a), was retained in every case.

When the anodized titanium plate was heat-treated at 1373 K in a nitrogen flow without a powder mixture, the anodic oxide film
was reduced and Ti$_2$N and TiN were formed as shown in Fig. 4. Al$_2$O$_3$ resulting from aluminum in the anodic oxide film was also recognized. However, the degree of change in TiO$_2$ and anosovite was too small compared with Fig. 3(d). A similar treatment has been carried out by Sugimoto et al. They have studied on the preparation of TiN fibers by heating TiO$_2$ fibers in a nitrogen flow, and have reported that the fibers consisting of a TiN single phase were obtained by heating at 1573 K for 18 ks in a nitrogen flow of 220 ml/min. Considering the result in Fig. 4 and the report by Sugimoto et al., it is noteworthy that thermodynamically stable titanium oxides were gradually converted to TiN with increasing heating temperature by using a mixture of iron, graphite and Al$_2$O$_3$ powders. As mentioned later, CO gas was detected during IPP treatment for anodized titanium plates. The CO gas was generated by a chemical reaction in the powder mixture, and was exhausted with the nitrogen flow from an electric furnace. Accordingly, oxygen in the furnace should be expelled. This is identical to a surface modification process of titanium plates, which is described in the introduction. Therefore, it is thought that an atmosphere with the low oxygen partial pressure forms around the anodized titanium plate in the powder mixture, and contributes to the decomposition of the oxide film and to the formation of TiN.

The change in XRD patterns was predicted by an external appearance of the specimen. The anodized titanium plate was gray white in color. This color was retained even after heating at 1073, 1173 and 1273 K in a nitrogen flow without a powder mixture. In these cases, the existence of TiO$_2$ and Al$_2$O$_3$ was confirmed by XRD measurements, since the anodic oxide film contained aluminum as already mentioned. At 1373 K, the surface of the specimen became black in color due to a certain degree of the reduction, as shown in Fig. 4. On the other hand, the black plate was obtained through IPP treatment at 1073 and 1173 K. At 1273 and 1373 K, the surface became golden brown in color, and such an appearance suggested the formation of TiN.

3.2 Cross-sectional observation

Figures 5(a) to 5(d) show optical micrographs of the cross section of anodized titanium plates after IPP treatment at 1073, 1173, 1273 and 1373 K for 3.6 ks, respectively. A film with a thickness of approximately 10 μm on the titanium plate corresponded to an anodic oxide film modified by the IPP treatment. There were five kinds of distinctive microstructures, indicated as I to V. Region I was located at the outermost side of the film. This region became thin with increasing heating temperature, and was not observed in Fig. 5(d). Figure 6 shows the results of elemental mapping for the anodized titanium plate after the IPP treatment at 1073 K for 3.6 ks. From Fig. 6(d), the anodic oxide film was found to contain aluminum as mentioned above. Although Al$_2$O$_3$ powder was used in the IPP treatment as one of three components of a powder mixture, it did not adhere to the specimen even after heating and was not directly related to aluminum in the film. In region I, titanium, aluminum and oxygen were detected, and TiO$_2$ and anosovite would mainly exist according to an XRD pattern in Fig. 3(a). On the other hand, the distribution of nitrogen was observed at the position corresponding to region II in Fig. 5(a). The oxygen concentration seems to be decreased in this region, as shown in Fig. 6(e). However, the distribution of carbon in region II is unclear due to
the influence of resin, which was used to mount the specimen. For this reason, the specimen prepared at 1073 K was also examined by using GD-OES analysis. An analytical result is shown in Fig. 7. Although the film thickness was estimated to be lower than those in Figs. 5(a) and 6, the enrichment of not only nitrogen but also carbon was recognized in region II. In addition, the oxygen concentration was decreased in this region. It is notable that carbon and nitrogen began to be concentrated in the vicinity of the film/plate interface. This would be attributed to a porous structure formed by anodic oxidation and to the existence of aluminum in the film.

As shown in Fig. 5, the thickness of region II increased with increasing heating temperature, and this region was spread over the whole film at 1373 K. In all cases, the nitrogen concentration in region II was much higher than the carbon concentration. This is the reason that main diffraction peaks in Fig. 3(d) were identified as TiN. Furthermore, aluminum and oxygen were detected in the film by EPMA and GD-OES analyses even after the IPP treatment at 1373 K, and consequently diffraction peaks for Al2O3 were observed in Fig. 3(d). These facts indicate that the IPP treatment enabled the reduction and carbonitriding of the anodic oxide film, although the complete removal of oxygen was not achieved.

Defects like a void were observed in the film side of the titanium plate, which was indicated as region III in Fig. 5. It is thought that such defects were introduced by the interdiffusion across the film/plate interface and by the damage during grinding and polishing, and its detail is still under investigation.8)

Regions IV and V were observed only in Fig. 5(d). Region IV points to a gap, and means the peeling of the film from the titanium plate. On the other hand, region V was produced by the diffusion of carbon, nitrogen and oxygen into the titanium plate. The average hardness of this region was more than HV = 1300, and was much higher than that of the titanium plate before IPP treatment. A formation mechanism of these regions is discussed in the next section.

3.3 CO gas generation during IPP treatment

As shown in Fig. 5(d), the film was separated from the titanium plate through IPP treatment at 1373 K. An SEM image of its film surface is shown in Fig. 8. Cracks indicated by single arrows were observed on the porous surface. Such cracks were introduced only in the anodized titanium plate after the IPP treatment at 1373 K. Therefore, the occurrence of the cracks has a close relation with the peeling at the film/plate interface. On the other hand, there were a lot of spherical fine particles on the porous surface. These were iron particles in a powder mixture used in the IPP treatment, and their existence was expected from Fig. 3(d).

From previous studies, CO gas is known to be generated during a heating step in the IPP treatment by a chemical reaction in a powder mixture.3,4) Figure 9 shows a measurement result of the CO gas concentration detected during heat treatment at 1373 K for 3.6 ks in a nitrogen flow using a powder mixture. The amount of the used powder was approximately 2 ml.
comparison with that in the heating step. Therefore, the continuous generation of the CO gas in the holding step is a distinctive phenomenon in modifying the anodic titanium oxide film. According to Figs. 3 and 5, this indicates that the reduction of the oxide film was further promoted at a heating temperature of 1373 K. In fact, the amount of the CO gas detected in the holding step at 1373 K was larger than that at 1273 K. A reduction reaction in the holding step would be also caused by a decrease in the oxygen partial pressure around the anodized titanium plate.

As shown in Figs. 6 and 7, the reduction and carbonitriding of the anodic oxide film began to occur in the vicinity of the film/plate interface. Therefore, it is thought that the CO gas, which resulted from the decomposition of the anodic oxide film, was accumulated near there, and then caused the peeling of the film. From this standpoint, the cracks in Fig. 8 appear to be a trace of releasing the CO gas from the film/plate interface. Such a situation would lead to the formation of a hardened area containing carbon, nitrogen and oxygen, as indicated by region V in Fig. 5(d).

Although oxygen was not completely removed from the anodic oxide film by IPP treatment, we succeeded in the diffusion of carbon and nitrogen into the film. In addition, it was confirmed that the anodic oxide film, which was a porous and insulating material, was converted to a conductive film. The anodized titanium plate modified by the IPP treatment is expected to be used in electrolytic devices and battery cells as a porous electrode.

4. Conclusions

Titanium plates covered with anodic oxide films with thicknesses of approximately 10 μm were embedded in a mixture of iron, graphite and Al₂O₃ powders, and then heat-treated in a nitrogen flow to verify the effectiveness of this heat treatment method (IPP treatment). The main results were as follows.

(1) The anodic oxide film on the titanium plate was composed of TiO₂ and anosovite. By applying the IPP treatment at 1373 K to this plate, diffraction peaks for TiN appeared clearly in an XRD pattern, and the surface color of the film changed from gray white to golden brown.

(2) After the IPP treatment at 1073 K, not only an increase in the concentrations of carbon and nitrogen but also a decrease in the oxygen concentration was confirmed in the vicinity of the film/plate interface. The thickness of this region increased with increasing heating temperature, and the distributions of carbon and nitrogen were spread over the whole film at 1373 K. These indicate that the IPP treatment enabled the reduction and carbonitriding of the anodic oxide film, although oxygen was not completely removed from the film.

(3) The film was separated from the titanium plate through the IPP treatment at 1373 K. Cracks were also observed on the porous surface of the film. These would be caused by the accumulation of CO gas near the film/plate interface, which was generated by the decomposition of the anodic oxide film.

Acknowledgements

The authors would like to express their appreciation to Dr. T. Yamamuro of Kumamoto University for his kind assistance in the experiments. We greatly appreciate support from JSPS KAKENHI Grant Number 15K06509.

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