The 2017 World Congress on
Advances in Nano, Bio, Robotics and Energy (ANBRE17)
28 August - 1 September, 2017, Ilsan(Seoul), Korea

Effects of surface fluorination on the coloring of Ti-based alloy materials

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ABSTRACT

The surface of Ti metal can be modified using F_2 gas. Titanium oxides can be changed into titanium oxyfluorides or titanium fluorides on the Ti surface. And washing process after surface fluorination can make to eliminate the fluorides layer on the surface. And it makes to change the surface roughness. From the AFM results, the colorization of Ti metal was depended on the surface roughness (Ra and P-V).

1. INTRODUCTION

Titanium is a lightweight, high-strength, low-corrosion structural metal and is used in alloy form for parts in high-speed aircraft. A compound of titanium and oxygen was discovered (1791) by the English chemist [1]. With a pure metal density of 4.51 g/cm^3 (which may increase or decrease in alloys) the other most appealing aspect of titanium and its alloys is the excellent specific strength, that is, mechanical resistance per unit weight, which is also maintained at high temperature. Especially, titanium aluminides based onα–TiAl are highly regarded for high-temperature applications in automotive, aerospace, and power generation industries [2-6]. Even once titanium has been obtained in metallic form, a nanometric layer of TiO_2 immediately forms [7-8]; this constitutes a protective film, which prevents the metal from corroding in most known environments, even in very harsh conditions. Titanium reacts with oxygen to form a clear

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[1)] Graduate Student, [2),3)] Professor oxide, TiO_2. This clear oxides filter out light waves, producing brilliant colors. The thickness of oxide varies the colors. Oxides form naturally on titanium leaving the metal a gray color, but applied heat and or electrochemical treatment will increase the oxide thickness to produce a spectrum of color similar to a rainbow. This same filtering effect can be seen in colors on soap bubbles. The colors produced by these metals are known as interference colors. There are no pigments or dies involved. They are generated by a transparent oxide film grown on the metal surface. The colors develop when part of the light striking the surface reflects and part pass through the film to reflect off the metal below. When the delayed light reappears and combines with the surface light waves they may either reinforce or cancel. This generates a specific color. The thickness of the oxide film dictates the color. Coloring can be generally achieved in two ways; thermal oxidation and electrolytic oxidation (anodizing). Both processes do essentially the same thing. Through electron excitation, the metals react with oxygen to form a thin transparent film. Thermal oxidation (heat coloring) is simple, but difficult to control. Anodizing is infinitely more predictable. When the oxide is of a thickness to generate interference colors, its depth is measured in angstroms. This layer can vary in thickness from 500 to 1,000Å depending on the color. It is not the oxide itself that is perceived by the viewer but its effect on light. However, all the colors of the light spectrum are not produced. True red and forest green are not generated. F_2 gas has high reactivity with the oxygen in TiO_2 and easily forms the oxyfluorides or fluorides replacing of TiO2 on the Ti metal.

And the formed the oxyfluorides or fluorides can be eliminated by the lower heating or washing with water.

In this study, we will try to control the thickness and surface morphologies of TiO_2 film on Ti metal by the surface fluorination with F_2 gas. And it can make to vary the colors of Ti metal.

2. EXPERIMENTAL DETAILS

2.1 Surface fluorination

Ti meal (99 %) was purchased from Nilaco corporation. For the surface fluorination, the Ti sample (20 x 25 mm) was put into the reactor (3.4 x 10^6 m^3) made of nickel. After the reactor was pumped out to less than 1 Pa, F_2 gas was introduced into the reactor. Reaction temperature, fluorine pressure, and reaction time were set at 200℃, 0.1 MPa, and for 1h, respectively. Details of the fluorination apparatus have been mentioned in our previous work [9].

2.2 Washing and sintering processes

After surface fluorination, the samples were sintered under different conditions of washing processes as shown in Fig. 1. And individual process was noted as T-1, T-2, T-3 and T-4 in Fig. 1. In case of T-1 samples, they were sintered without any washing. T-2 samples were reacted with H_2O_2 solutions, and dried and sintered at 300℃ for 1h without washing process. After T-3 and T-4 samples were reacted with H_2O_2 solutions, they were washed with water and dried and sintered at same conditions. Especially, when the T-4 samples are washing with water, they were cleaned and heated using the ultrasonic instrument.

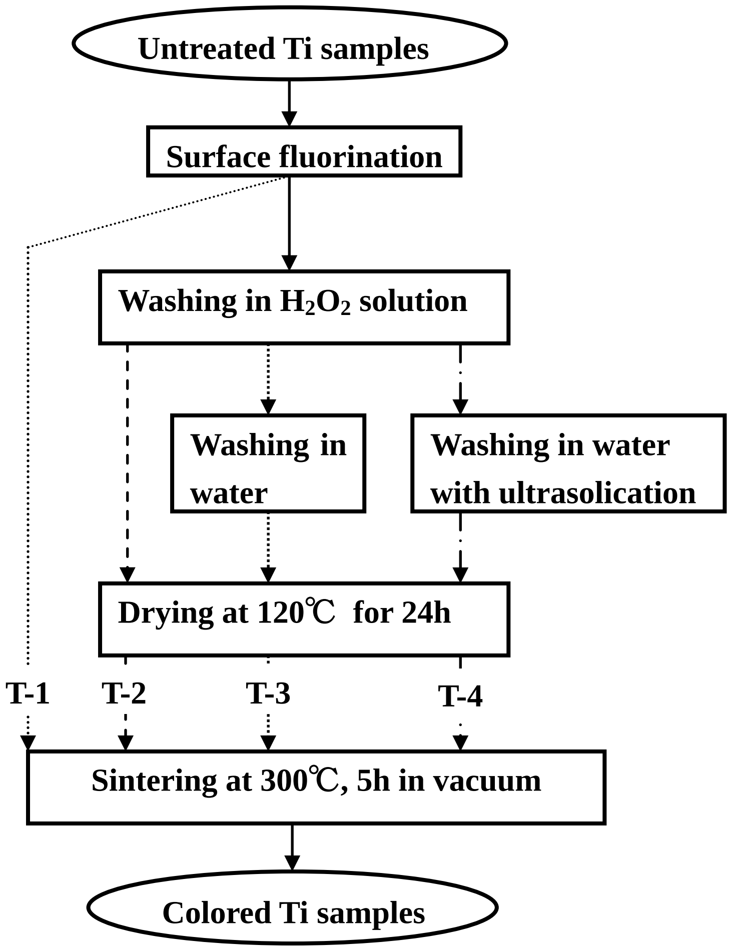

Fig. 1 Flow diagram for coloration of Ti samples

2.3 Measurements

The structural and electronic properties of the samples were investigated using powder X-ray diffraction (XRD, XRD-6100; Shimadzu Corp.) and X-ray photoelectron spectroscopy (XPS, XPS-9010; JEOL). The surface morphology of various samples was observed using a scanning electron microscope (SEM, s-2400; Hitachi Ltd.). And the surface roughness was measured using an atomic force microscopy (AFM, SPI-3700; JEOL). The coloration of samples was measured using a spectrophotometer (CM-3700d; Konica Minolta Corp.).

3. RESULTS and DISCUSSION

3.1 Photographs

Figure 2 shows the photographs of untreated and fluorinated samples. Comparing with Ti metal color of untreated sample, the surface coloration of fluorinated samples could be changed and depended on the washing process as shown in Fig.1.

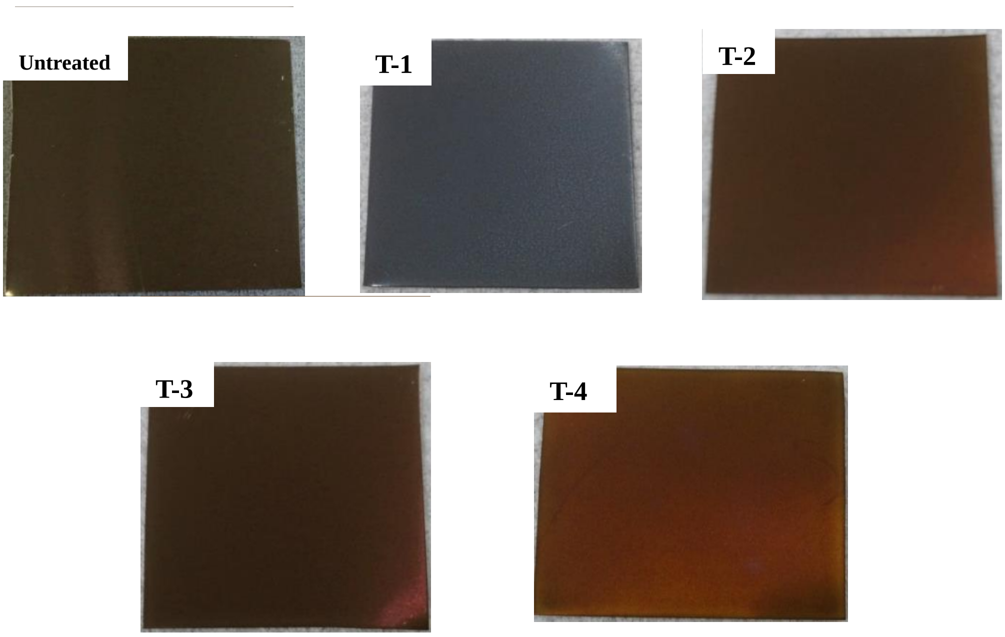

Fig. 2 photographs of color samples.

3.2 SEM images

Figure 3 shows the SEM images of various samples indicated in Fig.2. Comparing with untreated sample, the surface morphology of T-2, T-3, T-4 samples seems to be similar and it looks like a slanting line patterns. However, surface morphology of T-1 sample looks like network patterns. It may be reasoned for the residual of fluorides on the Ti surface.

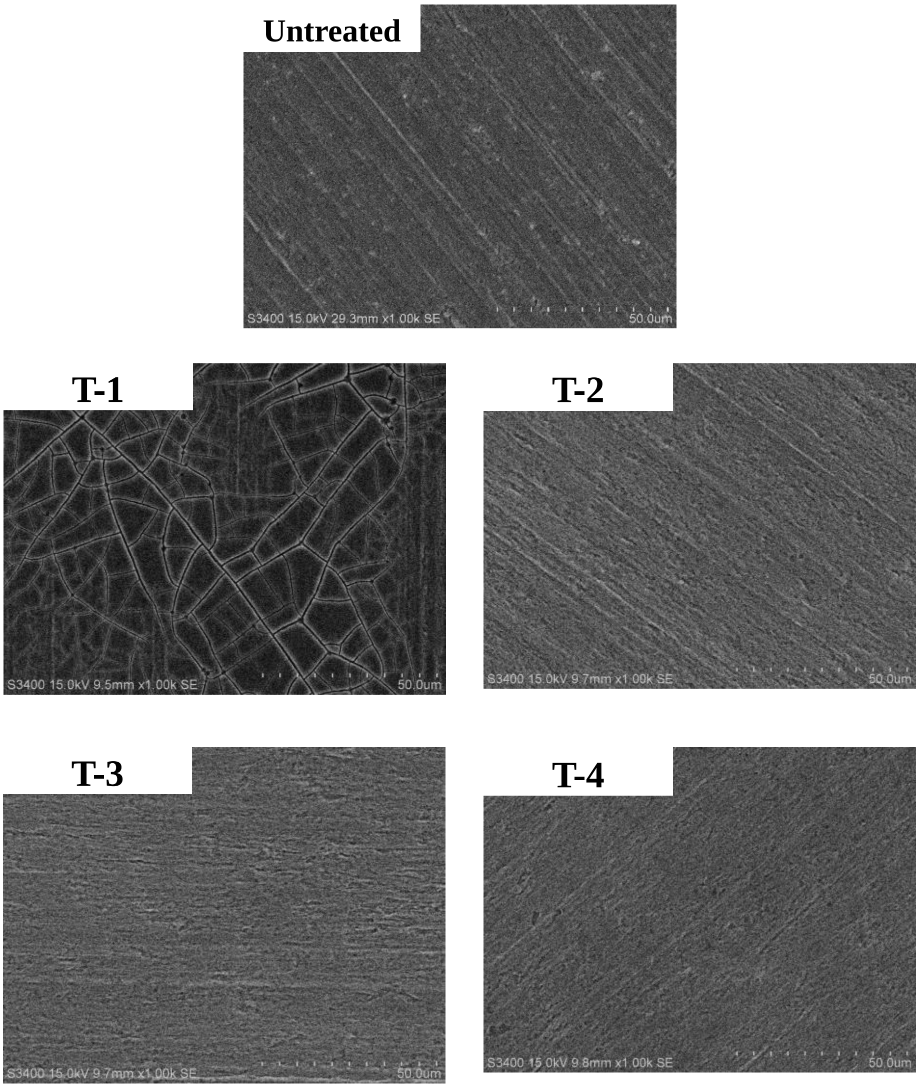

Fig. 3 SEM images of various samples.

3.2 Surface roughness

Figure 4 shows the average value (Ra) and size (P-V) of roughness on the Ti surface.

Depended on the washing processes, the roughness of sample surface can be controlled as shown in Fig.4. With increasing the roughness, the color changed from blue into red sides. However, though the roughness of T-2 and T-3 was almost same, the color had different things as shown in Fig. 5. As shown in Fig.6, the colorization and roughness size (P-V) are linearly changed. Namely, the changing color from blue to red side was depended on the roughness size (P-V) at this time.

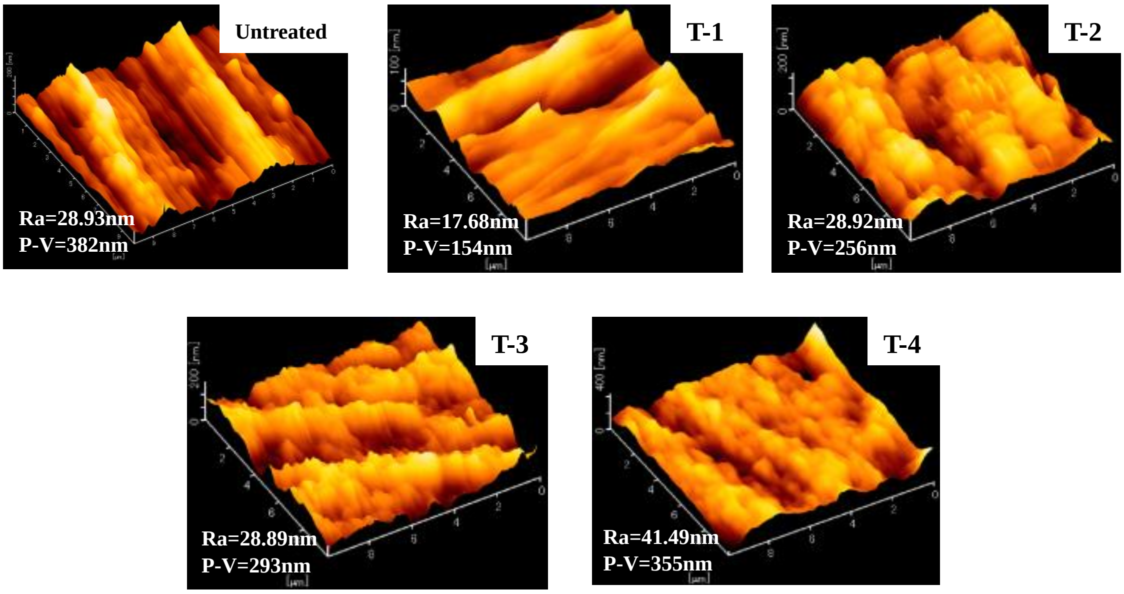

Fig. 4 AFM images of various samples.

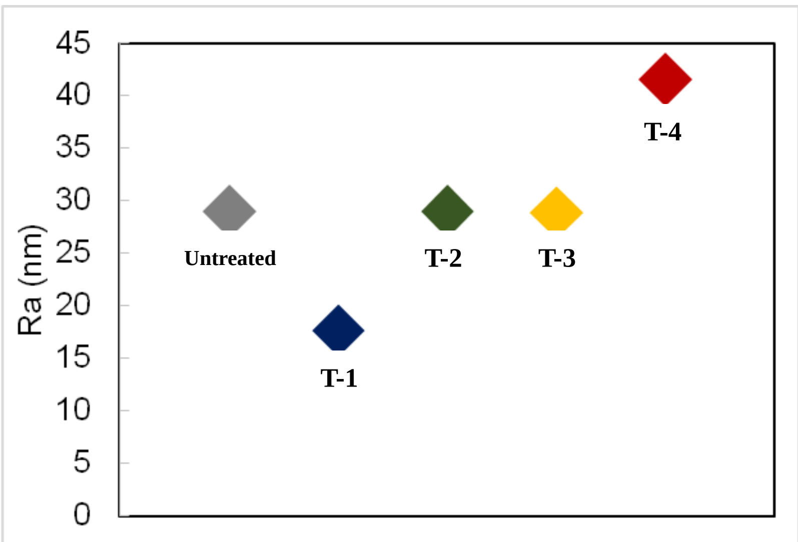

Fig. 5 The relationship between colorization and roughness value (Ra) of Ti surface.

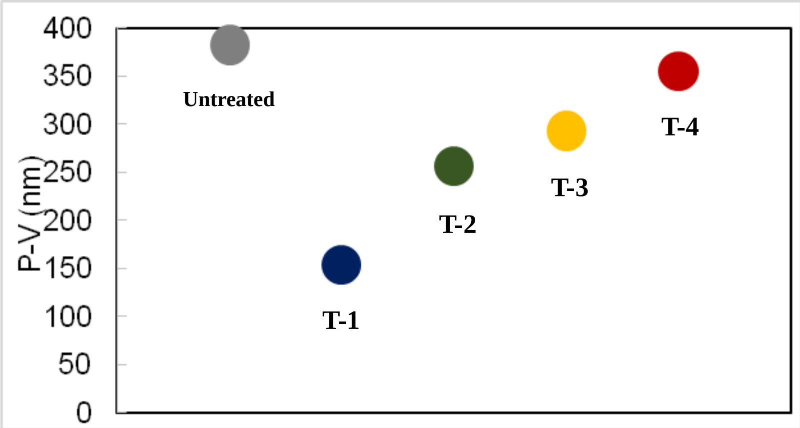

Fig. 6 The relationship between colorization and roughness size (P-V) of Ti surface.

4. CONCLISIONS

We have reported the effects of surface fluorination on the colorization of Ti metal. And the washing process after fluorination mainly affects the roughness of surface in this study. Especially, the colorization was depended on the roughness size (P-V) on the Ti surface. Namely the colorization of Ti meal can be controlled by adjusting the surface roughness as well as the thickness of TiO_2 layer.

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