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Enhancement of oxidation resistance in titanium by plasma treatment for high temperature applications

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Abstract. Titanium metal has many uses in various industries and applications due to its unique and distinctive properties, making it an important and effective material in daily use in many fields. However, they cannot be used for high-temperature applications for a long time due to their poor oxidation resistance at high temperatures. This study used compression plasma flows (CPFs) treatment to enhance the oxidation resistance of pure titanium samples in high-temperature environment. X-ray diffraction (XRD) was used to characterize air-annealed pure titanium samples with and without CPFs treatment. Without CPFs treatment, the XRD spectra of the samples annealed at 700 °C for 10 minutes and above consist of additional diffraction lines of (110), (101), and (211), representing the rutile TiO_2 phase, indicating the occurrence of oxidation. However, TiO_2 phases were absent in the XRD spectra of the samples treated with CPFs and then annealed under similar conditions. This indicates the effectiveness of the treatment and its ability to prevent oxidation at high temperatures. Moreover, the XRD investigation showed insignificant changes in the crystal structure of the samples annealed after plasma treatment. Thus, titanium and its alloys with CPFs treatment show potential for high-temperature applications.

1. Introduction

Titanium and its alloys, for example, are widely used engineering materials in the aviation, automotive, aerospace, biomedical, shipbuilding, petrochemical, nuclear, and power generation industries due to their numerous important properties including low density, high strength, low weight, superior biocompatibility, excellent corrosion resistance, etc. [1]. Although carbon fiber reinforced plastics have a higher specific strength than titanium alloys below 300 °C, the specific strength of titanium and its alloys is attractive at high temperatures [2]. However, the use of titanium and titanium alloys is still limited to temperatures below 550 °C due to their low oxidation resistance above 550 °C [3]. The possible chemical reactions involved in oxidation of titanium at high temperatures are reported elsewhere [2]. The oxidation of titanium leads to the lattice distortion and reduction in the mechanical performances. To improve the high temperature oxidation resistance of titanium and titanium alloys, several material modification techniques such as alloying, and surface modifications have been followed. Alloying modification by adding alloying elements into the titanium or its alloys is simple and effective technique to increase the high temperature oxidation resistance. Surface alloying and coating are two surface modification techniques to change the material properties. However, the addition of alloying elements changes the mechanical behaviour which can lead to the degradation of ductility and toughness of the alloy systems. Moreover, surface coatings are not stable for long term high-temperature applications [2]. The aforesaid techniques are inefficient in improving the oxidation resistance of titanium and its alloys. Plasma technologies have wide range of possible surface treatment of materials. Surface modification of materials can be performed by compression plasma flows (CPFs) produced in a quasi-stationary plasma accelerator of compact geometry, which has a comparatively long discharge time of ~ 100 μs, a high temperature of 1 – 3 eV and a high velocity of plasma particles of 4 – 7 × 10^6 cm/s [3]. Due to the plasma flows into the material, the treatment of CPFs on the materials leads to the thermal effects such as heating and melting of the surface layer, which subsequently results in a modified layer due to rapid cooling and crystallization. X-ray diffraction (XRD) is an effective analytical tool used in materials science to determine material's crystallographic structure, which involves irradiating the material with incident X-rays and measuring the intensity and scattering angle of those X-rays that leaves the material. This technique has many applications, such as determination of atomic arrangement, identification of crystalline phases, and determination of structural properties, i.e., phase composition, crystallite size and the lattice parameters. In this study, pure titanium was annealed in air atmosphere before and after the CPFs treatment to investigate the resistive behavior of pure titanium to oxidation. CPFs treatment modifies the surface layer of the materials. XRD was used to characterize the annealed and unannealed samples before and after the plasma treatment. The properties of metals are affected by the annealing and CPFs treatment. Thus, CPFs treated air-annealed pure titanium does not contain any XRD peaks corresponding to oxide indicating the effectiveness of the treatment and its ability to prevent oxidation at high temperatures.

2. Experimental

A magnetoplasma compressor of compact geometry produces intense pulsed CPFs in nitrogen atmosphere whose discharge duration was 100 μs, plasma velocity was 3 – 7 × 10^6 cm/s, and electron temperature was between 2 and 4 eV. The voltage between the electrodes was 4 kV. Six samples were annealed in air atmosphere at different temperatures (600 °C – 700 °C) and durations (5 – 15 min) without CPFs treatment. Other six samples were treated with CPFs and then exposed to the temperature between 600 °C and 700 °C for annealing in air atmosphere to observe the oxidation behavior. In addition, the crystal structure of titanium is affected when titanium is exposed to a high temperature. Titanium samples were heated to a certain temperature (600 °C – 700 °C) in a furnace and kept there for the desired period (5 to 15 min), and then it is naturally cooled in the air atmosphere. The samples were heated in the furnace for different periods and temperature ranges to expose the samples to a high temperature environment like various high-temperature applications. Metals are more likely to oxidize in high temperature conditions depending on their chemical properties. Aforementioned two sets of titanium samples were subjected to the annealing process to compare the oxidation behavior between the sets with and without CPFs treatment. The purpose of this heating process is to investigate if compression plasma flow treatment has any role in increasing the oxidation resistance of the pure titanium samples. The samples are named according to the processing conditions and are listed in the table 1 and table 2. X-ray diffraction (XRD) technique was used to characterize the samples. Pure titanium sample without annealing and plasma treatment is referred to as B61.

Table 1. List of annealed titanium samples without plasma treatment along with their nomenclature.

Sample Name	B51	B52	B53	B54	B55	B56
Annealing Temperature	600 °C	600 °C	600 °C	700 °C	700 °C	700 °C
Annealing duration	5 min	10 min	15 min	5 min	10 min	15 min

Table 2. List of annealed titanium samples after plasma treatment along with their nomenclature.

Sample Name	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Annealing Temperature	600 °C	600 °C	600 °C	700 °C	700 °C	700 °C
Annealing duration	5 min	10 min	15 min	5 min	10 min	15 min

3. Results and Discussion

Figure 1 shows the XRD spectrum of B61 which contains diffraction lines corresponding to (100), (002), (101), (102), (110), (103), (112), and (201) planes of pure titanium occurring at $2\theta = 35.2^\circ, 38.5^\circ, 40.2^\circ, 53.1^\circ, 63.1^\circ, 70.7^\circ, 76.3^\circ$, and 77.4°, respectively.

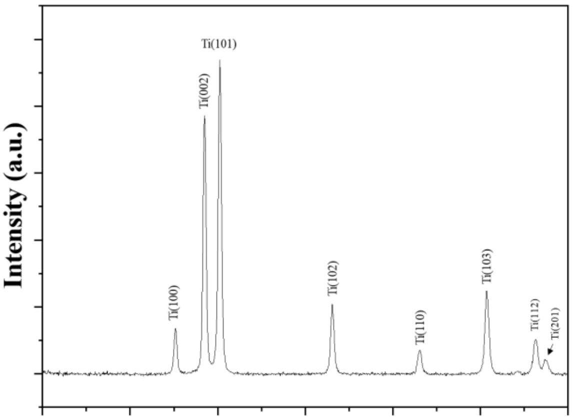

Figure 1. XRD spectrum of pure titanium sample without annealing and plasma treatment (B61).

Diffraction peak corresponding to (101) occurring at 40.2° represents the most dominant crystal orientation. The interplanar spacing d_{hkl} is determined by following the Bragg's condition [4]:

$$2d_{hkl} \sin\theta = n\lambda \qquad (1)$$

where θ is the Bragg angle, and n is the diffraction order which is 1 for the first order. The values of d_{hkl} corresponding to different diffraction peaks (100), (002), (101), (102), (110), (103), (112), and (201) planes of B61 are 2.549, 2.336, 2.239, 1.724, 1.473, 1.331, 1.277, and 1.247 Å, respectively. Since the pure titanium exhibits a hexagonal close-packed (HCP) crystal structure, the lattice parameters are determined by using the below equation [4]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\,\frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2} \qquad (2)$$

where a and c are the lattice parameters. The values of a and c are 2.94 and 4.67 Å, respectively, which are close to that of pure titanium.

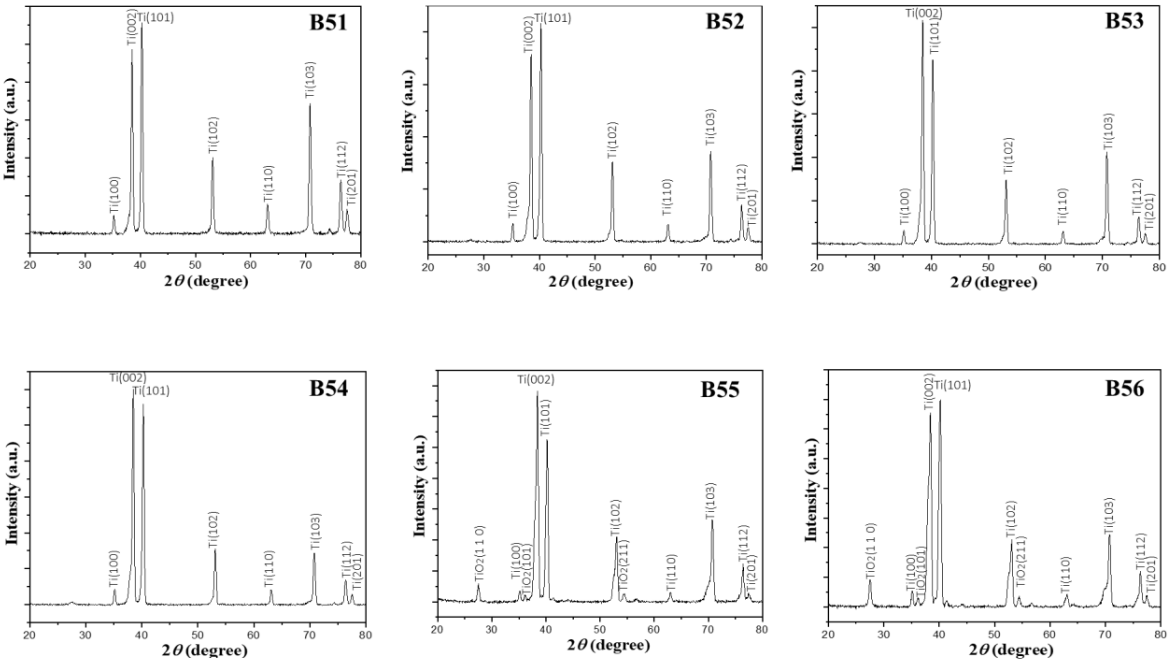

Figure 2. XRD spectra of the pure titanium samples annealed at 600 °C for 5 min (B51), 10 min (B52) and 15 min (B53), and at 700 °C for 5 min (B54), 10 min (B55) and 15 min (B56).

Figure 2 shows the XRD spectra of the samples B51, B52, B53, B54, B55, and B56. The samples annealed at 600 °C for all durations up to 15 min have XRD peaks corresponding to the pure titanium (B61). No new additional diffraction peaks, particularly diffraction lines corresponding to oxides are observed. However, linewidth broadening of diffraction peaks is noticed as the duration of annealing increases from 5 min to 15 min at 600 °C which is an indication of the degradation of the crystal structure. The samples annealed at 700 °C for 5 min (B54) shows similar behaviour which consists of diffraction lines corresponding to pure titanium with no additional diffraction peaks. The samples annealed at 700 °C for 10 and 15 min consist of same diffraction peaks as that of the pure titanium (B61) along with additional diffraction peaks occurring at 27.5°, 36.1°, and 54.3° corresponding to (110), (101) and (211) planes of the rutile phase of TiO_2. This indicates that the investigated pure titanium does not show significant oxidation behavior for the samples annealed at 600 °C up to 15 min and at 700 °C up to 5 min. Moreover, the intensity of diffraction peaks corresponding to rutile phase of TiO_2 observed for B55 and B56 increases with respect to that of pure titanium phase, which indicates increasing oxidation with increase in annealing duration. At annealing temperature of 600 °C, the dominant crystal orientation changes from (101) to (002) plane as annealing duration increased to 15 min, which could be attributed to thermal induced change in crystallinity since the dominant preferred crystal orientation is along c-axis. At annealing temperature of 700 °C, the dominant crystal orientation is along c-axis even for smallest annealing duration of 5 min and medium duration of 10 min. However, for the longest duration of 15 min, the dominant preferred crystal orientation is changed back to (101) plane, which could be attributed to the occurrence of additional processes including oxidation to form rutile phase of TiO_2.

Figure 3 shows the XRD spectra of sample 1 to 6. All XRD spectra contain diffraction lines corresponding to (100), (002), (101), (102), (110), (103), (112), and (201) planes of pure titanium. No additional diffraction peaks corresponding to the oxides are observed. Note that the samples 1 to 6 are annealed after the CPFs treatment. This indicates that CPFs treated samples are oxidation resistant up to 700 °C for 15 min. Moreover, the value of lattice constant c remains close to 4.71 Å which indicates no degradation of crystal structure due to CPFs treatment and post annealing. The most dominant crystal orientation is along (101) for all samples. The degree of crystal orientation in CPFs treated annealed samples along (101) is substantially larger than annealed and unannealed samples without CPFs treatment.

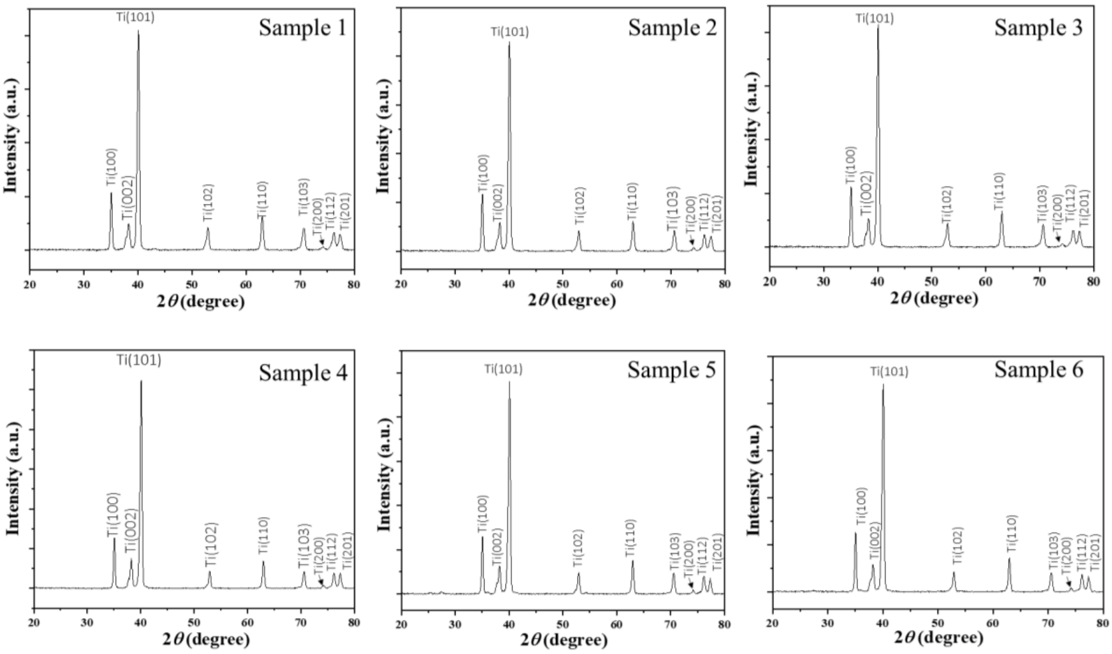

Figure 3. XRD spectra of the pure titanium samples annealed at 600 °C for 5 min (sample 1), 10 min (sample 2) and 15 min (sample 3), and at 700 °C for 5 min (sample 4), 10 min (sample 5) and 15 min (sample 6).

4. Conclusions

Compression plasma flows (CPFs) treatment is used to enhance the oxidation resistance of pure titanium samples in high-temperature environment above 550 °C at which high-temperature applications of titanium is limited [3]. The samples without CPFs treatment annealed in air atmosphere at 700 °C for duration above 10 minutes show formation of oxides. XRD analysis reveals that the formed oxide is rutile TiO_2 which shows diffraction lines in XRD spectra corresponding to (110), (101), and (211) planes. The samples annealed in air atmosphere after CPFs treatment does not show oxide diffraction lines in their XRD spectra up to 700 °C for 15 min. This betokens that the compression plasma flows treatment is quite effective in increasing the oxidation resistance of the pure titanium by modifying the surface layer. The plasma treatment technique can further be used for other metallic systems including titanium alloys to prevent the oxidation of metals at high-temperatures and to make them suitable for desired high-temperature applications.

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