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Laser Treatment of Pure Titanium Surface in Various Irradiated Media: Investigating Hardness Properties of Ablated Ti Surface

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Abstract

Titanium (Ti) has poor tribological and mechanical properties such as low hardness and wear resistance. In this study, we considerably improve Ti's hardness by laser ablation method. Ambient air, N_2 gas chamber and N_2/liquid water environments were separately selected as irradiation environments and their effect was comparatively studied on Ti treatment surfaces. The fabrication of titanium nitride (TiN) structure was successfully confirmed by XRD analysis in N_2 gas and N_2/liquid water as irradiation media. Accordingly, there was good adhesion between TiN structure and Ti's surface. Vickers hardness test indicated the laser treatment and TiN structure significantly improved Ti's hardness. The formed TiN structure in N_2/liquid water environment had the highest hardness value of 530Hv comparing to hardness of ablated Ti in N_2 gas (370Hv) and air (340Hv). The escalation of Ti hardness and generation of TiN structure with laser-treatment in N_2/liquid water environment is a favorable aspect of this method.

1. Introduction

Ti and its alloys have various applications in the industry owing to their remarkable chemical and mechanical properties including high strength, high melting point, light weight, and resistance to corrosion [1–3]. Despite the advantages of Ti properties, it has poor hardness and wear resistance, which limits its industrial uses. Therefore, surface modification techniques were applied to extend Ti application [4, 5]. Over the last years, laser approaches as powerful and essential methods are of interest in research to modify surfaces. Laser surface treatment methods include laser cladding [6], laser welding [7], laser additive manufacturing [8], laser surface hardening [9] and pulse laser deposition (PLD) [10, 11]. There are conventional methods such as chemical and physical vapor deposition (CVD and PVD) [12, 13], sputtering [14], ion plating [15], carburizing [16], and nitriding [17], which have been employed by researchers. Generally, coating a hard ceramic layer on the surface of Ti is a potential technique for improving the mechanical properties of Ti [18]. Among the ceramic materials, titanium nitride (TiN) with excellent hardness and wear resistance is a suitable candidate for overcoming the drawbacks of Ti in the industry [19, 20]. Compared to conventional methods, laser treatment techniques are very simple, clean, and low-cost ways to form TiN layers with high adhesion [11, 21]. In literature, the TiN layer has been deposited on Ti or its alloys' substrates with laser cladding [6], laser gas nitriding (LGN) [19, 22], and pulsed laser ablation (PLA) in nitrogen gas atmosphere [23, 24] to enhance wear and hardness properties of Ti surfaces.

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A brief description of PLA mechanism is presented in the following.

Ti plate is irradiated by a laser beam and its temperature gradually rises to reach at its melting point. Based on laser thermal processes, molecules and atoms are removed from the Ti solid surface followed by plasma plume generation [25]. The plasma plume forms exactly above the Ti target in the irradiation environment. By interaction between laser beam and plasma plume, the species including neutral atoms, ions, and electrons from target and environment increase rapidly leading to expand plasma plume [21]. In the case of gaseous medium, the plasma plume separates from the surface. However, the liquid environment traps the plume and prevents its expansion [21, 26, 27] and spreading plasma plume leads to the species' collisions, aggregations, and condensations. Then new materials will be formed in the plasma plume and redeposit on the Ti target and form a new structure on Ti's surface [25]. So far, there has been various investigations in numerous studies on the effects of laser irradiation parameters and scanning conditions (scanning speed, laser overlap rate, and the number of scanning cycles) [22, 28], the amount and thickness of TiN layer [24, 29], N_2 gas pressure [30] and the laser power [24] on the surface hardness and tribological properties of irradiated Ti surfaces.

In this research, the laser ablation was selected as an easy and cost-effective method to ablate the Ti plate in ambient air, N_2 gas chamber and N_2/liquid water environments separately. The effect of various media was comparatively studied on Ti hardness surfaces. The characterization of irradiated samples in different media was investigated by XRD method, which reveals the formation of TiN and TiO_2 structures as hard materials on the Ti surface leading to its increased mechanical hardness. N_2/liquid water medium has been used to produce a TiN structure so that a chamber of distilled water would be purged with N_2 gas. The merits of doing so are as follows; First, according to SEM analysis, the irradiated surfaces' morphology is more uniform in the liquid medium compared with irradiated surfaces in gaseous medium [31], which can affect the hardness of the irradiated surface. Second, laser ablation in liquid state is much simpler and cheaper in terms of N_2 gas usage.

2. Experimental Procedure

In order to improve Ti surface properties, a Ti sheet (0.6mm thick) was firstly cut into the required number of samples at $16 \times 16\text{mm}^2$ dimension. They were ground with different SiC papers and then they were washed with distilled water via an ultrasonic device for 15 minutes. In this work, two laser ablation methods have been proposed to construct the new structures on the surface of Ti in gaseous and aqueous environments; therefore, after preparing the samples, they were irradiated in air, N_2 gas, and N_2/liquid water media under the same irradiation condition using fiber laser (RFL-P30Q) with the wavelength of 1064nm, the repetition rate of 20kHz, the scanning speed of 200mm/s, laser power of 27W, and with a laser step of 50μm in x and y directions [31]. The laser ablation process was applied to Ti samples in different laser irradiation environments (similar laser parameters). The reference Ti (without any laser processes) and irradiated samples in air, N_2 gas, and N_2/liquid water media were named as S_R, S_A, S_N, and S_W, respectively. The preparation sequences of Ti samples for the laser ablation process are illustrated in Fig. 1. Regarding S_A, the Ti sample was placed in ambient air and then laser ablation process was performed on it. About S_N, the N_2-filled chamber was chosen as irradiated media at inlet gas pressure of 2 bar [31]. In this case, at first, the chamber should be filled with N_2 gas for about one min to remove inconvenient gases and also during the ablation process the injection of gas into the chamber must steadily continue. In the case of S_W, a chamber containing distilled water was purged with N_2 gas at a low flow rate of 25ml/s for about 15 minutes [32]. This N_2/liquid water was used as laser irradiation media. It should be noted that during the irradiated process, N_2 gas was continuously injected into the water chamber. The structures of S_R, S_A, S_N, and S_W were evaluated by XRD (ITALSTRUCTURE, ADP 200) over the 2θ range of 20°-80° at room temperature (RT). The scanning electron microscopy (SEM, JFC-1100 E) was employed to investigate the morphology of the samples. Microhardness measurements were performed on samples with Buehler (60044. USA).

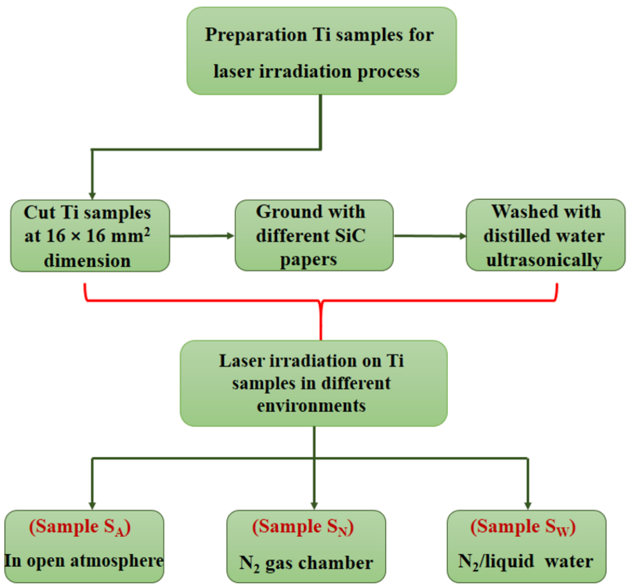

Fig. 1. The illustration of Ti samples' preparation for laser ablation process.

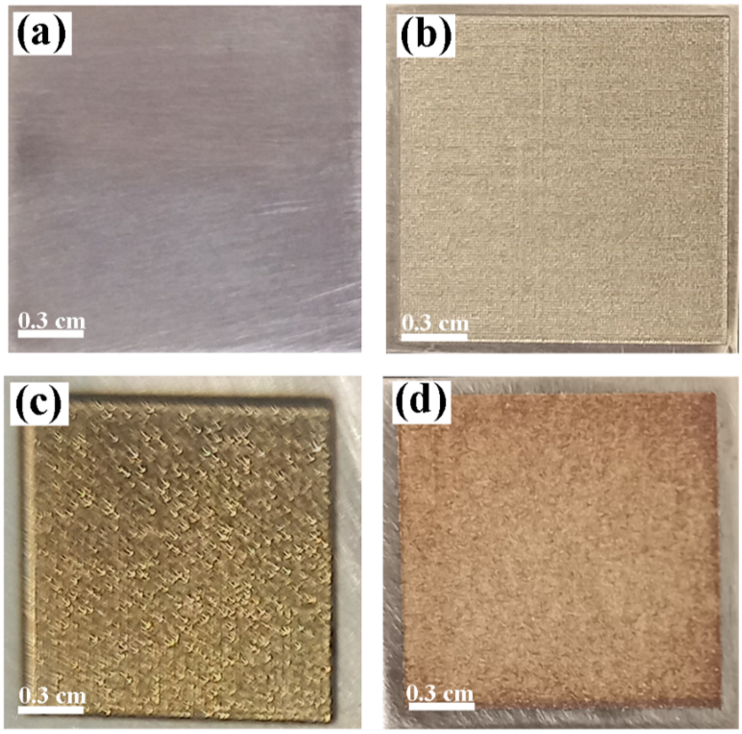

Fig. 2. Optical images of pure Ti metal a) and ablated samples S_A b), S_N c), and S_W d).

3. Results and Discussion

3.1. Characterization Analyses

After the laser ablation process, the color of the samples was changed as shown in Fig. 2. The discoloration of irradiated samples is the first sign of new structure fabrication on the surface of Ti. The color of S_A surface changed to gray (Fig. 2b), it might be due to titanium oxide (TiO_2) formation structure on S_A surface [33, 34]. The reason for the generation of TiO_2 can be related to the large amount of oxygen (O) in air, entering the Ti structure under laser processing [35]. According to Fig. 2 (c and d), the samples S_N and S_W turned golden yellow. The effect of the appearance of golden yellow color on the formation of TiN is well known [34]. During the laser ablation process, the hexagonal close-packed (hcp) lattice of Ti structure is occupied with nitrogen (N) atoms leading to TiN formation. Therefore, the irradiated surfaces of the Ti sheet in N_2 gas and N_2/liquid water turn desirable golden [34]. Of course, their golden color is different, which is probably due to their different morphology, which leads to a change in light absorption and reflection. For further investigation, XRD analysis of samples was performed to determine the new structure.

3.1.1. XRD Analysis

The XRD test results of samples are presented in Fig. 3. The diffraction patterns in Fig. 3a-d relate to samples S_R, S_A, S_N, and S_W, which S_A, S_N, and S_W irradiated in air, N_2 gas and N_2/liquid water media, respectively. As seen in Fig. 3, all these four XRD patterns indicate peaks at about 35.1°, 38.4°, 40.1°, 53.3°, 63.2°, 70.7° 76.2°, and 77.2° matched with Ti hexagonal peaks (ICDD Card No. 01-1198). Furthermore, two peaks are located at 25.3° and 70.4° in the XRD pattern of S_A corresponding to TiO_2 peak (ICDD Card # 16-0617). In the case of S_N and S_W, three peaks at about 37.2°, 42.9°, and 78.5° have appeared in their X-ray patterns; these peaks are related to (111), (200), and (222) Bragg planes of cubic titanium nitride (ICDD Card No. 06-0642) illustrating the TiN formation on the exposed Ti surface. In the case of air and N_2 gas irradiated environments, because they are both gaseous, the mechanism of laser-plasma formation is almost the same [35]. As explained in the introduction part, by irradiating the Ti surface in ambient air for S_A and in an N_2 gas chamber for S_N, the laser ablation process starts. By the effect of laser beam on Ti surface, its temperature rises. After the laser-irradiated area melted, plasma was created on the exposed spot of Ti surface by the evaporation process. Separation and ionization of air or nitrogen molecules was occurred by the pressure and the high plasma temperature [25]. Therefore, the irradiation environments such as ambient air containing oxygen or N_2 gas chamber play an important role in the formation of new structures and the properties of the material. Hence, in the case of S_A and S_N, the opportunity of TiO_2 and TiN formation on Ti's surface is strongly high which confirms with XRD test results and colors of the samples. In relation to sample S_W irradiated in N_2/liquid water, the conditions are slightly different due to the liquid environment. Under the laser ablation process, Ti surface is melted and surface tension differences caused a convective flow of liquid Ti [36]. The temperature of Ti surface rises by absorbing the laser beam. Its thermal processes change the physical properties of material and lead to evaporation [37]. The plasma plume is formed on the Ti surface contained of atoms, ions, and electrons from the irradiation environment and Ti target. The plasma plume movement is limited by liquids. Therefore, the generation, transformation, and condensation processes happen under the liquid confinement condition [21, 38]. Therefore, the probability of collisions between N and Ti atoms increases and causes the formation of a TiN structure due to the purging of N_2 gas in water to removal of dissolved oxygen. The X-ray diffraction pattern of S_W and its desirable TiN golden color confirms this claim.

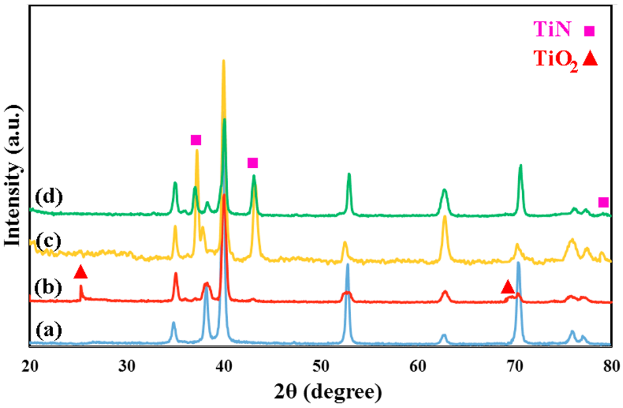

Fig. 3. XRD patterns of a) S_R and laser ablated samples; b) S_A, c) S_N, and d) S_W.

3.1.2. Scanning Electron Microscopy (SEM)

Fig. 4a shows a microscopic image of S_R. Fig. 4b and c indicate Ti surface after the ablation process in N_2 gas (S_N) and N_2/liquid water (S_W), respectively. As seen in the pictures, after the irradiation process, the effect of laser irradiation is completely visible and the pores are created on the surface of irradiated samples. By comparing SEM images of irradiated surfaces in different laser irradiation media, we found that with changing the environment from gaseous to liquid, the porosity is significantly reduced. The cavities are created due to the laser ablation effect in all sample surfaces but the sample irradiated in N_2/liquid water is more uniform because the molten material in liquid can better fill and cover the surface cavities (Fig. 4c).

3.2. Microhardness Measurement

Fig. 5 illustrates the microhardness diagram of S_R and the laser-ablated samples. Microhardness measurements were applied by microhardness tester with a load of 100g at hold time of 15s. From each sample, three samples were prepared in the same condition. Three hits were carried out on each sample to ensure the accuracy of the hardness data and their average was finally reported as the value of hardness. The basic rule of hardness measurements is the ability of material to plastic deformation resistance from a standard source [39]. In this test, the hardness value is introduced as the Vickers Pyramid Number (Hv) [39]. In the present work, it is clearly obvious that the hardness extremely rises with changing laser treatment media in a way that S_R has lower hardness compared to ablated samples S_A, S_N and S_W. The mechanical properties of the metal alloy such as micro-hardness and compressive stress can improve by laser treatment technique with a little bit increasing surface roughness and affecting microstructures [39]. According to our previous study [31], the Ti roughness was increased after laser ablation process in N_2 gas leading to increase hardness. Therefore, laser treatment is an effective factor in increasing micro-hardness of all irradiated samples. Another factor that can have an effect on Ti hardness is the ceramic coatings such as TiN, TiC, and TiO_2 on Ti surface [3, 38]. As exhibited in the XRD patterns of samples in Fig. 3, the operation of laser method leads to the formation of TiO_2 and TiN structure which represents higher hardness to the surface. Similar results were found in the literature [3, 8]. In addition, we find that the S_W has much more hardness value (530Hv) than those of samples S_A (340Hv) and S_N (370Hv). Although according to XRD results the deposited material on both of S_N and S_W surfaces is TiN, the SEM images show that the Ti irradiated in a liquid medium is more uniform and has less porosity compared to the gaseous one, which probably has resulted in greater hardness.

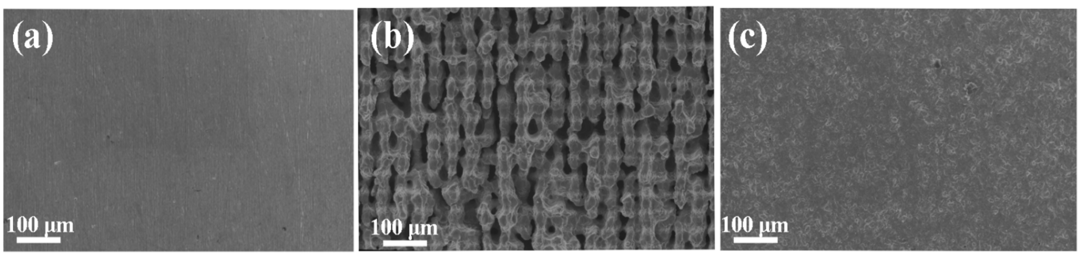

Fig. 4. Surface SEM images of a) S_R, b) S_N, and c) S_W.

In a similar work it has been shown that the escalation of Ti hardness is significantly related to increasing laser-treatment time that leads to a more uniform surface [38]. Therefore, the formation of the TiN ceramic structure and its surface morphology are important factors for improving the Ti hardness in laser treatment.

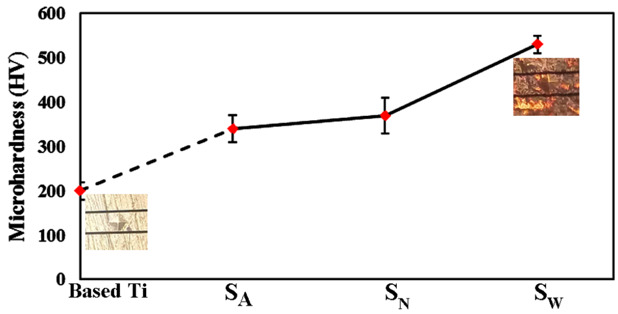

Fig. 5. Microhardness graph of the laser-irradiated Ti samples in different irradiation environments.

4. Conclusion

In summary, laser surface treatment as an easy and green technique was used to improve the Ti metal's mechanical properties. The Ti samples were irradiated in different laser irradiation environments including ambient air, N_2 gas and N_2/liquid water by fiber laser. As the first advantage of this method, we found uniform TiN structure could be formed on the Ti surface in N_2 gas and N_2/liquid water. As we expected, the laser treatment and ceramic TiN structure improved the microhardness of the Ti. One of the surprising aspects of this research is that the hardness of the samples irradiated in N_2/liquid water significantly increased to 530Hv. Hence, laser irradiation and its environment play an important role in enhancing surface properties and improving the quality of the formed new structure.

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