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Phase transformation under beam-target interactions during high-intensity pulsed ion beam irradiation at low pressure

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Abstract

Nitrides and/or carbonitrides formation of high efficiency was found on titanium target under irradiation of high-intensity pulsed ion beam (HIPIB) with a few shots at a low pressure of 10^{-2} Pa order, which is extraordinary in comparison with conventional thermo-chemical diffusion process such as gas nitriding and/or carbonitriding of metals necessarily heated at high temperatures during a processing time of hours. The underlying mechanism of the nitrides and carbonitrides formation on titanium targets was explored by a comparative study on three typical HIPIB sources, i.e., TEMP-6, TEMP-4M, and ETIGO-II, varying the irradiation intensity within several J/cm^2 per shot of a 60–70 ns pulse duration and the shot number of similar ion species. It is revealed that ambient gases and ion source material are the main sources providing the nitrogen and carbon species for the phase transformation on titanium target at the low pressures, whereas the ion species of HIPIB composition is negligible at a low implantation dose of 10^{13}–10^{14} ions/cm^2. The adsorbed gaseous species, the deposited layer of the ion source material, and *in-situ* formed compound top layer from reactions between ablation plasma and the ambient species during HIPIB irradiation, can be effectively incorporated into the irradiated target surfaces under a controlled HIPIB-target interaction.

Keywords: Carbonitriding; High-intensity pulsed ion beam; Irradiation; Nitriding; Phase transformation

1. INTRODUCTION

Nitriding, carburizing, and carbonitriding have been used as widespread thermo-chemical diffusion methods for surface treatment of metallic work-pieces made of titanium, aluminum, and their alloys as well as steels (Bell, 1992; Schaaf, 2002), where a compound surface layer with new phases of nitrides, carbides, or carbonitrides can be produced on the treated parts usually heated in a gaseous ambient from hundreds to a thousand degrees centigrade with inward diffusion of thermo-activated nitrogen or carbon atoms during a processing time up to tens hours. However, in many cases, the thermo-chemical diffusion treatments are unfeasible and inefficient for processing materials liable to microstructural changes and deformation of the work-pieces at the high temperatures and long processing period that may result in notable deterioration in the overall performance of treated work-pieces.

In recent years, a number of advanced plasma/ion-based and laser beam-based methods are developed with higher efficiency of processing for no more than several hours, such as plasma/ion nitriding or carburizing (Czerwiec *et al.*, 2000; Lei *et al.*, 2000; Möller *et al.*, 2000), ion implantation (Manova *et al.*, 2006), or laser nitirding (Schaaf, 2002; Schaaf *et al.*, 2002), where the processing efficiency and the surface quality can be considerably enhanced due to energetic ion bombardment, ion implantation at high temperatures or with post-annealing, or laser irradiation in a gaseous environment, respectively. Alternatively, it has been demonstrated that, nitrides/carbonitrides formation on a titanium target with extraordinarily high efficiency was resulted from irradiation of high-intensity pulsed ion beam (HIPIB) with a few shots in a vacuum condition of 10^{-2} Pa (Zhu *et al.*, 2005). The unique phenomenon of HIPIB-induced nitriding and carbonitriding is still not fully understood. Although the residual gaseous species in the vacuum chamber at the low pressure could be a major source providing nitrogen and carbon in the surface nitriding/carbointriding, formation of compounds in HIPIB-irradiated targets has also been found and attributed to the short-pulse ion implantation, such as nitrides and borides on titanium target under

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HIPIB irradiation of N and B mixed ions (Yatsui *et al.*, 1994), and silicon carbides on silicon target under irradiation of C ions (Remnev *et al.*, 2009). Note that, no unambiguous evidence of nitrides or carbonitrides formation was found in the investigations on HIPIB-irradiated titanium and its alloys by other researchers (Davis *et al.*, 1996; Hashimoto *et al.*, 2000; Lavrentiev *et al.*, 2001), as well as in some cases we also did not observe new phase transformation. It appears to be controversial on the HIPIB-target interaction among the different research groups where even the influence of HIPIB irradiation parameters on the compounds formation has not yet been clarified. In order to explore the underlying mechanism for HIPIB-induced nitrides and carbonitrides formation, a series of experiments on HIPIB irradiation with mixed hydrogen, carbon and/or oxygen ions onto titanium target were conducted on three different types of HIPIB apparatuses, i.e., TEMP-6, TEMP-4M, and ETIGO-II, respectively, by changing energy density and shot number. The effect of experimental conditions including residual gases, ion species, and base pressure, on the compounds formation on irradiated titanium target were compared to elucidate the mechanism of HIPIB-target interaction.

2. EXPERIMENTAL

The experiments of HIPIB irradiation onto titanium targets were performed in parallel on TEMP-6 (Dalian University of Technology), TEMP-4M (Tomsk Polytechnic University), and ETIGO-II (Nagaoka University of Technology), respectively. In all the apparatuses, magnetically insulated ion diodes (MIDs) with external magnetic field insulation were applied for ion beam generation, and polyethylene was used as the ion supply material of MIDs in TEMP-6 and ETIGO-II (Zhu *et al.*, 2003, 2007; Yatsui *et al.*, 1985) for generation of mixed hydrogen and carbon ions, and epoxy in TEMP-4M (Stepanov *et al.*, 2008) for mixed hydrogen, carbon, and oxygen ions. The MID in the TEMP-6 had a cylindrical focusing configuration, that in the ETIGO-II a spherically concave focusing MID, and in the TEMP-4M an annular focusing one, respectively. Due to the differences in the structure and operation principle of the MIDs, TEMP-6 and TEMP-4M normally worked at accelerating voltage in the range of 200–400 kV and ion current density of several hundreds A/cm^2 with a total energy up to about 10 J/cm^2 per shot, and ETIGO-II at a higher voltage of around 1000 kV and a thousand A/cm^2 with up to 100 J/cm^2 energy delivered per shot. In addition, the vacuum pumping systems also slightly differed on the apparatuses, where turbo-molecular pump package was used in TEMP-6 leading to a base pressure of $1.0–1.3 \times 10^{-2}$ Pa and oil diffusion pump package in the other two systems to a base pressure of $2.0–2.5 \times 10^{-2}$ Pa.

The titanium samples (99.9% purity) for the irradiation experiments were in dimension of $15 \times 15 \times 3$ mm^3, cut from a titanium sheet, prepared by using mechanical polishing with SiC abrasive papers and diamond paste in sequence, and followed by ethanol cleaning and air drying. The HIPIB irradiation was performed at the low pressures of $1.0–2.5 \times 10^{-2}$ Pa, at an ion current density varied in the range of 60 to 300 A/cm^2 with 1–50 shots, where an energy fluence of 1–6 J/cm^2 was delivered per shot on the three types of HIPIB apparatuses operated at different accelerating voltage of 300 or 1000 kV. The ion current density (energy fluence) of irradiation was adjusted by the distance between the MID and the target, and for the experiment on ETIGO-II, the samples had to be also placed off-axis for a relatively low intensity due to the extremely high energy density output. The details of experimental conditions in the HIPIB apparatuses were listed in Table 1. X-ray diffraction (XRD) analysis was applied to characterize the changes in phase structure on HIPIB-irradiated target surfaces.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of titanium targets irradiated at ion current density of 150 A/cm^2 and 300 A/cm^2 with 5 shots, respectively, on TEMP-6. No diffraction peaks from any new phases could be detected on the irradiated surfaces expect for the change in the relative intensity among the diffraction peaks of titanium, especially the apparent increase in the (100) and (110) peaks and decrease in the (002) peak against the originally strongest peak (101). The crystalline orientation was assigned to preferred recrystallization relative to the original microstructure with rolling texture. Moreover, the plastic deformation in the target surface layer under coupled thermal-dynamic process by HIPIB irradiation may also contribute to formation of the particular orientation upon specific lattice planes sliding and their interaction.

It has been demonstrated that, new phases of both nitrides and borides on titanium was resulted from HIPIB irradiation of N and B mixed ions generated from MID with BN source material due to ion implantation effect, where repetitive HIPIB irradiation up to a hundred shots was needed for the compounds formation (Yatsui *et al.*, 1994). Nevertheless, the ion implantation can not take effect in the present work

Table 1. *Typical HIPIB parameters of irradiation experiments on the three* apparatuses

Parameters	TEMP-6	TEMP-4M	ETIGO-II
Diode voltage (kV)	300	300	1000
Ion current density (A/cm^2)	150,300	60,150	60
Pulse width (FWHM, ns)	70	70	60
Energy density (J/cm^2)	3.0, 6.0	1.2, 3.0	3.5
Ion species	H^+, C ions	H^+, C, O ions	H^+, C ions
Base pressure (Pa)	$1.0–1.3 \times 10^{-2}$	$2.0–2.5 \times 10^{-2}$	$2.0–2.5 \times 10^{-2}$

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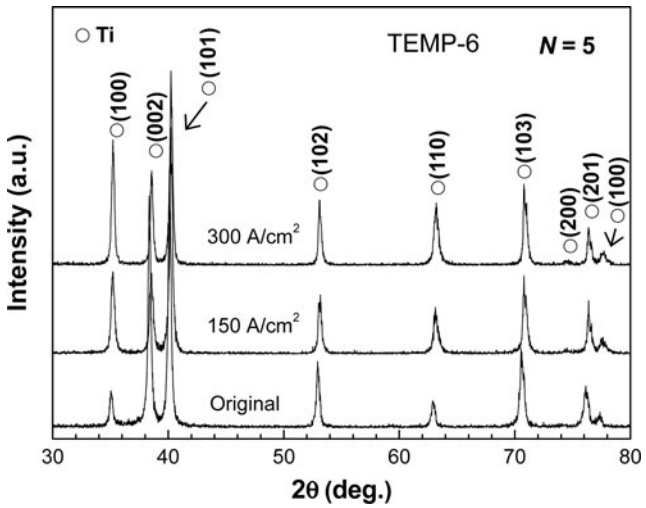

Fig. 1. XRD patterns of titanium targets irradiated at ion current density of 150 A/cm^2 and 300 A/cm^2 with 5 shots respectively on TEMP-6.

due to the HIPIB irradiation with only a dose of 10^{13}–10^{14} ions/cm^2 per shot of tens to hundreds A/cm^2 at pulse duration of 60–70 ns, i.e., about 2.6×10^{13} ions/cm^2 per shot for 60 A/cm^2, and about 6.5×10^{13} ions/cm^2, and 1.3×10^{14} ions/cm^2 for 150 and 300 A/cm^2. The respective total ion dose for the HIPIB irradiation at TEMP-6 was about 3.2×10^{14} ions/cm^2 (5 shots of 150 A/cm^2) and 6.5×10^{14} ions/cm^2 (5 shots of 300 A/cm^2), and at TEMP-4M was about 2.6×10^{14}, 5.2×10^{14} and 1.3×10^{15} ions/cm^2 (10, 20, and 50 shots of 60 A/cm^2) and at ETIGO-II about 2.6×10^{13}, 5.2×10^{13} and 2.6×10^{14} ions/cm^2 (1, 2 and 10 shots of 60 A/cm^2). Therefore, the results of new compounds on HIPIB-irradiated targets due to the short-pulse ion implantation, such as titanium nitrides and borides on titanium irradiated by N and B ions (Yatsui *et al.*, 1994) and silicon carbides on silicon irradiated by C ions (Remnev *et al.*, 2009), is in accordance with that of conventional ion implantation by which an dose of 10^{16}–10^{18} ions/cm^2 may result in a peak concentration of implanted ion species typically from several to tens at.% in a depth of ion range responsible for new phases formation (Hammerl *et al.*, 1999; Tsyganov *et al.*, 2000; Manova *et al.*, 2006).

In addition, for the HIPIB implantation of C ions, the C peak concentration in the target may be further lowered due to the C ions constituting only 20–30% in the HIPIB of mixed H and C ions at TEMP-6 and ETIGO-II using polyethylene as the ion source material, and the larger ion range at the HIPIB accelerating voltages of several hundreds kV as compared to that of tens kV for conventional ion implantation. Consequently, the expected peak concentration of implanted C was at the order of 10^{-3}–10^{-2} at.% at the total nominal dose of 10^{14} ions/cm^2 due to the HIPIB irradiation into titanium in this work. It should be pointed out that, the implanted dose can not proportionally grow by increasing the dose per shot (ion current density) of HIPIB irradiation, since the implanted dose thus can be greatly reduced as a result of substantial removal of the implanted top layer during a HIPIB shot due to considerable surface ablation at the higher ion current density. As a consequence, the C ion implantation into the irradiated titanium was not sufficient for carbides or carbonitrides formation, in good agreement with the results of no carbides or carbonitrides formation on the irradiated titanium in TEMP-6 experiment, as well as in the previous studies (Davis *et al.*, 1996; Hashimoto *et al.*, 2000; Lavrentiev *et al.*, 2001). Even for the HIPIB irradiation of a hundred shots, the new phases in the surface layers due to the ion implantation were usually limited to a small amount of content (Yatsui *et al.*, 1994; Remnev *et al.*, 2009). Therefore, ion implantation effect can be ignored for HIPIB irradiation of a few shots.

Figure 2 presents the XRD patterns for titanium targets irradiated on TEMP-4M at ion current density of 60 A/cm^2 with 10, 20 and 50 shots respectively. In this case, some small new diffraction peaks can be clearly identified in the range of $2\theta = 35$–$45°$. It is confirmed in the enlarged view of this range that, titanium nitrides and/or carbonitrides were formed on the irradiated surfaces of titanium targets,

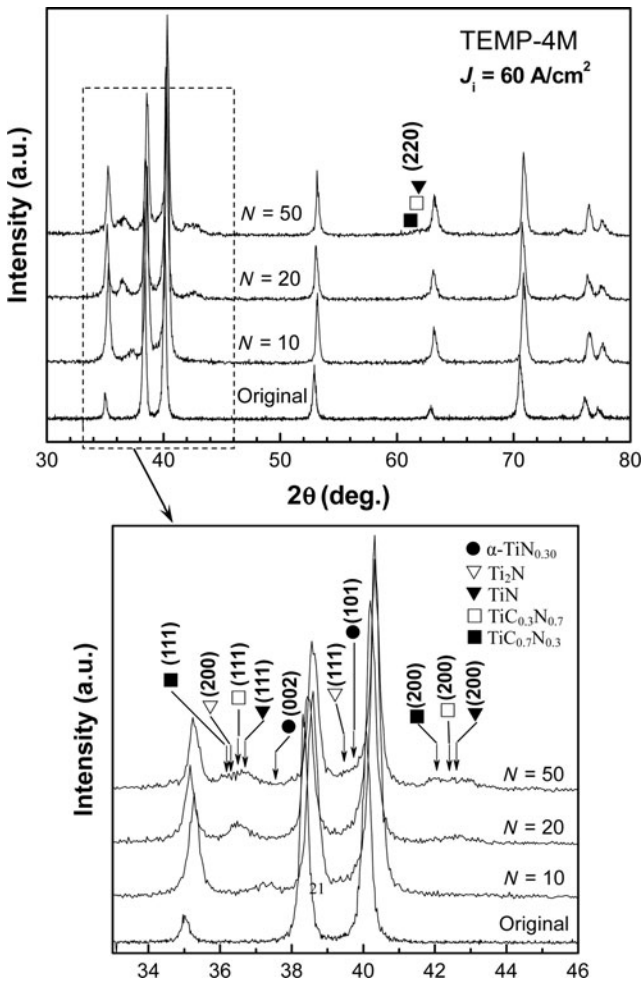

Fig. 2. XRD patterns of titanium targets irradiated at ion current density of 60 A/cm^2 with 10, 20 and 50 shots respectively on TEMP-4M.

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dependent on the shot number. Note that, less shot number led to formation of nitrides of lower nitrogen content such as α-$TiN_{0.30}$ at 10 shots, and irradiation with increasing shot number led to nitrides of higher nitrogen content including Ti_2N and TiN etc. up to 50 shots. Furthermore, carbonitrides of $TiC_{0.3}N_{0.7}$ and $TiC_{0.7}N_{0.3}$ can be found at 20 and 50 shots, and the compounds of higher carbon content was also favored at the higher shot number.

Since C ion implantation of HIPIB irradiation is negligible and not responsible for the surface carbonitrides formation, it is thus inferred that, external species other than the ions accelerated from the HIPIB source, are the main sources contributing to the compounds formation on titanium. On one hand, ion source material may be deposited onto the target surface, as a type of explosive emission of molecules/atoms, clusters and debris along with the ion beam generation process based on surface breakdown mechanism of polymeric materials. For instance, surface discharging channels or bubbles was observed on the anode materials under high-voltage surface breakdown in TEMP-6 and ETIGO-II apparatuses, indicative of surface emission of discharged debris (Zhu *et al.*, 2007). It was also observed that, a metal target surface was covered by polymeric debris after HIPIB irradiation generated from acrylic source material (Wood *et al.*, 1998). The deposited layer of polymeric materials on the target surface, as a source of C species, may be readily mixed into the molten surfaces during irradiation of the HIPIB shot and following shots. On the other hand, the possible and only source of nitrogen species is from residual gases in the vacuum chamber in the present experimental conditions, since the deposited layer from ion source material as a major source of carbon is just a precondition for formation of carbonitrides, and can not account for the nitriding aspect. The ambient gaseous species may interact effectively with the molten surfaces under HIPIB irradiation, and incorporated into target surface leading to the nitrides formation (Zhu *et al.*, 2005). However, in the experiments on TEMP-6 apparatus, no titanium nitrides could be detected by XRD analysis after irradiation at 150 A/cm^2 or 300 A/cm^2 with 5 shots (Fig. 1), as well as 60 A/cm^2 up to 30 shots in our previous studies, whereas small amount of nitrides can be identified on the irradiated titanium in TEMP-4M experiment after 10-shot irradiation at 60 A/cm^2 (Fig. 2). To further understand this phenomenon, HIPIB irradiation at 150 A/cm^2 up to 20 shots was also carried out in TEMP-4M, and the XRD patterns of the irradiated titanium were presented in Fig. 3. The titanium nitrides were detected after 10 shots, though the relative intensity of diffraction peaks for nitrides was weaker as compared to the results at 60 A/cm^2 (Fig. 2). This result indicates that there was a threshold pressure for the gaseous ambient, i.e. around 2×10^{-2} Pa, for nitrides formation. It is clearly shown that, the relatively higher residual pressure facilitate the reactions between gas molecules and irradiated surface. Furthermore, oil vapors from the oil pump systems in the TEMP-4M and ETIGO-II apparatuses may provide another

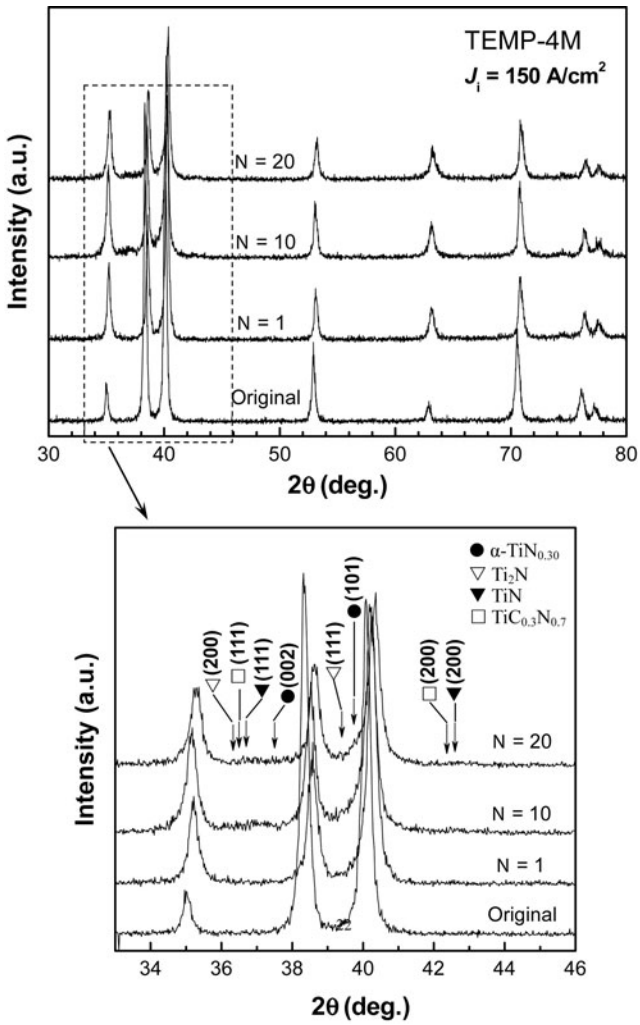

Fig. 3. XRD patterns of titanium targets irradiated at ion current density of 150 A/cm^2 with 10 and 20 shots respectively on TEMP-4M.

C source in the ambient gases for the carbonitrides formation. The surface reaction between ambient gases and irradiated surface can be greatly promoted by HIPIB mixing the adsorbed layer of the gaseous species on the target surface before each shot of irradiation.

Figure 4 presents the XRD patterns for titanium targets irradiated on ETIGO-II at ion current density of 60 A/cm^2 with 1, 2 and 10 shots respectively. The result indicates a similar trend of nitrides/carbontirdes formation process on the irradiated titanium as compared to that of TEMP-4M, i.e., low nitrogen/carbon compounds formed with less shot and high nitrogen/carbon phases was facilitated by repetitive irradiation, but carbonitrides became the major phase in the compound surface layer at 10 shots. It is clearly seen that, in comparison with the TEMP-4M experiment, formation of nitrides/carbonitrides in the ETIGO-II case had a much higher efficiency with nitrides formation (e.g. α-$TiN_{0.30}$) under only 1 shot irradiation. In addition, the carbonitrides phase formation with carbon incorporation became significant with increasing the shot number up to 10 shots, as

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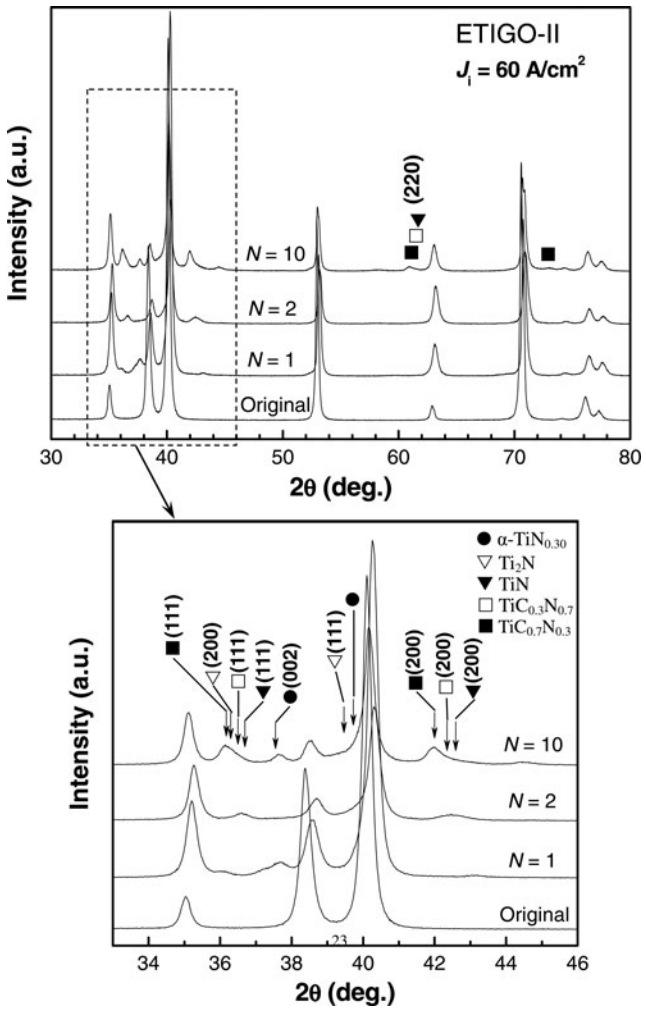

Fig. 4. XRD patterns of titanium targets irradiated at ion current density of 60 A/cm^2 with 1, 2, and 10 shots respectively on ETIGO-II.

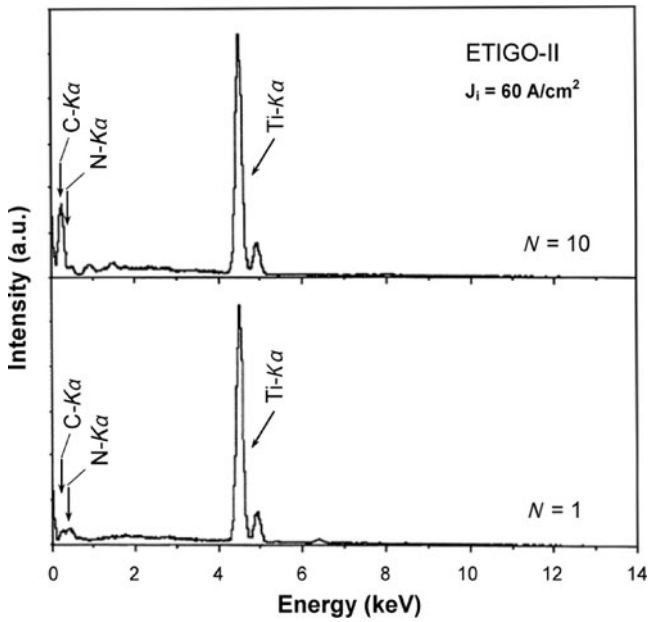

Fig. 5. Energy dispersive X-ray spectroscopy (EDS) result from titanium targets irradiated at ion current density of 60 A/cm^2 with 1 and 10 shots respectively on ETIGO-II.

evidenced by the fact that only nitrides could be observed at 1 shot, occurrence of $TiC_{0.3}N_{0.7}$ phase at 2 shots and predominant formation of $TiC_{0.7}N_{0.3}$ phase at 10 shots. Energy dispersive X-ray spectroscopy (EDS) analysis further confirmed the tendency of nitrogen and carbon incorporation into the irradiated surfaces, as shown in Fig. 5 where the peak-peak intensity ratio of C-*Kα* to N-*Kα* is considerably enhanced after 10 shots in comparison with that of 1 shot.

As excluding the contribution of ion composition effect at the irradiation up to several tens shots, the sources of N and C species for the nitrides/carbonitrides formation on the HIPIB-irradiated surface are mainly ascribed to residual gases and ion source materials, where the residual gases mainly provide N species at such a working pressure (base pressure) of 10^{-2} Pa order with partial pressure of nitrogen comparable to that in air (about 4:1 ratio of N_2 and O_2), and the ion source material (polyethylene or epoxy) dissociation under the HIPIB irradiation may work as a C source. Subsequently, the compound formation mechanism is discussed with HIPIB irradiation parametric influence on the compounds formation process, based on the significant thermal and dynamic characteristics of HIPIB-target interactions.

Firstly, the HIPIB irradiation intensity, determined by the energy density per shot at the similar pulse duration, has a fundamental influence on the surface interaction for nitrides/carbonitrides forming. The higher the irradiation intensity was, the more significant surface melting and ablation resulted from the irradiation. With one-dimensional approximation of heat transfer, it was theoretically estimated that the melting threshold of titanium target was about 0.5 J/cm^2, and evaporating at 3.7 J/cm^2 under the HIPIB irradiation of a pulse duration 60–70 ns (Zhu *et al.*, 2005). As for ion current density intensity of 300 A/cm^2 (6.0 J/cm^2) in TEMP-6, the mixing layer for compound formation in target could be entirely ablated during irradiation of a pulse, hence, accumulation of the alloying elements in the surface layer are not feasible at this high material removal regime. Even for the middle intensity of irradiation at 150 A/cm^2 (3.0 J/cm^2), considerable local ablation on the target could lead to material removal in a molten state, as evidenced by noticeable droplet ejection occurred at ion current density higher than 100 A/cm^2 for titanium target in TEMP-6 (Dong *et al.*, 2006). Therefore, surface melting with controlled ablation is preferred for both the surface reactions and compound retention, and noticeable nitrides and carbonitrides formation was found at a low irradiation intensity of 60 A/cm^2 in TEMP-4M and ETIGO-II (Fig. 2 and Fig. 3). It should be mentioned that, although the energy density per shot at 60 A/cm^2 in ETIGO-II, was about 3 times of that in TEMP-4M, due to the much higher kinetic energy of 1000 keV H^+, the effective deposited energy per unit volume

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could be comparable due to the larger ion range at the higher kinetic energy according to numerical calculation (Xin *et al.*, 2009).

Secondly, the compound formation may grow rapidly with the shot number once the criterion of irradiation intensity has been satisfied, i.e. under a limited surface ablation. The repetitive HIPIB irradiation could build an accumulation of N and C incorporated into the irradiated target from residual gas and ion source material. The deposited and/or adsorbed layer on the target from ion source material and ambient gases can be effectively mixed in a molten state with convection mechanism as long as the surface ablation is limited, with efficiency greatly higher than the conventional ion beam mixing upon collisions between the implanted ions and the film-substrate system atoms. The Raleigh-Taylor instability caused by different melt densities was proposed to explain the fast mixing in Ti/Al film-substrate system under HIPIB irradiation (Bystritskii *et al.*, 1999). However, that mechanism unlikely explains the data in the present case, since the top surface layer with carbon/nitrogen or compounds is not heavier than the titanium target. The disturbance of melting layer on the target under HIPIB irradiation may promote the chemical reactions for compounds formation. In any case, the ion beam mixing by HIPIB irradiation mainly involved convection mechanism due to surface melting under HIPIB irradiation, faster and more effective than collision mechanism of conventional ion beam mixing processing.

Finally, ablation plasma generation and propagation may be crucial on the compounds formation of high efficiency. In the ETIGO-II experiment, the formation of nitrides can be found after 1-shot irradiation, and carbonitrides formed after 2-shot irradiation. The high efficiency of reactions likely benefits from the experimental scheme in ETIGO-II, different from the other two, where the samples were set axis-off with a certain distance away from the ion beam center to obtain the irradiation intensity much lower than the central area. In the irradiation experiment at the low irradiation intensity of 60 A/cm^2, some samples were also placed in the central area or a large titanium plate was used as the sample holder to avoid introducing additional impurities from the HIPIB ablation on the holder. The dense ablation plasma from the titanium holder can expand laterally when interacting with incoming beam during a pulse. The dynamics of plasma expansion and interacting with objects may lead to an effective deposition of thin layer on the substrate as demonstrated in film deposition even in a backside configuration (Sonegawa *et al.*, 1996). During its expansion, the ablated Ti plasma can actively react with ambient gaseous species and emitting ion source material, i.e. titanium nitrides/carbonitrides can be produced *in situ* during the plasma expansion, and then a compound coating onto the irradiated surfaces can be resulted from the hydrodynamic characteristics of the expanding plasma. A similar mechanism was proposed for laser nitriding of metals where the laser nitriding process may be regarded as laser deposition of a nitride coating onto the target itself at high gas pressures higher than 0.05 bar (Schaaf, 2002; Han *et al.*, 2003). However, the HIPIB-target interactions proceeded at a low pressure of 10^{-2} Pa, with the pressure of 5 orders lower than the laser nitriding. Therefore, the significance of the HIPIB nitriding/carbonitriding process lies in the high-efficiency coupling of HIPIB and target (Davis *et al.*, 1996), and the ablation plasma or even ejected droplet from the target surface can be also further ionized and defragmented by the incoming beam during a single shot, since the HIPIB has a beam cross-section area of 100 cm^2 order well covering the entire irradiated targets. The highly reacting efficiency between ablation plasma and ambient gases has been also revealed in our study of HIPIB irradiation onto Si target at ETIGO-II, where HIPIB generated Si plasma reacted with residual oxygen of the low pressure of 10^{-2} Pa to form Si oxides thin film or nanoparticles. Therefore, the nitrides/carbonitrides formation process can be of extraordinarily high efficiency by the HIPIB mixing and modifying the deposited layer of in-situ formed nitrides and carbonitrides into the substrates.

4. CONCLUSIONS

A series of experiments were carried out on TEMP-6, TEMP-4M and ETIGO-II HIPIB apparatuses to elucidate the unique process of HIPIB-target interaction for nitrides and carbonitrides formation on titanium. Main conclusions are drawn as follows: (1) The main sources for surface nitrides/carbonitrides formation are attributed to residual gases (major nitrogen and minor carbon) and ion source material (major carbon), and the contribution of HIPIB ion composition (carbon ion implantation) can be neglected for several shots at a ion current density of 100 A/cm^2 order. (2) The surface interaction for compound formation is facilitated by repetitive irradiation at an optimal intensity with limited surface ablation, where incorporated species of nitrogen and carbon can be effectively accumulated during the multi-shot irradiation. (3) Ablation process from the HIPIB-irradiated target itself may play a crucial role on the nitriding/carbonitriding process due to ablation plasma-ambient species reaction and hydrodynamics during HIPIB irradiation, by which nitrides and carbonitrides layers forming on the target can be readily incorporated into substrate under HIPIB mixing with extraordinarily high efficiency. (4) Due to the HIPIB-target interaction characteristics, a certain pressure of ambient gas will promote the reaction process for compound formation, where a threshold value is found to be around 2×10^{-2} Pa for nitrides and carbonitrides formation on titanium.

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