Enhanced Diffusion and Compositional Change in Near Surface Layers of TiC under Hydrogen Ion Bombardment

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Received, October 20, 1983
Revised March 6, 1984

The compositional change of the surface and near surface layer of TiC coating has been studied under 1 keV hydrogen ion bombardment at various target temperatures. Depth profiles near the surface were observed by Auger electron spectrometer combined with Ar ion etching. The carbon composition decreases by a factor of 1.3 at the TiC surface bombarded at room temperature, indicating preferential sputtering. The carbon composition increases exponentially to the bulk value with increasing depth from the surface. The thickness of the altered layer is about 5 nm, which is almost a half of the projected range. No carbon depletion, however, was observed at the target temperature of 700°C. The diffusion coefficient of carbon atoms in the altered layer, calculated from the steady-state depth profile at room temperature, is about $8 \times 10^{-18}$ cm²/s which indicates enhanced diffusion in this layer.

KEYWORDS: tokamak devices, coating materials, limiters, walls, titanium carbides, surface analysis, sputtering, hydrogen ion beams, depth profile, enhanced diffusion, irradiation, radiation effects, steady state

I. INTRODUCTION

The performance of present large tokamaks closely depends on plasma surface interaction. In order to reduce radiation loss from the plasma, low to medium atomic number (Z) materials have been considered for use as limiters and walls. Compound materials, such as TiC and SiC, are promising candidates for the limiter and the wall because of their refractory nature\textsuperscript{1(2)} and low chemical sputtering\textsuperscript{(3)}. Coatings of these materials are usually used because of the difficulty in making full size units using these materials. The TiC coating has been successfully used as the limiters in ISX-B\textsuperscript{(4)} and in Doublet III\textsuperscript{(5)}. An all TiC coated limiter experiment has been carried out in JIPP T-II\textsuperscript{(6)}, and the mean effective ionic charge obtained in the experiment is about 1.

Energetic hydrogen ions and neutrals escaping from the confined plasma cause physical and chemical sputtering of the limiter and the first wall, leading to compositional change of the surface. It has been found that the carbon atoms of TiC and TaC are depleted from the surface by hydrogen ion bombardment because of preferential sputtering\textsuperscript{(7)}. It has also been shown that the extent of carbon atom depletion at the surface is larger with lower target temperature and lower bombardment energy for the case of TiC\textsuperscript{(8)}.

The compositional changes of the surface and near surface layers during ion bombardment have been studied in Cu-Ni alloys\textsuperscript{(9)}. The long range depletion of copper on the order of 100 nm in thickness has been observed. It has also been shown that the ion bombardment leads to enhanced diffusion of copper in the altered layer. The compositional change under ion bombardment has been formulated for a general case of binary alloy,
including sputtering and enhanced diffusion. In the present experiment, depth profiles of TiC after 1 keV hydrogen ion bombardment were observed in various target temperatures. Carbon composition decreased by a factor of 1.3 at the TiC surface bombarded at room temperature, while no carbon depletion was observed at the target temperature of 700°C. The diffusion coefficient of carbon atoms in the altered layer, estimated from the steady-state depth profile at room temperature, is about $8 \times 10^{-18}$ cm$^2$/s, indicating enhanced diffusion in this layer.

II. EXPERIMENTAL

The TiC samples coated on Poco graphite were prepared by chemical vapor deposition. Sample size is $15 \times 10 \times 2$ mm and TiC coating thickness is about 20 µm. Chemical composition of the TiC coating was analyzed by Electron Probe Micro Analysis (EPMA). The composition rate of carbon to titanium is about 1.0. As-deposited TiC coating was degreased in an ultrasonic bath of acetone before insertion into the vacuum chamber.

Figure 1 shows the experimental apparatus, which consists of low energy ion beam system and analysis chamber. The ion beam system is differentially pumped by a turbomolecular pump and an ion pump. The analysis chamber was evacuated by a 270 l/s turbomolecular pump. The ultimate pressure is less than $10^{-8}$ Pa after baking at 250°C for 24 h.

The TiC coating sample, mounted on the tantalum strip heater, can be heated up to 1,000°C. The target temperature is measured by a Pt-PtRh thermocouple which is fixed in a hole prepared in the target. Chemical composition of the TiC surface is observed using Auger electron spectrometer (AES). The surface composition is observed without any movement of AES-target system. Therefore, the system has the advantage of simultaneous analysis on the same fixed surface position on the target during ion bombardment. The surface composition is calculated from peak-to-peak value in the Auger spectra. Sensitivity values calculated for Ti and C composition are 0.31 at 387 eV and 0.28 at 273 eV, respectively.

A duoplasmatron is used as an ion source. The TiC coating was bombarded by hydrogen ions at the energy of 1 keV. The hydrogen beam current at the target, with positive bias for secondary electron suppression, is 14.5 µA. The angle of the beam to the target normal is 50°, hence the irradiation area is elliptical in shape, $3 \times 4.5$ mm. The ion beam was not mass analyzed, therefore molecular ions and a small amount of impurity ions may exist. The pressure during ion irradiation is $3 \times 10^{-6}$ Pa in the analysis chamber.

The same duoplasmatron ion source is used for argon ion etching. The depth profiles of the TiC after hydrogen ion bombardment was measured by AES during argon ion etching. The argon ion energy is 3 keV and the target current is 1 µA. In these condition, we confirmed that the ion induced Auger electron emission was not observed during argon ion etching. Only little compositional change has been observed in the surface of TiC by argon ion bombardment at 500 eV and 3 keV. It can therefore be considered that TiC is not preferentially sputtered by argon ion etching. The pressure during argon ion etching...
etching is about $5 \times 10^{-7}$ Pa in the analysis chamber. The sample was left in vacuum for 1 h before argon ion etching to evacuate the ion source chamber below $3 \times 10^{-6}$ Pa which is about 1/1,000 of the operating pressure. The target temperature during argon ion etching was measured to be room temperature.

The argon ion etching speed of TiC at room temperature is calibrated by thin TiC coating. Coating thickness, measured by an electron microscope, is 330 nm. The sputter etching time of TiC coating layer is 14 h. Therefore, the argon etching speed of TiC is 0.39 nm/min at room temperature.

### III. RESULTS

Figure 2(a) shows a depth profile of the TiC coating bombarded by 1 keV hydrogen ions at room temperature. The hydrogen ion fluence employed in this experiments is $5 \times 10^{18}$ ions/cm$^2$. It has been shown that surface composition at the TiC surface is saturated in this fluence. It is thus considered that the depth distribution observed after irradiation of $5 \times 10^{18}$ ions/cm$^2$ is also saturated. The equilibrium carbon concentration at the outermost layer of TiC is less than the bulk value probably because of preferential sputtering of carbon atoms from the surface. The carbon composition near surface layers in TiC increases exponentially to the bulk value with increasing depth from the surface, whereas the titanium composition decreases. The thickness of the altered layer, estimated from this compositional change, is 5 nm. The projected range of 1 keV hydrogen ions in TiC estimated from the LSS theory is around 9 nm which is somewhat larger than the altered thickness. Surface oxygen contamination, which is probably because of adsorption of residual gases, was observed to be less than 2 %. Moreover, oxygen contamination of the surface layer was within a thickness of about 1.5 nm. The compositional change observed in this experiment is, therefore, considered to be independent from oxygen contamination on the surface.

Figure 2(b) shows the depth profile obtained after 1 keV hydrogen ion irradiation at 700°C with the same ion fluence as that at room temperature. The result is obtained at room temperature after quenching the sample. The initial quenching rate at 700°C is 6.5°C/s, which is almost the same as Swalzfager. Since the volume diffusion coefficient of carbon in TiC at 700°C extrapolated by assuming the Arrenius expression is quite
small\(^{(15)}\), carbon diffusion during quenching in the altered layer appears to be negligible. Oxygen contamination on the surface is also less than 2 % in this case. It should noted that the depletion layer of carbon atoms, observed at room temperature, is not found at 700°C. Furthermore, carbon atoms are enriched slightly within 1 nm from the surface, which may be caused by segregation of carbon atoms.

Figure 3 shows depth profiles obtained at the following various target temperatures: room temperature, 100, 300, 500 and 700°C. The ratio of carbon to titanium (C/Ti ratio) at the outermost TiC surface is 0.68 for room temperature. The C/Ti ratio for the outermost surface increases gradually as the temperature rises. The C/Ti ratio at 700°C is 1.14, which is slightly higher than the bulk ratio (1.1). The altered layer thickness is less than 5 nm for all the target temperature. The C/Ti ratio increases exponentially to the bulk value with increasing depth from the surface for temperatures between room temperature and 500°C.

IV. DISCUSSION

Ion induced compositional changes near surface layer of multi-component material have been observed in many systems, such as Cu-Ni\(^{(9)}\), Ag-Au\(^{(16)}\) and others. In these studies, preferential sputtering and enhanced diffusion are considered as the mechanisms for compositional change of the surface. Recently, surface segregation has come to be recognized as an important mechanism\(^{(14)}\).

The C/Ti ratio for the outermost TiC surface after hydrogen ion irradiation at room temperature is less than the bulk value as shown in Fig. 3, indicating preferential sputtering of carbon atoms\(^{(17)}\). The C/Ti ratio increases gradually as the target temperature rises, and depletion of carbon atoms in the altered layer decreases. Since chemical sputtering yield is decreased with temperature up to at 700°C\(^{(8)}\), the saturated surface C/Ti ratio increases with higher target temperatures. Furthermore, surface segregation and diffusion of carbon atoms appear to play some role in increase of the C/Ti ratio with high temperature.

No surface segregation for TiC was observed at room temperature irradiation, as shown in Fig. 2(a), which is similar to the result obtained by Varga\(^{(7)}\). The segregation is usually observed at higher temperature, but the surface carbon atom enrichment at 700°C in this experiment is very small, as shown in Fig. 2(b). Furthermore, no surface segregation of carbon atoms has been observed under heat treatment of 1,000°C for TiC\(^{(12)}\). It has also been observed that segregation of carbon atoms is low with argon ion bombardment in 500 to 1,000°C\(^{(12)}\). It can therefore be considered that surface segregation plays minor role in the case of TiC during hydrogen ion bombardment.

A model for compositional change in the altered layer has been proposed by Ho\(^{(19)}\) and Eltoukey\(^{(18)}\). In the steady-state, the distribution of carbon atoms \(\theta\) as a function of depth \(x\) is given by

\[
\frac{d\theta}{dx} = -D_\text{diff} \frac{d^2\theta}{dx^2} - D_\text{sput} \frac{d\theta}{dx} + \frac{\theta}{K} \frac{dK}{dx}
\]
where \( C \) is the bulk concentration, \( v \) the sputtering recession velocity during ion bombardment and \( D \) the diffusion coefficient. Figure 4 shows normalized logarithmic plots of the carbon composition at room temperature in Fig. 2(a), after subtracting the bulk value. The slope of the line fitted to the data is \(-v/D\) in Eq. (1).

The value of \( v \) was estimated by utilizing the sputtering yield of TiC for 1 keV hydrogen ions obtained by Bohdansky\(^{(19)}\). The diffusion coefficient at room temperature was obtained to be about \(8 \times 10^{-18} \text{ cm}^2/\text{s}\) at 1 keV. Furthermore, no appreciable difference was observed at 500 eV. The diffusion coefficient is, therefore, considered to be independent on ion energy, as is suggested by Elthoukey\(^{(18)}\) and Morita\(^{(20)}\). The diffusion coefficients at temperatures ranging 100~700°C could not be estimated, because the composition change from the bulk value is small in the altered layer.

Figure 5 shows comparison between the diffusion coefficient of carbon atoms in TiC measured by Sarian\(^{(15)}\) at a temperature above 1,750 K. The extrapolated volume diffusion coefficient at room temperature, estimated by assuming the Arrhenius expression, is about \(2 \times 10^{-69} \text{ cm}^2/\text{s}\). The volume diffusion coefficient at room temperature is quite small, compared with the value obtained in this study. Thus, it is clear that enhanced diffusion of carbon atoms in the altered layer occurs during hydrogen ion bombardment. It also is consistent with the fact that the altered layer is about a half of the mean projected range.

Typical diffusion time \( t \) of the carbon atoms in the altered layer is

\[
  t = \frac{l^2}{D},
\]

where \( l \) is e-folding length of carbon concentration after subtracting the bulk value. The diffusion time, calculated using the enhanced diffusion coefficient is approximately 30 min at room temperature. Since the hydrogen ion bombardment time is twice as large as this value, it is considered that the compositional change in the altered layer is almost in the steady state.

As mentioned in Chap. II, the sample
was left in a vacuum chamber from 1 h before depth-profiling. However, the carbon atom increment during this period is only 7%. It is thus concluded that carbon diffusion during depth-profiling preparation plays a minor role in determining the results shown in Fig. 4.

V. CONCLUSION

Compositional change of TiC coating was studied under 1 keV hydrogen ion bombardment in various temperatures. Depth profiles near the surface were observed by Auger electron spectrometer combined with argon ion etching. The carbon composition at the surface bombarded at room temperature decreases by a factor of 1.3 at the fluence of $5 \times 10^{18}$ ions/cm$^2$. This means that the carbon atoms are preferentially sputtered in room temperature. The carbon composition increases exponentially to the bulk value with increasing depth from the surface. The altered layer thickness is about 5 nm which is almost a half of the projected range. No carbon depletion, however, was observed at 700°C. The outermost surface C/Ti ratio increases and depletion of carbon atoms in the altered layer decreases as the target temperature rises. These phenomena are considered to be the results of composite effects of preferential sputtering, surface segregation and diffusion.

The diffusion coefficient in the altered layer was estimated by applying the model considering the sputtering recession speed of the surface. The coefficient calculated from the normalized logarithmic plots of the carbon distribution at room temperature, is about $8 \times 10^{-18}$ cm$^2$/s. This value is much larger than the extrapolated volume diffusion coefficient, indicating enhanced diffusion in this layer.

ACKNOWLEDGMENT

The authors wish to thank Dr. H. Yamato for continuous encouragement. They also wish to thank Drs. S. Takatsu and K. Shibuki in Toshiba Tungaloy Co., Ltd. for preparing the coating samples.

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