Criterion for Self-Sustaining Coating in Metal- or Carbide-Coated Graphite Limiter

K. Morita and H. Ohno

Abstract. We have studied the conditions for self-sustaining coatings of a nickel and titanium carbide layer deposited on graphite, and a nickel layer deposited on nickel carbide film. Segregated carbon atoms are responsible for the self-sustaining nature of the coating. Both the concentration of carbon atoms at the surface and the sputtered flux of carbon atoms from the nickel and titanium carbide deposited on the graphite substrate are calculated as a function of ion flux. It is shown that the critical ion flux for a self-sustaining coating depends on the rate constant of segregation to the bombarded surface, on the diffusion constant, and on the rate constant of dissolution from graphite into the deposited layer. The experimental results on the ion flux dependence of the sputtered flux of carbon and on the critical ion flux are compared with the calculated results and, the rate constant of segregation of carbon on the Ni surface is determined to be 57 s^{-1} at 650° C. That on the TiC surface is determined to be 0.1 s^{-1} at 900° C. It is pointed out that segregation from the grain boundary to the surface of the deposited layer, grain boundary diffusion, and dissolution from graphite into the grain boundary are important factors for self-sustaining coating.

INTRODUCTION

Graphite is a candidate material for limiters in toka-mak-type fusion devices and has been tested under various conditions. The enhanced erosions observed at high temperatures, namely chemical sputtering [1–5] and radiation-enhanced sublimation [6,7], are its drawback. Some efforts to reduce the chemical sputtering have been done by means of coating the graphite surface with a metal layer [8] or metal carbide layer [9]. It has been shown that a thin nickel layer deposited on graphite reduces the reaction probability of CH_4 formation responsible for chemical sputtering by a factor of 4–5 [8].

Moreover, it has been found that the yield of CH_4 formation for the TiC layer deposited on graphite is much less than that for graphite [9]. In those cases the suppression of sputtering of coated high Z elements is a main problem. On the other hand, recent probe experiments with large fusion devices show that the

graphite limiters are covered by deposition of metal atoms sputtered off from the first walls and the neutral injection liners [10]. Such deposition of a metal layer under irradiation at elevated temperatures varies erosion behavior of graphite because of modification of the surface properties, as well as reduces the chemical sputtering as described above. Therefore, it is required to know how the erosion of graphite is modified by deposition of the metal layer.

When a metal layer is accumulated on graphite under irradiations with the high flux of multiparticles and energy, carbon atoms are dissolved into the metal layer from graphite. In some cases metal carbide phases [11] are produced due to thermally activated and/or radiation-enhanced processes. Furthermore the carbon atoms are segregated on the surface of the metal or metal carbide layer as well. In recent papers [12,13], it has been shown that when nickel-layer deposited graphite is bombarded with Ar^+ ions below certain current density at elevated temperatures, continuous coverage of the surface with the carbon atoms segregated in a self-sustaining way protects the nickel layer from being sputtered. Since the deposited metal layer reduces the chemical sputtering of graphite, this result indicates

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that the graphite limiter may show a favorable performance. Since erosion and deposition on graphite limiter in fusion devices are so complicated, it is important to study using simple systems, in which metal or metal carbide layer does the self-sustaining coating take place, and what is the limitation to the self-sustaining coating: the thickness of the layer to be protected, temperature, ion flux, and so on.

The coverage of the material surface with a segregated layer is essential for the self-sustaining coating. The surface coverage seems to be determined by a balance between the sputtered flux and the fluxes of segregation from inside to the surface and of dissolution in the reverse direction. Extending the theoretical treatment of the sputtering of binary alloys [14], we have shown that the surface concentration of segregated atoms depends on the rate constants of segregation and dissolution at the surface, on the diffusion constant, and on the sputtering (or desorption) cross section [13], based on an assumption that the rate constants of segregation and dissolution at the interface between the graphite and deposited layer are sufficiently large compared with those at the surface. The critical ion flux and critical thickness for the self-sustaining coating have been expressed as a function of the relevant rate constants.

In this paper, we present first an improved treatment including the rate constants of segregation and dissolution at the interface, to evaluate the surface concentration of segregated atoms and to describe the criterion for the self-sustaining coating in detail. Next, we show briefly the experimental results on the surface segregation of carbon atoms on nickel-deposited graphite obtained by means of the AES technique. Further we present the experimental results, obtained by means of the RBS technique, on the critical ion flux, for a TiC-deposited graphite [15] bombarded with a 1 keV hydrogen ion beam at 900° C and for a nickel-deposited graphite and a nickel/nickel carbide bilayer bombarded with a 5 keV argon ion beam at 650° C. Comparing the experimental values with the calculated ones of the critical ion flux, the key rate constants of segregation and dissolution are estimated.

regation of carbon atoms at the surface leads to a steady state. The segregation may be enhanced by ion bombardment [16]. Such a problem has been previously treated by the present authors [13]. We extend the treatment more generally to discuss the critical ion fluxes for the self-sustaining coating obtained experimentally.

We consider a composite system composed of carbon atoms and metal atoms, where the fractional concentrations of the carbon atoms in the bulk and at the top surface are represented by $C_b(x,t)$ and $C_s(t)$, respectively, where x is the depth from the surface and t is the time after the start of ion bombardment. Referring to Figure 1, the surface concentration $C_s(t)$ of main interest in this study is obtained by solving the following equations:

$$\frac{dC_s(t)}{dt} = k_2C_b(0,t) - k_1C_s(t) - \sigma\phi C_s(t) \qquad (1)$$

$$\frac{dC_b(x,t)}{dt} = D\frac{d^2C_b(x,t)}{dx^2} \qquad (2)$$

where k_2 and k_1 are the rate constants of segregation and dissolution given in the units of s^{-1}, D is the diffusion constant of carbon atoms, σ is the sputtering cross section for carbon atoms, and ϕ is the ion flux. The boundary condition at $x = 0$ for Eq. (2) is given by the relation

$$D\frac{dC_b(x,t)}{dx}\bigg|_{x=0} = k_2aC_b(0,t) - k_1aC_s(t) \qquad (3)$$

Furthermore, the boundary condition at the back surface of the composite layer is similarly given by the relation

$$D\frac{dC_b(x,t)}{dx}\bigg|_{x=L} = k_4aC_{subst}^0 - k_3aC_b(L,t) \qquad (4)$$

where C_{subst}^0 is the fractional concentration of carbon atoms in graphite, namely unity; k_4 and k_3 are the rate

CRITERION FOR SELF-SUSTAINING COATING

We suppose a carbon–metal composite layer on graphite, of which carbon atoms tend to be segregated at the surface. The surface is usually covered with an amount of carbon atoms at given elevated temperature because of Gibbsian segregation. When such a surface is bombarded with energetic ions at the elevated temperature, a balance between the sputtering and seg-
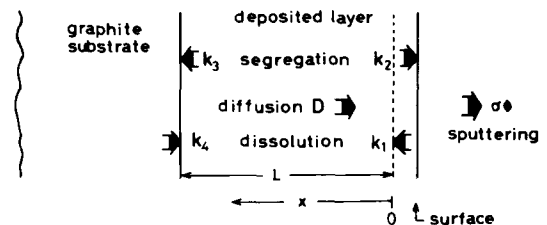

Fig. 1. Processes inducing fluxes of carbon atoms migrating in a metal–carbon composite layer, with a thickness L, deposited on graphite under ion bombardment.

constants of dissolution from the graphite into the deposited layer and its reverse process, respectively; L is the thickness of the deposited layer, and a is the planar spacing. Equation (4) is different from the boundary condition used in the previous treatment based on the assumption that the dissolution rate is large enough compared with the diffusion rate. In practice, when the deposited layer is polycrystalline, the short circuit grain boundary diffusion is a dominant process for carbon atoms to be supplied to the surface through the whole deposited layer from the graphite substrate. When the thickness of the deposited layer is sufficiently large compared with the range of bombarding ions, $C_b(x,t)$ should be replaced by $C_g(x,t)$; D should be replaced by D_g, and k_2 should be replaced by $k_2'(2a/r)$, where C_g, D_g, and k_2' and k_3' are the fractional concentration at the grain surface, the grain boundary diffusion constant, and the rate constants of segregation from the grain boundary to the surface and to the interface, respectively, and r and a are the spherical grain radius and the average thickness of the grain boundaries.

Equations (1) and (2) can be solved easily at a steady state, where $dC_s(t)/dt = 0$ and $dC_g(x,t)/dt = 0$, as observed experimentally in the previous work [13]. The steady state solution for the fractional concentration $C_s(\phi)$ of the carbon atoms is given by

$$C_s(\phi) = \frac{C_s^0}{1 + (\sigma\phi/k_1)(1 + Q_1 + Q_2)} \quad (5)$$

where $C_s^0 = (k_2'k_4/k_1k_3')C_{subst}^0$, $Q_1 = k_2'/k_3'$ and $Q_2 = k_2'(2a/r)/(D_g/La)$. C_s^0 is the fractional surface concentration at Gibbsian equilibrium segregation and Q_2 represents the ratio of the segregation rate from the grain boundary at $x = 0$ to the surface, to the diffusion rate from the graphite to the surface through the grain boundary. The removal flux $R(\phi)$ for carbon atoms from the specimen is expressed by multiplication of $C_s(\phi)$ by $N_s\sigma\phi$, as follows:

$$R(\phi) = \frac{N_s\sigma\phi C_s^0}{1 + (\sigma\phi/k_1)(1 + Q_1 + Q_2)} \quad (6)$$

where N_s is the surface density of graphite of monolayer thickness. If the relevant rate constants are mainly contributed by the thermally activated process, σ can be determined from the slope of $R(\phi)$ at low ϕ and moreover $(1 + Q_1 + Q_2)/k_1$ can be determined from the saturation level at high ϕ using the relation between R versus ϕ obtained experimentally.

We consider the conditions for the self-sustaining coating. The condition of $Q_1 < 1$ and $Q_2 < 1$, namely $k_2' < k_3'$ and $k_2'(2a/r) < (D_g/La)$ is the segregation-

limited case; the condition of $Q_1 < 1$ and $Q_2 > 1$, namely $(D_g/La) < (2a/r)k_2' < (2a/r)k_3'$ is the diffusion-limited case; and the condition of $Q > 1$ and $Q_1 < 1$, namely $(D_g/La) > (2a/r)k_2' > (2a/r)k_3'$ is the dissolution-limited case. The critical thickness for the segregation- and dissolution-limited cases is given by the relation $Q = 1$, namely $L_c = D_g/(2a^2/r) \cdot k_2'$.

Using Eq. (5), the condition for the self-sustaining coating is derived as follows: (a) $C_s^0 = 1$ and (b) $(\sigma\phi_c/k_1)(1 + Q_1 + Q_2) \leq 0.1$. Condition (b) represents the competition of enrichment due to segregation with the removal due to sputtering. The value of 0.1 is chosen for the critical ion flux for self-sustaining coating to be effectively determined, because $C_s(\phi)$ is less than unity at $\phi > 0$. When $Q_2 << 1$, namely $L << L_c$, ϕ_c depends on k_2' or k_4, and not on L. When $Q > 1$, ϕ_c depends on L. Therefore, the experiments to determine the rate constants of k_2' and k_1 from the critical ion flux had better be done under a condition of $L < L_c$. When the carbon layer segregated at the surface of deposited layer has the same structure as the graphite, one can regard that $k' = k'$, thus $Q = 1$. In such a case the critical ion flux for the self-sustaining coating is by a factor of 2 smaller than that for the segregation-limited case.

EXPERIMENTAL PROCEDURE

The specimens used were nickel-deposited and TiC-deposited graphites and nickel/nickel carbide bilayer films. The nickel-deposited graphite was prepared by vacuum deposition of nickel layer ($\sim$5000 Å) on mechanically polished Poco-graphite with a size of 10 × 15 × 2 mm^3. The nickel layer deposited was tested by means of a 1 MeV transmission electron microscope. It was found that the nickel film is polycrystalline and the average size of crystalline grains is 200–300 Å in diameter. The TiC layer was prepared by chemical vapor deposition and the thickness was about 3000 Å. The chemical composition of the TiC layer was analyzed by both electron probe microanalysis (EPMA) and RBS techniques. The EPMA analysis showed that the composition ratio of carbon to titanium is about 1.0. On the other hand, the RBS analysis showed that the ratio is also 0.94. The scanning electron microscope (SEM) observation of the TiC surface showed that the average grain size is 1000–2000 Å in diameter. The preparation of nickel/nickel carbide bilayer films was described elsewhere [12].

Experiments on nickel-deposited graphites and nickel/nickel carbide bilayer films were carried out using a conventional ultra-high vacuum (UHV) chamber at a base pressure of 5 × 10^{-10} torr equipped with a manipulator and a sputter ion gun. The specimen, in contact with a ceramic heater placed on the manip-

ulator, was bombarded with a 5 keV Ar^+ beam perpendicular to the surface. Ar^+ ion current density was uniform over a spot of 5–6 mm in diameter and varied in the range between 1 and 40 $\mu A/cm^2$. The surface composition of the specimen was determined by means of the AES technique. The depth distribution of carbon atoms in the specimens was determined using the RBS measurement with a 1.3 MeV H^+ beam of 1 mm in diameter. The sputtering yield of nickel was obtained from the difference between the depth distributions before and after the ion bombardment, as a function of the ion flux.

Irradiation of TiC-deposited graphite with a 1 keV hydrogen ion beam was done in Toshiba Corp. using experimental apparatus which consists of a low-energy ion beam system and a UHV chamber. The detailed description of the apparatus was given elsewhere [17]. The hydrogen ion beam was generated by duo-plasmatron and the current density at the target was varied in the range between 20 and 700 $\mu A/cm^2$. The angle of the beam to the target normal was 50° deg. and the irradiation area was elliptic in shape, 3 × 4.5 mm. The pressure in the chamber during hydrogen ion bombardments was about 3 × 10^{-8} torr. The TiC-deposited graphite specimen, mounted on a tantalum strip heater, could be heated up to 1000° C. The temperature was measured with a Pt–PtRh thermocouple which was fixed in a hole prepared in the specimen. The specimen was analyzed using the RBS measurement with a 2 MeV He^+ beam of 0.4 mm in diameter. The RBS energy spectra were obtained at several points inside and outside of the irradiated area on the specimen. The sputtering yield of titanium atoms was determined from the difference between the thicknesses of the TiC layer in the irradiated and nonirradiated parts of the specimen.

EXPERIMENTAL RESULTS

Ni-Deposited Graphite

The Ni-deposited graphite specimen, as prepared, was bombarded with a 5 keV Ar^+ beam at room temperature in order to remove the oxide layer at the surface. Immediately after the ion bombardment, the specimen was heated for 2.5 hr at 650° C. Before and after the heating, the specimen was characterized by means of the AES and RBS techniques. In Figure 2, are shown typical AES spectra from a Ni-deposited graphite specimen. In the spectrum (a) obtained before the heating, one can find a main signal from nickel and small signals from residual impurities of carbon and oxygen at the surface. In the spectrum (b) after the heating, one can see clearly that the carbon signal has grown by the heating. The growth of the carbon signal
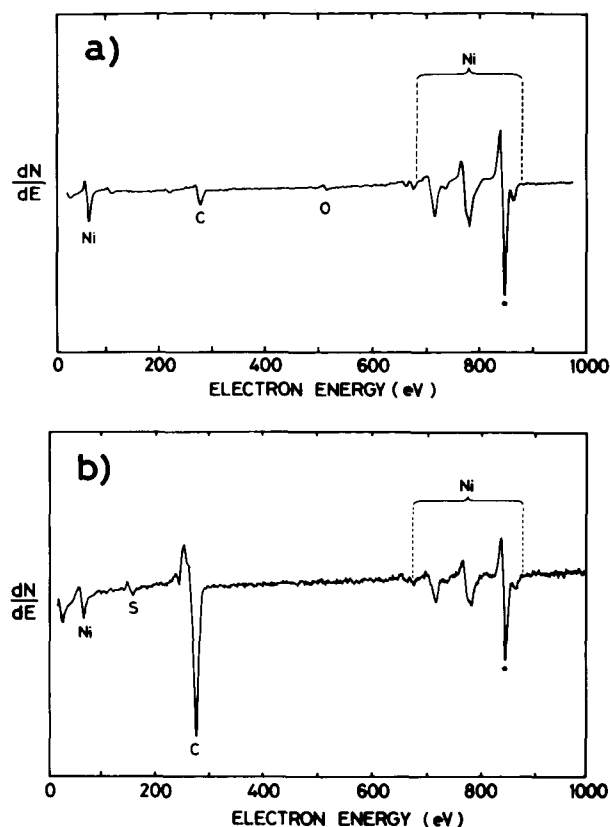

Fig. 2. Auger electron energy spectra from a nickel layer deposited on graphite: (a) after bombardments with 5 keV Ar ions at room temperature, and (b) after subsequent heating for 2.5 hr at 650° C.

is ascribed to the carbon atoms which are dissolved into the nickel layer from graphite and are segregated to the surface via grain boundary diffusion. The shape of the carbon signal observed was identified to be the same as that for graphite. This result corresponds to the experimental observation by Shelton et al. [18] that at temperatures below 1065 K the surface of nickel-bearing carbon is covered with segregated (or precipitated multilayer) graphite. Thus, one can conclude that the segregated carbon layer in this case is a graphitic layer.

The segregation of carbon atoms is also found in a typical RBS energy spectrum of 1.3 MeV H^+ beam from the specimen, shown in Figure 3. In this spectrum, H^+ ions backscattered from the nickel layer form a broad peak and those from a graphite substrate form a flat continuum below the channel marked by the interface. A clear small peak, which is produced by the heating, at the channel marked by C^s indicates the carbon atoms segregated to the nickel surface. Small counts between the marks of the interface and C^s indicate that the concentration of carbon atoms solute in the nickel layer is very small. From the area of the small surface
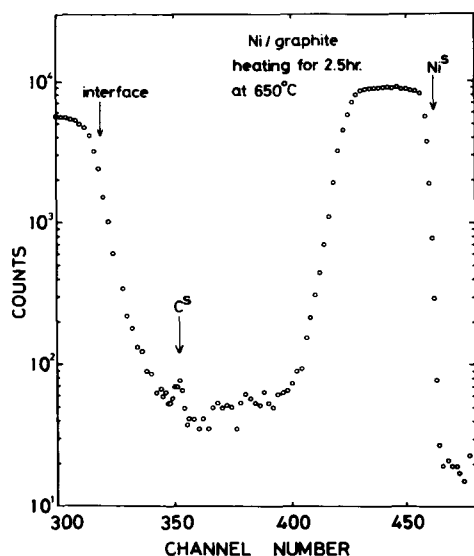
Fig. 3. RBS energy spectrum of a 1.3 MeV H^+ ion beam from a nickel layer deposited on graphite heated for 2.5 hr at 650° C.

peak, the effective thickness of the segregated carbon layer is estimated to be about 2 monolayers.

Since the width of the nickel peak is proportional to the thickness of the nickel layer, the sputtering yield of nickel was determined from reduction in the width caused by the 5 keV Ar^+ ion bombardments. The reduction in the width by the bombardment at different current densities at 650° C is shown in Figure 4. It is seen from Figure 4 that the width of nickel peak at each current density decreases linearly with increase in the ion fluence. It was observed also that the surface peak of the segregated carbon layer keeps almost a constant level at each case. These facts indicate that the Ni-deposited graphite attains a steady state during
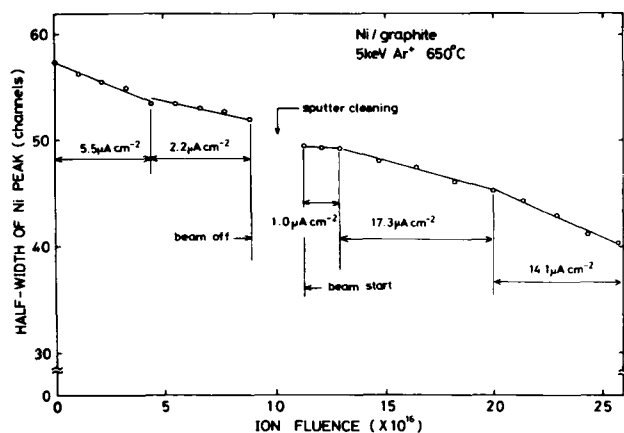

Fig. 4. Variation of the width of Ni peak with the ion fluence for a Ni-deposited graphite bombarded with 5 keV Ar^+ ion beams of different current densities at 650° C.

each Ar^+ bombardment. The sputtering yield of nickel was calculated from the slope of linearly decreasing width. The experimental results were presented in the previous paper [13]. Therefore, only the experimental results for the Ni-deposited graphite and self-supporting Ni/Ni carbide bilayer at 650° C are shown in Figure 5. One can see that the sputtering yield of nickel atoms for both specimens are almost zero at ion fluxes below 5×10^{12} ions/cm$^2 \cdot$ s and 1.7×10^{13} ions/cm$^2 \cdot$ s, respectively. It is also seen that as the ion flux increases beyond the critical ion flux, the sputtering yield of nickel atoms increases and then decreases to a constant value. This change has been discussed in terms of the radiation-enhanced segregation elsewhere [19].

TiC-Deposited Graphite

Since it is already known that the carbon layer segregated at the surface of TiC-deposited graphite heated above 700° C and it has a graphitic structure [17], we have investigated, by means of the RBS technique, only the partial sputtering yield of titanium atoms. In Figure 6, typical RBS energy spectra of 2 MeV He^+ beam from a TiC-deposited graphite are shown which is bombarded with 1 keV H^+ beam of 20 μA/cm^2 by a fluence of 2 A $\cdot$ s/cm at 900° C. In Figure 6, the counts between the 200 and 500 channels represent scattering from Ti atoms in the specimen and the counts below the 160 channels represent that from carbon atoms. The crossed points indicate the spectrum obtained at the outside of the irradiation area and the open circles that obtained at the center. The counts for Ti and C between marks of the interface and Ti^s (or C^s) represent scattering from the deposited TiC layer
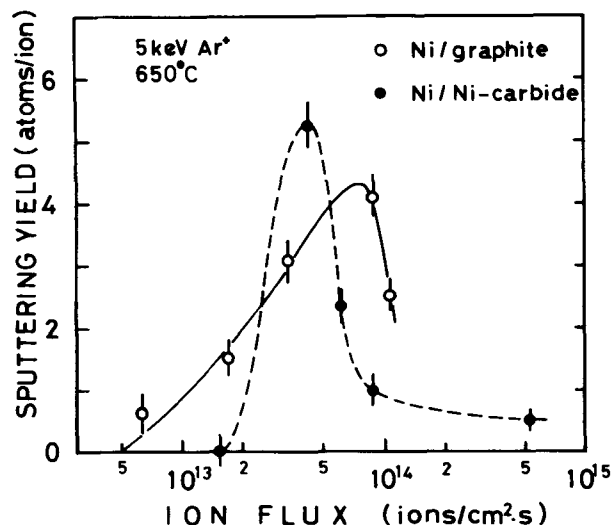

Fig. 5. Ar^+ ion flux dependence of the sputtering yield for nickel atoms from a Ni-deposited graphite and from a Ni/ Ni carbide bilayer, bombarded with 5 keV Ar^+ ions at 650° C.
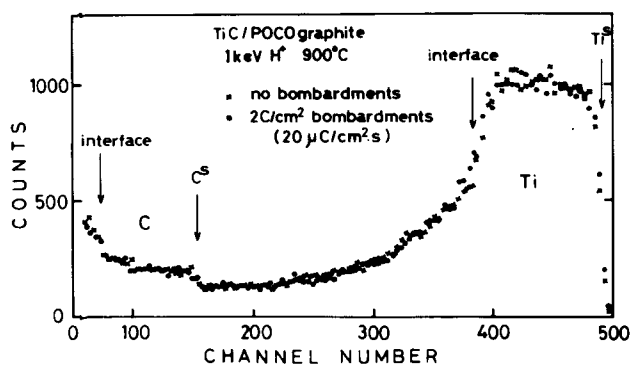
Fig. 6. RBS energy spectra of a 2 MeV He$^+$ ion beam from TiC-deposited graphite bombarded with a 1 keV H$^+$ ion beam of 20 μA/cm^2 at 900° C.

and the counts for Ti tailed to the lower channels from the interface means that Ti atoms are distributed into the graphite substrate. Comparing both spectra, it is found that the width of the Ti peak is not reduced by the irradiation, although an appreciable reduction in the peak width was produced by the same irradiation at room temperature. Moreover, the counts for Ti atoms at the channels around the mark of the interface in the irradiated spectrum are found to be increased. These results indicate that the hydrogen ion bombardment of the specimen at 900° C and at 20 μA/cm^2 does not reduce the thickness of the TiC layer, but it increases the composition ratio of Ti/C at the interface, namely, it removes the carbon atoms from the interface of the specimen. It is also seen that the ratio of the average counts of Ti and C for the TiC layer, namely the composition ratio of Ti/C is not changed by the hydrogen ion bombardment. From these facts, one can conclude that the sputtering of Ti atoms from the TiC-deposited graphite is prohibited by the self-sustaining coating under irradiation at a current density of 20 μA/cm^2 at 900° C. Similar results [15] are observed for the specimens irradiated at the ion current densities of 40 and 80 μA/cm^2.

On the other hand, it is found that the width of Ti peak for the specimen irradiated at the higher ion current density is clearly reduced. Moreover, the composition ratio of Ti/C at the interface is also found to be increased. The sputtering yields of Ti atoms obtained at different ion current densities at 900° C and at room temperature are shown as a function of the ion flux in Figure 7. The sputtering yield, 1×10^{-2} atoms/ion, of Ti atoms at room temperature is found to agree well with the result at normal incidence obtained by Brossa et al. [20], when taking into account the factor caused by the difference between the incident angles in both experiments. It is seen from Figure 7 that the sputtering yield of Ti atoms at 900° C is
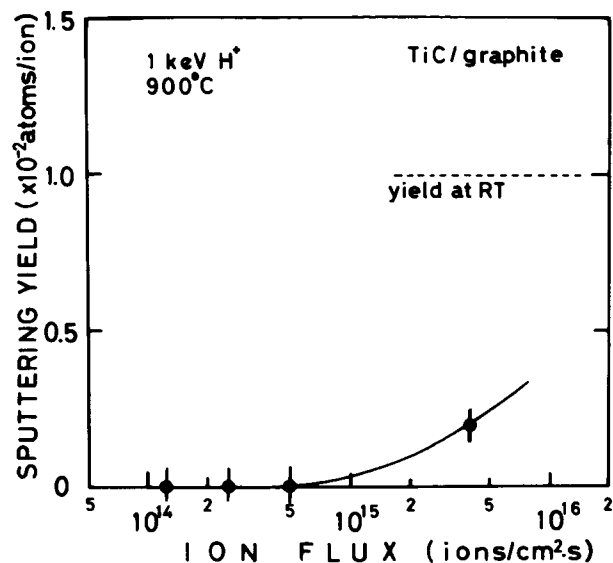

Fig. 7. H$^+$-ion flux dependence of the sputtering yield for Ti atoms from a TiC-deposited graphite bombarded with 1 keV H$^+$ ions at 900° C. The dotted horizontal line represents the sputtering yield for the H$^+$ bombardment at room temperature.

almost zero at low ion fluxes and seems to increase with increasing the ion flux beyond a critical ion flux of 5×10^{14} ions/cm$^2 \cdot$ s.

DISCUSSION

It has been experimentally shown that when Ni-deposited graphite, Ni/Ni carbide bilayered and TiC-deposited graphite are bombarded with energetic ions at certain elevated temperature, the sputtering of metal atoms is substantially suppressed by the self-sustaining coating with segregated carbon layer below certain critical ion flux. The critical ion fluxes for the Ni-deposited graphite and Ni/Ni carbide bilayer bombarded with 5 keV Ar$^+$ ions at 650° C are 5×10^{12} ions/cm$^2 \cdot$ s and 1.7×10^{13} ions/cm$^2 \cdot$ s, respectively. On the other hand, the critical ion flux for the TiC-deposited graphite bombarded with 1 keV H$^+$ ions at 900° C is 5×10^{15} ions/cm$^2 \cdot$ s. Here, using the criterion for the self-sustaining coating derived, we discuss which parameter makes a main contribution to the critical ion flux.

When the substantial suppression of metal sputtering takes place, one can regard the condition (b) of $(\sigma\phi_c/k_1)(1 + Q_1 + Q_2) \leq 0.1$ to be satisfied. As described above, the values of $(1 + Q_1 + Q_2)/k_1$ are determined from the curve of the removal flux $R(\phi)$ obtained experimentally, since the relevant rate constant k_2' is mainly caused by the thermally activated process in this case. In a previous paper [13], we have

obtained the removal flux of carbon atoms as a function of the ion flux of a 5 keV Ar^+ beam using the self-supporting Ni/Ni carbide bilayer film, of which the thickness is sufficiently small compared with L_c. The values of σ and $k_1/(1 + Q_1 + Q_2)$ are determined to be $0.43 \times 10^{-15} cm^2 \cdot s$ and $0.17 \ s^{-1}$, respectively. Using these values, the critical ion flux is computed to be 4×10^{13} ions/$cm^2 \cdot s$, which corresponds well to the value of 1.7×10^{13} ions/$cm^2 \cdot s$ determined from the experimental result on the sputtering yield of nickel atoms. Therefore, one can conclude from this fact that the phenomenological treatment developed in the present study is applicable to evaluate the critical ion flux for the self-sustaining coating.

Next, we consider which parameter makes a main contribution to the critical ion flux. If the rate constants of k_1, k_2', k_3', and k_4 are available, it is easily known from condition (b). Unfortunately, there exist no available data on the rate constants. When the thickness of the deposited layer, L, is much smaller than L_c, as shown later, condition (b) is rewritten into the relation $\phi_c = 0.1(k_1/\sigma)/(1 + k_2'/k_3')$. The relation indicates that the difference between the critical ion fluxes observed for the two nickel–carbon composite systems is due to the difference in the values of k_2'/k_3', since the values of σ and k relevant to the surface of the deposited layer are the same for the two systems. As shown in Figure 2, the carbon layer segregated at the nickel surface is a graphitic phase. This result indicates that for the Ni-deposited graphite the dissolution rate constant k_1 of carbon atoms from the graphitic layer at the surface into the nickel layer may be regarded to be the same as the dissolution rate constant k_4 from the graphite into the nickel layer when the contribution of the radiation-enhanced segregation is assumed to be small, namely, it holds that $k_2' = k_3'$ at equilibrium segregation. On the other hand, for the Ni/Ni carbide bilayer, the value of k_3' is expected to be much larger than the value of k_2', because the nickel carbide phases are metastable, thus the dissolution rate constant k_4 from the carbide into the nickel layer being much larger than the dissolution rate constant k_1 from the stable graphitic phase. In such a case, the ratio k_2'/k_3' is sufficiently small compared with unity. Based on these considerations, the critical ion flux for the Ni/Ni carbide bilayer is expected to be by a factor of 2 larger than that for the Ni-deposited graphite. On the other hand the ratio of the critical ion fluxes observed experimentally for the two systems is 3.4. The larger value of the experimental ratio may be partly attributed to a contribution of the radiation-enhanced segregation to k_2'.

Using $Q_1(= k_2'/k_3') \sim 0$ for the Ni/Ni carbide bilayer, the dissolution rate constant k_1 is determined to

be $0.17 \ s^{-1}$ at 650° C. For Gibbsian equilibrium segregation, $C_s^0/s = (2a/r)k_2'/k_1$ is suggested to hold [19], where s is the solubility of carbon in nickel in the units of the fractional concentration. The solubility of carbon in nickel at 650° C is experimentally determined by Coad and Riviere [21] to be 0.30 at. wt. %. Thus, the value of $(2a/r)k_2'$ is computed to be $57 \ s^{-1}$. So, we can confirm that the condition of $Q_2 << 1$ is satisfied in the present study. The nickel layer deposited is polycrystalline, thus the grain boundary diffusion constant should be used. Since it is not available, we use the bulk diffusion constant of carbon in nickel, $5 \times 10^{-10} \ cm^2 \cdot s$ at 650° C. For the thickness of the deposited nickel layer, $\sim 5000 \ Å$, Q_2 is computed to be 0.11. Since the grain boundary diffusion is, in general, larger than the bulk diffusion constant, the value of Q_2 indicates that the values of k_1 and k_2' determined are very reasonable.

Here, we discuss, briefly, the critical ion flux for the TiC-deposited graphite. It has been also observed that the carbon layer segregated at the TiC surface is a graphitic phase. Thus, in this case, we may put also that $k_2'/k_3' = 1$. However, we have no available experimental data on k_1 and σ. Therefore we estimate the value of k_1 from the experimental critical ion flux. The sputtering cross section σ for the carbon layer at the TiC surface is approximated by the physical sputtering cross section for graphite [23], $\sim 10^{-17} cm^2$. When $Q_2 << 1$, the value of k_1 is computed to be $0.05 \ s^{-1}$ for $\phi_c = 5 \times 10^{14}$ ions/$cm^2 \cdot s$. For Gibbsian equilibrium segregation, the relation $C_s^0/C_g(0) = (2a/r)k_2'/k_1$ is regarded to hold. Using $C_s^0 \sim 1$ and $C_g(0) \sim 1$, the value of $(2a/r)k_2'$ is obtained to be $0.1 \ s^{-1}$. The grain boundary diffusion constants of C in TiC have been experimentally determined by several authors, $5 \times 10^{-13} \ cm^2/s$ at 900° C [24]. Using these values, Q_2 is computed to be 0.1 for the thickness of the TiC layer, $\sim 3000 \ Å$, used in the present study. This indicates that the value of k_1 estimated is also very reasonable.

Finally we emphasize that the critical ion flux and the critical thickness for the deposited layer to be protected from resputtering can be evaluated using the phenomenological treatment developed in the present study and that the rate constant of segregation from the grain boundary to the surface and the grain boundary diffusion constant included are important parameters. Especially, available data on the rate constants of segregation and dissolution are required.

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