DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**AN IN-SITU SPECTROSCOPIC
EROSION YIELD MEASUREMENT WITH
APPLICATIONS TO SPUTTERING AND
SURFACE MORPHOLOGY ALTERATIONS***

W.K. Leung, Y. Hirooka, R.W. Conn,
D.M. Goebel, B. LaBombard, R. Nygren

UCLA-PPG-1167

July, 1988

Department of Mechanical, Aerospace, and Nuclear Engineering
Institute of Plasma and Fusion Research
University of California, Los Angeles 90024

An In-situ Spectroscopic Erosion Yield Measurement with Applications to Sputtering and Surface Morphology Alterations

W. K. Leung, Y. Hirooka, R. W. Conn, D. M. Goebel, B. Labombard, R. Nygren

Mechanical, Aerospace and Nuclear Engineering Department and Institute of Plasma and Fusion
Research, University of California, Los Angeles, USA

Abstract

An in-situ spectroscopic erosion yield measurement is developed and used to monitor material surface erosion during bombardment by a plasma. The experiments are performed in a plasma that has the characteristics of a fusion tokamak boundary plasma but the technique is applicable to many processes where plasma erosion is important. Erosion yield of materials bombarded in a high flux (up to 10^{18} ion/cm²/s) plasma environment has been previously studied using weight loss measurements. In the present study, the sputtered flux from a material is monitored by the line emission intensities of atoms eroded from the surface. The line intensities can be used to infer erosion yields after proper calibration. The method agrees well with results from weight loss measurements. Earlier work established that the material surface structure can substantially influence the erosion yield. When a change of surface morphology (e.g. cone formation) occurs, weight loss methods cannot be used to determine the erosion yield. However, the in-situ erosion measurement is suitable and is used to investigate the relation between the on-set of morphology changes and alternations in erosion yield during plasma bombardment. Experiments are reported for copper, as an example of a pure material, and stainless steel, as an example of an alloy system. The formation of surface cones is observed only when both the sample temperature is above a critical value and surface impurities exist. If the source of impurities is removed, or the sample temperature is lowered below the critical value, a surface rough with cones will be returned to a smooth state.

1. Introduction

Erosion of wall, limiter or divertor target plate material by energetic particle bombardment in fusion plasma devices is one of key mechanism for impurity introduction [1]. It is important to investigate experimentally such plasma erosion of materials and to monitor, if possible, the erosion

process. In earlier work, we reported on an extensive series of experiments in the PISCES plasma device [2] in which both plasma-induced erosion as well as plasma ionization and redeposition of eroded material is observed [3,4,5]. The plasma operates continuously over a range of plasma density and temperature. Shown in Fig. 1 is a schematic view of the general experimental setup, with a material sample located in a plasma produced in the PISCES facility [2].

It was found earlier that the erosion yield of a material can be changed substantially if the surface morphology is changed. In particular, cone structures [6] can be formed on the surface under certain specific conditions. The modification of surface morphology by plasma bombardment and its relation to the erosion yield is not well understood. Conventional erosion yield measurements using the weight loss method are not applicable here because the time scale of the morphology change is much faster than that of a measurable weight change. An in-situ erosion diagnostic is thus indispensable in this case. Laser excited fluorescence measurements [7] have been used by others to measure the sputtering yield but the complex nature and stringent requirements of such a diagnostic make it difficult to use this technique as an on-line, real time measurement.

In this paper, the development, investigation and results of a spectroscopic method to continuously measure the erosion yield in-situ and apply it to diagnose surface morphology changes is presented. The intensity of neutral atom emission in front of the material sputtered by the plasma is used to determine the yield. The problem of converting the intensity into erosion yield is discussed and solutions are demonstrated. Investigations reported here used both copper and stainless steel samples to demonstrate the applicability of this method for both pure materials and alloys. In addition, basic differences between these materials in terms of yield and surface morphology can be examined. In particular, we use the in-situ spectroscopic erosion yield technique to study the dependence of surface cone formation on substrate temperature and impurity content.

2. Experimental arrangement

An illustrative view of the experimental set-up is shown in Fig. 2. The plasma is generated from the source upstream and guided by a uniform magnetic field toward the sample. Samples are supported from behind and at the center of the plasma. Water cooling lines and a thermocouple are introduced from the back. A movable Langmuir probe can be positioned in front of the sample to measure the electron density and temperature of the plasma. A detailed description of the PISCES facility is given in reference 2.

Line emission spectrometry as used in this work is based on the excitation of an atom from

a lower to a higher state and its subsequent transition back to the lower state by spontaneous radiation. The intensity is proportional to the density of atoms in the upper level and to the transition rate. To convert a line intensity signal into particle density, one must calculate the excited state density. The plasma electron density and temperature must be known.

A McPherson 209 1.3m Czerny-Turner monochromator is used to view the plasma through the center and at a location about 0.5 cm in front of the sample. Exposed samples are 3.8 cm in diameter. An electrical bias of up to -500 V can be applied to the sample to provide ions with a specific energy for sputtering. The plasma can be hydrogen, helium, nitrogen, argon or other gases. Argon is used for all the experiments reported here because its higher sputtering yield.

3. The atomic density determination

In an optically thin plasma, the line intensity for a transition in an atom from the n th to the m th state is

$$I(n,m) = 1/4\pi \int n_p(n) A(n,m) ds \quad (1)$$

where $n_p(n)$ is the density of particle at state n and $A(n,m)$ is the atomic transition rate from the n th state to the m th state. The integration is over the depth of the plasma. In the experiments reported here, the transition lines monitored are Cu I at 3247.5Å ($4s - 4p$ ($^2S_{1/2} - ^2P_{3/2}$)), Cr I at 4254.35Å ($3d^5 4s - 3d^5 4p$ ($a^7S_3 - z^7P^o_4$)) and Fe I at 3859.9Å ($3d^6 4s^2 - 3d^6 4s 4p$ ($a^5D_4 - z^5D^o_4$)), respectively. All the transitions are of the type $\Delta n = 0$. The transition rates are strong so that the coronal model [8] can be used. In this model, the electron impact excitation line emission radiation contains two following processes:

(a) The excitation of the atoms from the lower state level (the ground energy level) to the higher state level by absorption of the energy from the electrons in the plasma;

(b) The spontaneous emission of radiation in the form of one of the spectral lines when the excited atom transits to the lower lying energy level.

The population density of the excited states is determined by the balance between the rate of excitation from the ground level and the rate of spontaneous radiative decay, expressed as

$$n_e n_p(g) X(Te,g,n) = n_p(n) \sum_{r < n} A(n,r) \quad (2)$$

where n_e is the electron density, $n_p(i)$ is the density of the particles in the i th state, and $X(Te,g,n)$ is

the excitation rate coefficient. The intensity of the line $I(n,m)$ is then

$$I(n,m) = 1/4\pi \int n_e n_p(g) X(T_e, g, n) A(n,m) / \sum_{r < n} A(n,r) ds \quad (3)$$

The excitation rate coefficient used here is based on the Bethe-Born approximation for an optically allowed transition [9], i.e.,

$$X(T_e, m, n) = 1.6 \times 10^{-5} f g(\beta) \exp(-\beta) / (E T_e^{1/2}) \quad (4)$$

Here, the excitation rate coefficient, X is in cm^3/sec , T_e , the electron temperature, and E , the energy difference between the transition levels m and n , are in eV, β is E/T_e , f is the absorption oscillator strength, and $g(\beta)$ is the average effective Gaunt factor. For the Gaunt factor, the interpolation formula proposed by Mewe [10] is used,

$$g(\beta) = A + (B\beta - C\beta^2 + D) \exp(\beta) E_1(\beta) + C\beta \quad (5)$$

where $A = 0.6$, $B = C = 0$, $D = 0.28$ (for $\Delta n = 0$ transition), and E_1 is the exponential integral function. When the coronal model cannot be applied, one must determine an effective excitation coefficient by a detail collisional balancing of the transitions among the different energy states. A treatment of this process is beyond the scope of this paper but a description of different models can be found in reference 8.

4. Determination of the atomic density and flux of sputtered particles

Conversion of the sputtered atom density into flux requires knowledge of the mean velocity of the sputtered particles. One may either measure or obtain from the Thompson formula [11] the velocity distribution function. In our experiments, the mean velocity of sputtered particles is not measured. Instead, a calibration factor is determined by comparing with results of weight loss measurements under different, well-defined conditions of erosion at normal incidence and at different energies. The erosion yield is deduced by the measurement of line intensity, electron temperature and electron density once the calibration factor is obtained.

The sputtering of particles from a plane target has been discussed by Hintz et al. [7]. The particle flux leaving the target can be written as

$$\Gamma = \sum \Gamma_i \quad (6)$$

where i denotes the different constituents of the metal. We make the following assumptions as in reference 7. First, the contribution of polyatomic particles can be neglected. Second, for a clean surface the number of particles sputtered as ions is negligible. Third, the occupation of the energy levels in the fine structure is according to the statistical weight of the levels because the electron temperature is much greater than the energy difference between the levels.

For a large surface the flux density of the i th sputtered particles is

$$\Gamma_i = n_i v_i \quad (7)$$

where n_i is the atomic density, and v_i is the averaged velocity of the sputtered atoms perpendicular to the target. In principle, n_i can be measured by the line emission radiation while v_i can be obtained from the energy and angular distribution of the sputtered particles [12] corrected for the finite size of the target. With this approach, one obtains the sputtered flux density from equation (7) and thus the sputtering yield. In practice, a calibration is made of the spectroscopic technique by normalizing to a weight loss measurement. Since Γ is proportional to the weight loss and, for a uniform plasma, n_p is proportional to I (equation (1)), one can obtain the ratio of weight loss to the intensity as a calibration. So long as the plasma density and temperature are held fixed, the calibration factor remains the same.

When the electron temperature or density changes, two effects must be included. One is the change in measured intensity due to the dependence of I on the plasma temperature and density, as indicated in equation (3). This can be readily normalized from knowledge of the electron density and temperature. The other effect is that some sputtered atoms may be ionized in the plasma prior to escaping and be redeposited onto the target [4,5]. Hence, the weight loss can depend on the ionization mean free path, λ , even if the sputtered flux is the same.

In the following treatment, we parametrize the effective sputtered flux by,

$$\Gamma_{\text{Eff}} = \alpha(\lambda) \Gamma \quad (8)$$

where $\alpha(\lambda)$ is the fraction of sputtered atoms escaping the plasma, i.e., not redeposited onto the target. We call $\alpha(\lambda)$ the erosion factor. The measured weight loss is proportional to Γ_{Eff} . In the

limit that the mean free path is long, the factor $\alpha(\lambda)$ approaches one, as illustrated in Fig. 3, based on data reported earlier [3,4,5]. In Fig. 3, the normalized erosion yield is plotted against the ionization mean free path for two materials, copper and stainless steel. The normalized erosion yield is obtained by dividing the measured yield (determined via weight loss) by the calculated sputtering yield. The data shows that the normalized yield is small for small λ but approaches one, as λ becomes large (greater than 20 cm in this case).

As a consequence of Fig.3, a calibration can be found using the weight loss method for a fixed mean free path. The calibration factor is simply proportional to $\alpha(\lambda)$, and the value of $\alpha(\lambda)$ itself is deduced by knowing the calibration factor as a function of ionization mean free path. The results presented for the experiment reported here are obtained using this procedure.

5. Erosion yield measurements

In Fig. 4, the erosion yield of copper, bombarded by an argon plasma at a bias voltage of -50 to -200V, and measured by spectroscopy is shown plotted against the erosion yield determined by weight loss, after the calibration procedures mention in section 4 have been made. In this case, the mean free path of a copper atom is 12 cm. In the calculation of the ionization mean free path, the semi-empirical prescription of Lotz [13] for the ionization rate coefficient is used. Measurements made of the ionization mean free path of metals in the PISCES plasma [14] are in good agreement with values calculated.

In Fig. 5, a similar plot is shown for a 304 stainless steel sample. In this case, both the Fe I and the Cr I lines are monitored. The intensities of Fe I and Cr I lines are each calibrated to the stainless steel weight loss independently and the yields of Fe and Cr are proportional. That is, no differential sputtering is observed during these experiments.

As described in section 4, the calibration factor at different mean free path is proportional to $\alpha(\lambda)$. One can normalize the value of calibration factors to that at very long mean free path to obtain $\alpha(\lambda)$ at different λ . A plot of the erosion factor $\alpha(\lambda)$ obtained in this way is shown in Fig. 6. In this graph, the longest value of λ is 38 cm. Note that the erosion factors obtained in this way agree reasonably well with the calculated values in Fig. 3.

6. Application of the in-situ erosion yield measurement to monitoring metal surface morphological changes

It is well known [15-19] that smooth metal surfaces can be modified to form cone

structures under certain specific plasma and material conditions. The conditions are as follows. First, the sample temperature must be above a critical value, T_c . This temperature apparently determines the mobility of impurities on the surface via surface diffusion. Second, there must be impurity atoms on the surface whose sputtering yield differs from that of the substrate. In the case of PISCES, the plasma must be in the redeposition regime, i. e., the majority of sputtered particles are ionized and redeposited onto the surface. Without redeposition, impurities are removed from the surface by sputtering and the clean surface does not develop cones, regardless of temperature. Scanning electron microscope pictures of a smooth surface and a modified cone surface are shown in Fig. 7. Since the erosion yield depends on the surface morphology, one can monitor the cone formation process on a metal surface by monitoring the erosion yield. As noted earlier, the weight loss method is not suitable for this because of its poor time resolution and the fact that it is not an in-situ monitor.

Reported here are first quantitative results using the in-situ spectroscopic erosion yield measurement technique to examine the surface changes due to cone formation on copper and stainless steel samples. In the copper erosion experiment, the electron temperature and density are 7.2 eV and $5 \times 10^{12} \text{ cm}^{-3}$ respectively, and the sample bias voltage is -100 V. Impurities are introduced deliberately by sputtering the molybdenum tip of a Langmuir probe placed in the plasma in front of the sample. The temperature increase of the sample is obtained by the heating associated with plasma bombardment. Shown in Fig. 8 is a plot of the relative erosion yield of an originally smooth copper surface as a function of time. The temporal sample temperature measured by a thermocouple is plotted on the same graph.

The measured erosion yield remains constant until the copper temperature reaches about 520 K. This is the critical temperature, T_c , for copper above which cone formation is triggered, resulting in a reduction in erosion yield. The yield drops continuously to about half the original value and then remains constant, suggesting that cone formation and erosion have come to equilibrium. The spectroscopic erosion monitor proves to be an effective way to determine the critical temperature for the onset of surface morphology changes, particularly cone formation. The decrease in yield of a factor of two for a cone-covered surface is consistent with earlier findings [3,4]. Experimental and theoretical studies of retrapping effect on structured surfaces have been done by Auciello [20]. A likely reduction in sputtering yield on a cone covered surface is indicated.

Measurements of erosion yield for a smooth copper surface and for a cone-modified copper surface, determined by ion beam sputtering, were made and the results are shown in Fig. 9. The yield is reduced by a factor of two for the cone modified surface. Importantly, if the source of

impurity is removed (in this case, the impurity is molybdenum), the surface returns to smooth even if the temperature remains above the critical temperature.

A temporal plot of yield versus temperature for a stainless steel sample is shown in Fig 10. In this case, the critical sample temperature is higher, about 550 K. The electron temperature and density are 26 eV and $1.2 \times 10^{12} \text{ cm}^{-3}$ respectively. The final erosion yield of the surface is close to 60% of the starting value. It is again found that the cones are eroded away and the surface becomes smooth if the sample temperature is lowered below the critical temperature or if the impurity seed is removed from the plasma.

Although not shown here, the rate of change of erosion yield is found to be faster at a higher plasma flux, suggesting that the rate of cone formation is flux dependent. However, along with the increase in flux, the temperature of the sample also increases. The possibility that the temperature increase may affect the cone formation rate cannot be ruled out. Further investigation of each of these two effects separately requires an approach to maintain the sample temperature at a fixed value.

7. Summary

An in-situ spectroscopic erosion yield measurement has been described. Atoms eroded by plasma bombardment are detected in front of the eroding surface by the line emission radiation induced by electron excitation. The measured density of the sputtered atoms in the plasma can be used to deduce the sputtered flux leaving the surface. After calibrating directly with weight loss, the erosion yield can be obtained spectroscopically without removing the sample or disturbing the experiment. The calibration is done in two step. First, the calibration of the erosion yield is obtained for the sputtered particles in the plasma that results in the same ionization mean free path, λ . Second, the erosion factor, $\alpha(\lambda)$ is obtained by comparing the variation of the calibration factor in different plasmas having different ionization mean free paths for the eroded particles. Step two is necessary because the fraction of particles redeposited onto the sputtered surface depends on the ionization mean free path. The erosion yields of copper and stainless steel are measured in this way, and compared with results of weight loss, and excellent agreement is obtained.

It has been shown that under certain plasma conditions, the morphology of a material surface may be changed and in particular, cone-type structures are formed. There are two necessary conditions. First, the sample temperature has to be above a critical value, T_c . Second, there must be impurities present on the surface of the material. The technique mentioned above is suitable to

determine the critical temperature. Values of T_c are found to be 520 K for copper and 550 K for the alloy 304 stainless steel. The reduction of erosion yield due to the formation of cone structures is also measured. The erosion yield of copper when the cone surface is fully developed is found to be a factor of two less than that of a fresh, smooth surface. This is consistent with earlier results [3, 4]. Sputtering yield measurements using the ion beam technique has been carried out for both the smooth and cone-modified surface. The results agree with the spectroscopic determination. The reduction of yield for stainless steel is found to be about 40%. When the plasma flux is reduced, the rate of erosion yield reduction is also reduced, suggesting a flux dependence of the rate of cone formation. However, a temperature dependence cannot be ruled out.

It is clear from these results that the in-situ erosion yield measurement is sensitive to and tracks with the surface morphology modification. When coupled with other surface analysis methods [16], this spectroscopic approach can be used to investigate the cone formation processes. The material surface can be characterized by in-situ monitoring up to a specific stage, after which the sample is removed to determine the distribution of surface cones concentration, height, and the impurity distribution using techniques such as scanning Auger microscopy, secondary ion mass spectroscopy, and scanning electron microscopy etc., to follow the formation processes.

Acknowledgment

We appreciate the contribution of the PISCES technical staff, especially K. Andrews and K. Sheedy for computer data acquisition and G. Gunner, V. Low, and T. Sketchly for PISCES machine maintenance. This research is supported by the U.S. Department of Energy under contract #DE-AS03-84ER52104.

References

1. D. Post and R. Behrisch, editors, 'Physics of Plasma-Wall Interactions in Controlled Fusion', Plenum Press, New York (1986).
2. D. M. Goebel, G. A. Campbell and R. W. Conn, *J. Nucl. Mater.*, 121 (1984) 277.
3. Y. Hirooka, D. M. Goebel, R. W. Conn, W. K. Leung and G. A. Campbell, *J. Nucl. Mater.*, 141-143 (1986) 193.
4. Y. Hirooka, D. M. Goebel, R. W. Conn, G. A. Campbell, W. K. Leung, et al., *Nucl. Instr. and Meth. in Phys. Research*, B23 (1987) 458.
5. D. M. Goebel, Y. Hirooka, R. W. Conn, W. K. Leung, G. A. Campbell, et al., *J. Nucl. Mater.*, 145-147 (1987) 61.
6. S. Morishita, Y. Fujimoyo and F. Gkuyama, *J. Vac. Sci. Technol.* A6 (1988) 217.
7. E. Hintz, D. Rusbueidt, B. Schweer, J. Bohdanský, J. Roth and A.P. Martinelli, *J. Nucl. Mater.*, 93&94 (1980) 656.
8. McWhirter, R. W. P, in 'Plasma Diagnostics Techniques', Ed. by Richard H. Huddleston and Stanley L. Leonard, Academic Press 1965.
9. H. Van Regemorter, *Astrophys. J.*, 136 (1962) 906.
10. R. Mewe, *Astron. Astrophys.*, 20 (1972) 215.
11. M. W. Thompson, *Phil. Mag.* 18 (1968) 377.
12. For example, J. Roth in 'Physics of Plasma-Wall Interactions in Controlled Fusion', D. E. Post and R. Behrisch, editors, Plenum Press, New York (1986).
13. W. Lotz, *Z. Physik* 220 (1969) 466.
14. W. K. Leung, B. LaBombard, R. W. Conn, Y. Hirooka, Y. J. Ra, G. Tynan, *Bull. Am. Phys. Soc.* 32 (1987) 1940, 9P3.
15. A. Guenther-Schulze and W. V. Tollmien, *Z. Phys.* 119 (1942) 685.
16. A. D. G. Stewart and M. W. Thompson, *J. Mater. Sci.* 4 (1969) 56.
17. I. H. Wilson, *Radiat. Eff.* 18 (1973) 95.
18. G. K. Wehner, *Appl. Phys. Lett.* 43 (1983) 366.
19. G. K. Wehner, *J. Vac. Sci. Technol.* A3 (1985) 183.
20. A. Auciello, *Radiat. Eff.* 60 (1982) 1.

Figure Captions

- Fig.1 An illustrative view of a sample eroded by plasma bombardment in the PISCE experiment. Plasma guided by an axial magnetic field uniformly illuminates the sample. Atoms sputtered from the same may escape or being ionized in the plasma depending upon plasma conditions. Ionized sputtered atoms can be redeposited onto the sample surface.
- Fig. 2 The experimental arrangement for the in-situ erosion yield measurement.
- Fig. 3. A plot of the normalized erosion yield as a function of ionization mean free path. The data are obtained for copper and 304 stainless steel. The ionization mean free path of iron is used for stainless steel. The erosion experiments are done using Ar, He and D plasmas.
- Fig. 4 The erosion yield measured by spectroscopy plotted against the erosion yield measured by weight loss for copper samples in an argon plasma. The ionization mean free path for copper is 12 cm
- Fig. 5 The erosion yield measured by spectroscopy plotted against the erosion yield measured by weight loss for 304 stainless steel samples in an argon plasma. Iron and chromium intensities are calibrated separately to the stainless steel weight loss. The ionization mean free path for chromium in this case is 8.5 cm.
- Fig. 6 The erosion factor of equation obtained by comparing the calibration factor at different ionization mean free paths for copper.
- Fig. 7 Scanning electron microscope pictures of a smooth and cone-covered surface of copper. Conditions for obtaining each surface are discussed in the text.
- Fig. 8. The erosion yield of a copper surface as a function of time and temperature. The on-set of cone formation correlates with the decrease in yield that begins at about 520 degree K.
- Fig. 9. The erosion yield of copper obtained by ion beam sputtering of smooth and cone-modified samples.
- Fig.10. The erosion yield of 304 stainless steel as a function of time and temperature. As with the results for copper shown in Fig. 8, the decrease in yield beginning at about 550 degree K surface temperature correlates with the on-set of cone formation.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Smooth

Cone

Fig. 8

Fig. 9

Fig. 10