CONF-850310--46

For presentation at the 6th Topical Meeting on the Technology of Fusion Energy, San Francisco, CA March 3-7, 1985.

CONF-850310--46

DE85 009740

SELF-SUSTAINING COATINGS FOR FUSION APPLICATIONS - COPPER LITHIUM ALLOYS*

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ABSTRACT

Dilute binary alloys have been discussed previously as a means of producing self-sustaining coatings for fusion applications. The anticipated advantages of such coatings are described in a companion paper.[11] Issues addressed in this paper concern experimental observation of the formation of a low-Z coating by solute segregation in a Cu-Li alloy, maintenance of the coating in a sputtering environment, and a comparison of the calculated net erosion for W, Mo, and Cu-Li when used as either the divertor plate or the bottom limiter for INTOR.

Auger electron spectroscopy has been used to monitor the surface composition of an alloy consisting of 3.0 at.% Li in Cu while sputtering with 1-3 keV Ar^+ or He^+ at a flux of 10^{12} - 10^{14} cm^{-2} sec^{-1} (corresponding to a gross erosion rate of several mm/yr) at temperatures up to 430°C. It is found that the alloy is capable of reproducibly maintaining a complete lithium overlayer. The time-dependent thickness of the overlayer depends strongly on the mass and energy spectrum of the incident particle flux. It has been experimentally demonstrated that a significant fraction of the sputtered lithium is in the form Li^+ and is returned to the surface by an electric field such as the sheath potential at the limiter, or a tangential magnetic field such as the toroidal field at the first wall; consequently, the overlayer lifetime is essentially unlimited.

The TRIM computer code has been used to calculate the sputtering yield for pure metals and the partial sputtering yields of binary alloy components for various assumed solute concentration profiles. It is found that even with very low-Z coatings, the majority of the sputtered atoms originate in the uppermost atomic layer and that the partial sputtering yield of an alloy component is significantly reduced if that component is excluded from the uppermost atomic layer. It is predicted that the self-sputtering behavior of Cu-Li when used as a limiter or divertor plate will compare very favorably with that of tungsten.

Calculations using the REDEP code bear out this expectation. At low plasma edge temperatures (< 50 eV), the net erosion (erosion minus redeposition) due to D,T,He and self-sputtering is nearly zero, while the gross erosion is less than that of Mo. For edge temperatures > 50 eV, W, and Mo are unusable due to self-sputtering. It is calculated that in the intermediate edge temperature regime (50-200 eV), a limiter made of copper with a lithium coating 1.5 monolayers thick would show net growth or erosion of < 3 mm per year. Consequently, Cu-Li alloy may be the only material suitable for use with intermediate plasma edge temperatures.

INTRODUCTION

The use of low-Z plasma side materials provides a potentially effective means of reducing plasma contamination arising from the erosion of first wall and limiter surfaces by light ion impact, and of suppressing potentially disastrous effects of runaway self-sputtering of limiters and divertors. However, for reactor use, the thermal and mechanical properties of most low-Z materials require that they be used as a coating or cladding on an actively cooled substrate. Cooling requirements and the need for thermal shock resistance dictate that the coating be thin. Gross erosion and redeposition rates on the order of 100-1000 cm/yr, however, dictate the use of thick coatings for mechanical stability and adequate operating life.

The concept of using very thin self-sustaining coatings as a means of meeting these

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*Work performed under the auspices of the Division of Magnetic Fusion Energy, U.S. Department of Energy.

requirements has been described previously.[1-11] In brief, the concept utilizes the radiation environment and elevated temperature of a fusion device as a means of promoting the segregation of the minority component of a dilute alloy to the surface. The segregated material, by the manner in which it is formed, does not accumulate to very great thickness, but is continuously replenished as surface material is lost. Only atoms originating in the first 1-2 atomic layers are sputtered.[8,11] Consequently, a low-Z coating only 1-2 monolayers thick is sufficient to greatly reduce the erosion of the high-Z alloy component. By choosing the alloy in such a way as to guarantee that the low-Z component sputters primarily as a secondary ion, the loss of surface material can be minimized since secondary ions are trapped at the surface by the sheath potential[1,2] at limiter and divertor surfaces, and by the toroidal magnetic field at the first wall.

It has been predicted[5] and experimentally observed that lithium segregates very strongly in copper alloys[4,5] and forms a stable overlayer in a sputtering environment. The effects of Gibbsian segregation, preferential sputtering, radiation-induced segregation, radiation-enhanced diffusion, and cascade mixing on the near-surface lithium concentration profile have been calculated,[9] and it is predicted that the stability of the surface layer depends strongly on the sample temperature and on the mass and energy distribution of the projectile particles.

For 1-3 keV Ar^+ bombardment, it has been determined by Auger spectroscopy that it is possible to maintain a stable lithium overlayer while sputtering. The required temperature is, however, highly flux dependent. At a flux of 7×10^{11} Ar^+ cm^{-2} sec^{-1}, a temperature of 140°C is sufficient to maintain the lithium overlayer.[5] At a flux of 4×10^{12} Ar^+ cm^{-2} sec^{-1}, the lithium surface is rapidly depleted at 140°C but can be maintained at 230°C.[7] At an Ar^+ flux of 2×10^{14} cm^{-2} sec^{-1}, it is possible to maintain the lithium overlayer at temperatures > 300°C.

If, however, an electric field is applied to the sample to simulate the effect of the sheath potential, it is possible to maintain the overlayer at significantly lower temperatures as a result of Li^+ trapping. For high flux, light ion bombardment, preliminary experiments[12] indicate that when lithium secondary ions are electrostatically trapped, a lithium overlayer sufficient to significantly inhibit the erosion of copper can be maintained for at least several hours under 100 eV He^+ bombardment at a flux of 1×10^{17} cm^{-2} sec^{-1}.

It is the purpose of the present paper to examine the thickness of the lithium overlayer formed during light ion bombardment and to obtain a measure of the charge state of the sputtered lithium atoms. The results are compared with previous data for Ar^+ bombardment and interpreted in terms of the expected behavior of a Cu-Li alloy limiter for INTOR, based on the use of the TRIM computer code to predict the sputtering properties and the REDEP code to model the erosion and redeposition behavior.

EXPERIMENTAL

The Cu-Li samples were prepared in two steps, the first of which has been described elsewhere,[4] and results in the formation of a high lithium concentration alloy. The second step consists of arc melting this material with additional copper to produce the desired lithium concentration. Typically, little or no lithium is lost during the repeated arc melting steps used to insure uniformity. More recently, larger samples have been produced by heating copper-lithium ingots to 1100°C for one-half hour, also with negligible lithium loss.

Once prepared, the material is rolled or cut into a disk of the desired diameter and mounted in a UHV surface analysis system, also described elsewhere.[4]

RESULTS

The lithium surface concentration of a Cu-3 at.% Li sample was determined by the ratio of the peak-peak heights of the Li(KLL) and Cu(MNN) Auger lines. This ratio is shown in Fig. 1 as a function of elapsed time. The sample was subjected to a continuous 3 keV He^+ bombardment at a flux of 1.1×10^{14} cm^{-2} sec^{-1}. Initially, the sample was at room temperature. At the time indicated by the arrow, the sample heater was turned on and the sample temperature rose to 290°C in about 15 minutes. The surface lithium concentration rose more slowly, reaching a peak after about 40 minutes and then decreasing to a level near the original value.

This behavior is in marked contrast to the previously reported results for Ar^+ bombardment[7] but is qualitatively consistent with the expectation that for a solid alloy the steady state surface concentration is determined by the preferential sputtering condition:

$$C_A{}^1/C_B{}^1 = C_A\, S_B{}^*/C_B S_A{}^* \qquad (1)$$

where C_A, C_B are the bulk concentrations of the alloy components; $C_A{}^1$, $C_B{}^1$, are the first layer atom fractions of A and B; and S_A^* and S_B^* are the effective sputtering yields of species A and B. If a fraction β^+_A of species A is sputtered as a secondary ion, then in the presence of an external electric or magnetic field,

$$S_A^* = (1-\gamma\beta_A^+)S_A \qquad (2)$$

where γ is the efficiency with which ions are trapped by the field and S_A is the sputtering yield for species A in the alloy. If A and B differ greatly in mass, as is the case for copper and lithium, S_A and S_B may be significantly different from the yield expected for pure elements. In the absence of any external fields, the steady state surface lithium concentration predicted by Eq. 1 is ~8%, while the second layer lithium concentration is expected to be much lower.[5] If as a result of radiation-induced segregation, the subsurface lithium increases as calculated to a level sufficient to cause precipitation of a Cu-Li compound, then Eq. 1 would not correctly predict the first layer lithium concentration. It has been pointed out previously[6] that there is experimental evidence suggesting the formation of a subsurface compound. The Cu(MNN) 920 eV Auger line was chosen for analysis rather than the 61 eV Cu(LMM) line because it is not as sensitive to chemical effects.

However, the mean free path for the Cu(MNN) Auger electron is 10 Å, compared with 4 Å for the Li(KLL) electron. In order to interpret the Auger data in terms of surface lithium concentration, it is necessary to specify the shape of the lithium concentration profile. We have interpreted the data of Fig. 1 in terms of two assumed concentration profiles, using elemental sensitivity values obtained from standard tables.[13] In the surface layer model, the lithium is assumed to be present as an overlayer of specified thickness on top of a pure copper substrate. In the uniform concentration model, the lithium is assumed to be distributed uniformly throughout the Auger sampling depth. The steady state lithium concentration represented by the data of Fig. 1 corresponds to 20% if interpreted on the basis of the uniform concentration model, or to 0.6 monolayers in the overlayer model. The dashed line represents the Li(KLL)/Cu(MNN) Auger signal ratio for one monolayer of lithium on a copper substrate. In either model, the surface lithium concentration is significantly greater than specified by Eq. 1.

The ratio of the lithium secondary ion signal to the intensity of the lithium Auger line represents a measure of the relative lithium secondary ion fraction, β_{rel}^+. The ratio is plotted in Fig. 2 versus the surface lithium concentration obtained from the Auger data in terms of the overlayer model. X-ray diffraction data for Cu-Li by Klemm and Volavsek[14] indicate that lithium undergoes charge exchange with the copper and is present in a partly ionized state. As the lithium concentration increases, it is expected[15] that the repulsive dipole-dipole interaction will result in depolarization of the lithium, with a consequent decrease in the lithium secondary ion fraction, in accord with the data shown in Fig. 2. The absolute magnitude of the lithium secondary ion yield is not known and β^+_{rel} is normalized to unity at low surface lithium concentration.

When a 45 V bias is applied to the sample, a strong lithium Auger line is still seen, but the steeply rising background of secondary electrons makes quantitative analysis of the Auger data difficult. The bias results in the trapping of about 97% of the secondary ions. The remaining 3% which escape because of irregularities in the electric field geometry are sufficient to permit surface analysis by secondary ion mass spectroscopy (SIMS). The SIMS data qualitatively follow the Auger data in that an increase or decrease in the lithium signal obtained by one technique is matched by a similar response in the signal obtained by the other technique.

The Li^+/Cu^+ ratio is shown as a function of elapsed time in Fig. 3. The two curves represent the SIMS data with (▲) and without (●) applied bias. The samples were initially at room temperature, and the sample heater was turned on at time indicated by the arrows. The ultimate temperature was 290°C. The data are scaled to match at the peak.

In the absence of an external electric field, the lithium SIMS data exhibit the same behavior as the Auger signal, rising to a peak as the sample is heated and then dropping to a steady-state value. When a bias is applied to the sample and the sample is heated, the SIMS signal rises sharply and again drops. However, this drop in signal is very slight, followed by a slow increase in the Li^+ yield. This gradual increase in the Li^+ yield is not reversible by cooling and appears to be associated with a surface phase transformation.[6] This behavior is similar to that previously reported for Ar^+ bombardment and is attributed to the formation of a subsurface region of high lithium concentration and subsequent change of phase. The principal difference between He^+ and Ar^+ bombardment is that it takes longer for the phase change to occur, probably as the result of the greater damage depth for light ion impact.

IMPLICATIONS

Many of the key parameters affecting the sputtering properties of a Cu-Li alloy in a divertor or limiter application depend on the amount and depth distribution of the segregated lithium. If the lithium resides primarily on the surface, a thicker overlayer results in reduced copper erosion, as shown in Fig. 2 of Ref. 11, although there is little benefit expected for lithium layers thicker than two monolayers. The calculated copper erosion rate is reduced by more than one order of magnitude for a lithium thickness of only 1.25 monolayers. As the thickness increases, however, it is expected that the number of atoms comprising a monolayer will decrease and that the lithium secondary ion fraction will also decrease, in accord with the experimental results of Fig. 2. Consequently, lithium will be lost at a greater rate. A determination of the steady-state lithium surface concentration and absolute lithium secondary ion yield under various bombardment conditions is necessary for a definitive calculation of the performance of Cu-Li alloy in a fusion reactor environment. This information will be provided by an experiment under development in our laboratory. It has been determined by preliminary weight loss measurements,[12] however, that enough lithium can be retained at the surface to substantially reduce the sample erosion relative to that of pure copper, even for 100 eV He^+ fluxes in excess of 1×10^{17} cm^{-2} sec^{-1}.

Calculations based on a range of parameters consistent with experimental results and theoretical expectations have been made using the computer code TRIM to calculate the copper and lithium sputtering yields for various lithium concentration values and depth profiles. The REDEP code has been used to calculate the gross and net erosion (erosion minus redeposition) rates for a model material consisting of 1.5 monolayers of lithium on a copper substrate, assuming a Li^+ fraction of 0.9, in accord with thermal evaporation data.[16] The copper self-sputtering yield as calculated by TRIM for a pure copper surface is ~5x higher than for the Cu-Li model system.[11] Similar results hold for the light ion sputtering behavior.[10] At normal incidence the threshold for runaway self-sputtering of pure copper is 340 eV; for the model Cu-Li system, this value is 3400 eV.[9,11]

The calculated sputtering yields provide input for the REDEP code.[10] The results are presented in Fig. 4 for a design based on the INTOR limiter for a plasma edge temperature of 100 eV. The gross erosion (redeposition not included) for light ion and self-sputtering combined is in the range 10-20 cm/yr, well below the comparable values for low-Z materials. Tungsten is completely unusable at this edge temperature due to self-sputtering. When redeposition is considered, there is almost no net change in limiter thickness. At lower edge temperatures (20-50 eV) appropriate for divertor applications, the copper-lithium system still performs well and represents one of the few alternatives to tungsten (Table I).

Table I. INTOR Divertor REDEP Analysis

Plate Coating Material	Plasma Edge Temperature (At Separatrix) (eV)	Gross Sputtering Rate at Divertor Center Due to DT + He cm/yr	Total Gross Sputtering Rate at Divertor Center cm/yr	Net Erosion Rate at Divertor Center cm/yr
Beryllium	20	382	682	14.0
	30	313	688	9.1
	40	256	666	5.4
	50	212	624	4.1
Titanium	20	134	266	.025
	30	190	658	.036
	40	225	2750	.42
Molybdenum	20	12	21	~0
	30	25	64	~0
	40	31	142	~0
Tungsten	20	0.07	0	~0
	30	0.40	1.1	~0
	40	0.57	3.1	~0
	45	1.3	13.7	~0
Copper - 1.5 ML Li	30	35	42	0

The maximum calculated plasma edge temperature for which Cu-Li can be used as a limiter material depends on the actual value of β^+_{Li}, as shown in Fig. 5. The calculated performance is clearly superior to that of tungsten provided that $\beta^+_{Li} > 0.6$.

SUMMARY

It has been experimentally demonstrated that dilute alloys of lithium in copper are capable of producing a self-sustaining low-Z coating during both medium-Z and low-Z ion bombardment, although there are qualitative differences in the time evolution and possibly in the steady-state coating thickness. Preliminary measurements of the steady state thickness and secondary ion fraction of the low-Z alloy component have been made for 3 keV He^+ sputtering, but more precise values are needed.

Representative values of the layer thickness and lithium secondary ion fraction have been used to calculate the erosion and redeposition properties of copper-lithium alloy used as a limiter or divertor for INTOR, and it is calculated that Cu-Li alloy should have the low sputtering rates for light ion impact which are characteristic of high-Z materials but should be usable at significantly higher plasma edge temperatures than tungsten.

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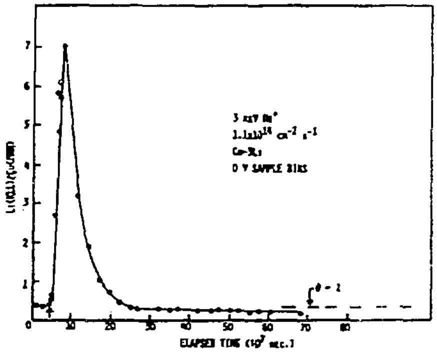

Fig. 1. Ratio of Li(KLL) to Cu([illegible]) peak-to-peak Auger signal vs. elapsed time. The dotted line represents the signal expected for 1 monolayer of lithium on a copper substrate. Sample heater turned on at arrow.

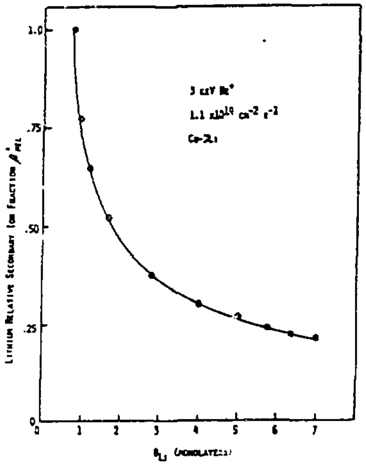

Fig. 2. Relative secondary ion fraction β^+_{rel} for sputtered lithium vs. lithium surface concentration. β^+_{rel} is normalized to unity at low lithium concentration.

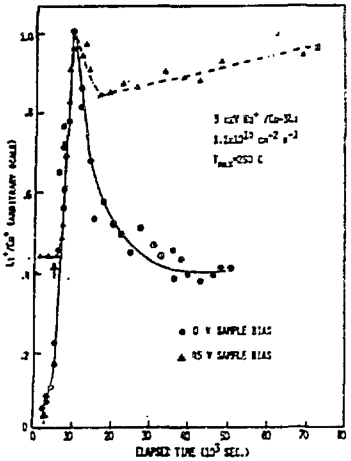

Fig. 3. Ratio of Li^+/Cu^+ SIMS intensities vs. elapsed time. (Δ) represents data taken with [illegible], and (●) represents taken in the absence of sample bias. The intensities are scaled to match at the maximum occurring immediately after heating starts (arrow).

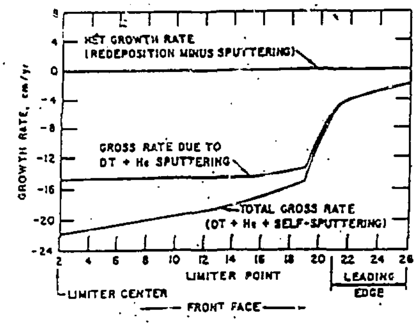

Fig. 4. REDEP calculation for INTOR limiter, T_o = 100 eV, copper coated with 1.5 ML Li.

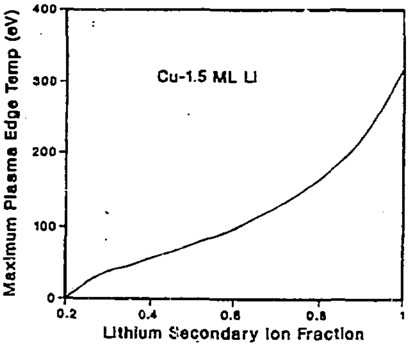

Fig. 5. Maximum plasma edge temperature vs. lithium secondary ion fraction