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SPUTTERING PROPERTIES OF COPPER-LITHIUM ALLOYS
AT REACTOR-LEVEL TEMPERATURES AND SURFACE EROSION RATES*

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Previous experiments on copper-lithium alloys at temperatures up to 250°C and with erosion rates of .01-.1 monolayer per second have shown that in the electric and magnetic field environment of a magnetic-confinement fusion reactor, it is possible to maintain a lithium over-layer which will significantly reduce the copper erosion rate. We have extended these experiments to the reactor-relevant regime of 350-400°C, with erosion rates approaching one monolayer per second. By comparison with the lower flux experiments, it is found that radiation damage effects start to dominate both the surface concentration and depth profile of the lithium. The subsurface region of enhanced lithium concentration is broadened, while the surface concentration is not

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depleted as rapidly per incident ion as in the low flux case. The time-dependent lithium depth profile is calculated using a computer code developed at Argonne which includes both Gibbsian segregation and radiation-induced effects. The experimental results are compared with these calculations. It is found that the sputtering behavior of the copper-lithium alloy is highly dependent on the mass and energy spectrum of the incident particles, the sample temperature, subsurface structure, and the partial sputtering yields of the alloy components.

INTRODUCTION

Because of its high thermal conductivity, copper is considered a likely material for high-heat-flux applications; for instance, as a Tokamak limiter. The sputtering yield of copper, however, is unacceptably high; in particular, the self-sputtering yield reaches unity at about 330 eV [1,2]. Assuming that the sputtered copper re-emerges from the plasma with a charge state of +3, it is expected that a self-sputtering cascade would occur with an edge temperature as low as ~ 30 eV [3]. Consequently, the copper must be coated, preferably with a low-Z material. The requirements of this coating are very stringent: (1) The coating must have a very long lifetime until depletion. (2) Regeneration procedures must be relatively simple and preferably performed in-situ. (3) The surface of the coating must have good thermal contact with the copper substrate, and the coating should therefore resist building up arbitrarily thick layers. (4) The interface should not be subject to thermal shock failure or act as a sink for accumulated gases. In order to meet these requirements, we have proposed the use of a dilute alloy of lithium in copper [4-8].

It was predicted by Gibbs [9] that, at thermodynamic equilibrium, the surface composition of a binary alloy corresponds to the lowest possible surface free energy. It can be calculated using, for instance, the model of Williams and Nason [10] or that of Miedema [11,12] that for Cu-Li, which forms a solid solution at lithium concentrations < 18 at.% [13], thermodynamic equilibrium corresponds to a surface consisting almost entirely of lithium [8]. The rate at which the equilibrium surface composition is approached increases directly with temperature, but because of increasing back-diffusion, the equilibrium concentration of the segregating species decreases at higher temperatures. For temperatures appropriate to copper in a fusion environment (300-400°C), it is predicted that the surface concentration of Li in a dilute Cu-Li alloy exceeds 95 at.%. In principle, therefore, we have identified a means of producing a low-Z coating which is self-sustaining and self-limiting, provides exceptionally low thermal resistivity to the substrate, and avoids thermal mismatch and gas accumulation at the interface.

In a radiation environment, a number of competing processes determine the surface composition [14,15]; preferential sputtering and displacement mixing tend to deplete the dominant surface species. Radiation-enhanced diffusion does not alter the thermodynamic driving force but strongly increases the diffusion coefficient of the alloy components. Radiation-induced segregation, i.e., the preferential coupling of one of the alloy components with mobile point defects, can either enhance or diminish the surface concentration of the segregating species.

A number of key issues must, therefore, be addressed in order to determine the usefulness of this means of producing self-sustaining low-Z coatings:

(1) Formation rate and completeness of the overlayer: These factors are strongly influenced by the temperature, sputtering rate, and damage profile.

(2) Thickness and structure of the overlayer and corresponding degree of substrate protection: If the low-Z overlayer is only one atomic layer thick (as predicted for the thermal process), the surface binding energy will be greater than that of elemental Li, and the low-Z sputtering yield will be correspondingly reduced [16]. However, such a thin layer may not provide adequate protection of the substrate. If the lithium overlayer is several atomic layers thick, it will behave like bulk lithium rather than as an adsorbed overlayer and will evaporate quickly at elevated temperatures. If the lithium has a concentration gradient as a function of depth, the sputtering yield of both lithium and copper atoms originating in a given atomic layer will depend strongly on the atomic composition of the immediately adjacent layers [17].

(3) Bulk depletion rate due to thermal loss and preferential sputtering.

(4) Self-sputtering properties.

(5) Mechanical properties such as tensile strength and hardness must be determined both for the as-prepared material and, after continued irradiation and thermal cycling, possibly resulting in grain boundary cracking, has occurred.

(6) Neutronics: The mechanical properties of this material, after prolonged neutron irradiation, are unknown. The tritium build-up within the material has been estimated and does not appear to represent a serious problem.

Items 1-4 are addressed in this paper both on a theoretical basis and experimentally, for temperatures ranging up to 430°C, with monolayer removal rates up to 0.4 layers per second.

EXPERIMENTAL

Samples of Cu-2.6 at.% Li weighing up to 25 grams have been prepared by first reacting copper and lithium in an argon atmosphere to form Cu_4Li , and then arc melting the product with additional copper to form the dilute alloy [6]. The pellet was re-melted a total of four times to guarantee uniformity. The amount of lithium lost during arc melting has been found to be negligible provided that the Cu_4Li is wrapped in the additional copper. The resulting pellet was sliced and pressed between polished dies to produce a foil ~ 0.5 mm thick and 6 mm dia. The sample was mounted on a heatable stage and placed in a bakeable metal vacuum system with a base pressure of $1-2 \times 10^{-10}$ Torr. The surface composition was analyzed by Auger spectroscopy while the sample was being sputtered. The temperature was varied step-wise between room temperature and 430°C. The primary ion beam consisted of 1.5 keV Ar^+ at a flux of $2.1 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$. With a sputtering yield of 3.5 for copper [2], this flux corresponds to a removal rate of 2.6 seconds per monolayer.

The Li(KLL), Cu(LMM), and Cu(MNN) Auger lines were repetitively scanned and data was stored in an LSI11/23 computer. Data presented

here represent the peak-peak amplitude of the Auger lines. The Li(KLL) and Cu(MNN) Auger transitions represent 41 and 58 eV electrons, respectively, with a corresponding electron mean free path of 4 Å. The Cu(LMM) line corresponds to a 920 eV electron with a 10 Å mean free path.

RESULTS

The sample temperature was ramped repeatedly over a range between room temperature and 430°C over a period of six weeks. For about half this period, it was subject to irradiation by a beam of 1.5 keV Ar⁺ at a flux of 2.1×10^{14} ions/cm² sec. The relative Auger signal strengths at thermal equilibrium (ion beam off) are shown in Figure 1 for lithium and copper as a function of temperature for a sample containing 2.6 at.% bulk lithium concentration. The surface lithium concentration is strongly enhanced, in qualitative agreement with the Gibbsian process. The Cu(MNN)/Cu(LMM) Auger peak ratio derived from Figure 1 does not correspond to that of pure copper, and the lithium/copper signal ratio is higher than expected for a single atomic layer of lithium, indicating an interaction between the lithium and copper conduction bands. The temperature at which back-diffusion appears to become significant is lower than predicted [8]. It should be noted however, that Figure 1 represents a composite of six scans through a temperature range from room temperature to 430°C, and that the surface composition was reproducible at a given temperature over a period of several weeks. Subsequent analysis by atomic absorption spectroscopy showed no measurable change in the bulk lithium concentration.

When the ion beam is turned on, it is expected that the lithium depth concentration will change from that represented in Figure 2A, i.e. a highly enriched first atomic layer and relatively dilute lithium concentration in subsequent layers, to something closer to that of Figure 2B. Preferential sputtering will erode the topmost layer, depleting the surface lithium, while recoil mixing will result in increased subsurface lithium concentration. Experimental results consistent with this picture have been reported for Al-Li alloys sputtered at room temperature [6]. It was found in that experiment that the initial rate of lithium depletion corresponded exactly to the sputtering yield predicted by the TRIM computer program for a single atomic layer of Li on Al. Previously reported experimental results [7] for the depletion of lithium on the surface of a Cu-Li alloy undergoing irradiation by 3 keV Ar^+ at a flux of 3.6×10^{12} ions/cm², and a temperature of 140 C are presented in Figure 3. The slope of the linear portion of the semi-log plot can be interpreted in terms of an effective desorption cross-section, $\sigma_d^{eff} = 5.5 \times 10^{-17}$ cm². Use of a higher ion beam flux resulted in a correspondingly shorter depletion time at that temperature.

The effective desorption cross section, however, corresponds to a sputtering yield about 50 times smaller than that calculated by TRIM. This result was explained in terms of simultaneous replenishment of the sputtered lithium, a conclusion which was reinforced by the fact that the application of an electrostatic potential to the sample in emulation of the sheath potential at the limiter resulted in the return of sufficient lithium sputtered as secondary ions to the surface to completely eliminate the observed lithium depletion.

Figure 4 shows similar data for sputtering by 1.5 keV Ar^+ at a flux of 2.1×10^{14} ions/cm². The sample temperature was increased stepwise and reached thermal equilibrium usually by the time the second data point was collected. The horizontal axis represents the product of the Ar^+ flux and the time elapsed since the temperature step. The vertical axis represents the $\text{Li}(\text{KLL})/\text{Cu}(\text{MNN})$ signal ratio. At 230°C, the surface lithium concentration is decreasing with time but at a rate which corresponds to an effective sputtering yield 3.1×10^4 times smaller than the calculated sputtering yield. At 260°C the surface lithium is still decreasing but at an even slower rate. At 290°C and 320°C the surface lithium concentration is increasing with time. The exact concentration of lithium is not known because of the previously discussed mixing of copper and lithium electronic states and because, although the mean free path of the Auger electrons is only 4 Å, there is some contribution to the signal from the second, third and fourth atomic layers, and the depth profile of the lithium distribution is unknown. If it is assumed that the lithium concentration is constant over the depth sampled, and the published Auger atomic sensitivity factors are used [18], the observed equilibrium signal intensity at 320°C corresponds to a lithium concentration of 94 at.%. As shown in Figure 4, the application of an electrostatic bias to the sample further increases the surface lithium concentration and maintains it at this value for an extended period of time. However, the Li concentration at 320°C was already so high that the effect is not as significant as it was at 140°C (Figure 3).

DISCUSSION

The general features of the experimental data can be understood in terms of computer calculations using the TRIM [19] code as modified by DeWald [20] to simulate sputtering from multi-component, multi-layer materials, and the Johnson-Lam model for synergistic processes in segregating alloys [15]. A number of details involved in the calculation are not yet fully resolved and a more thorough discussion is presented elsewhere [17]. A brief outline of the results is presented here to enable comparison between the experimental results and the general trends of the calculations.

At time $t=0$, it is assumed in the calculation that the lithium profile corresponds to that of Gibbsian segregation. As the surface and subsurface composition changes with time, the partial sputtering yields of lithium and copper change and may differ significantly from the yields for elemental lithium and copper [17,22]. For example, the sputtering yield for 3 keV Ar^+ on lithium is 0.68 and the yield for 3 keV Ar^+ on copper is 3.98. The lithium yield for 3 keV argon ions incident on a mono-layer of lithium on a substrate consisting of 97.4 at.% copper and 2.6 at.% lithium is 3.5. The sputtering yields are calculated by TRIM and the profile is allowed to evolve under the influence of the various processes described in the introduction. At each time step, the partial sputtering yields are recalculated according to the current concentration profile. Results of a typical calculation are presented in Figure 5 for 3 keV Ar^+ at a flux of 3.1×10^{13} ions/cm². Initially, the first layer lithium concentration decreases at a rate determined by the partial sputtering yield of a lithium monolayer on a substrate consisting of the bulk composition. Lithium from the

second and third layers flows to the surface to replace the sputtered surface lithium, producing a region of subsurface lithium depletion. Further down, at the region of peak displacement damage, radiation-induced segregation quickly establishes a lithium-enriched region which then spreads toward the surface, producing significant lithium enrichment in the near-surface layers. When this region crosses the surface, the first layer lithium concentration starts to increase. The time required for the turn-around depends on the incident particle flux, damage profile and peak damage rate. The extent of surface depletion before the turn-around depends on temperature. In the example of Figure 5, the first layer lithium concentration reaches a minimum value of 0.26 at about 40 seconds and then increases to 0.8 monolayers.

The expected Li-Cu Auger peak ratios for another set of calculations are presented in Figure 6. At 140°C, the surface lithium is strongly depleted while the region of peak displacement damage shows strong lithium enrichment. In reality the model would break down in this region because precipitation of a Cu_4Li phase would occur. It should be noted, however, that the existence of compound formation at low temperature was inferred from an experimental study of the $\text{Cu(LMM)}/\text{Cu(MNN)}$ Auger peak ratios [7].

At 400 C, the calculation shows little depletion in the first atomic layer with time, and a slight increase with time of the subsurface lithium concentration over an extended depth. As a result, the lithium-copper Auger signal ratio shows a net increase with time as is in fact observed experimentally at high temperature. The calculational result that at high temperature the surface lithium concentration is only negligibly less than the Gibbsian value is also consistent with the

experimental observation that biasing the sample to insure the return of lithium secondary ions has a much smaller effect on the measured lithium concentration than at low temperature.

The second layer lithium concentration may, as shown in Figure 5, be relatively insignificant compared with the first layer concentration. In the latter case it is important to determine the extent to which an essentially mono-atomic layer of lithium can reduce the erosion rate of the primarily copper substrate. This question can be answered by use of TRIM provided that the absolute number of lithium atoms in a monolayer is known, or equivalently that the atomic radius of lithium in the alloy is known. It was assumed in earlier publications [7,8] that surface lithium would have the same atomic radius as elemental lithium. However, X-ray diffraction experiments on copper-lithium alloys by Klemm and Volavšek [13] indicate that the atomic radius of lithium is much smaller than that of elemental lithium, being quite close to that of copper which it replaces in the lattice. It was assumed for the purpose of the present calculation that lithium on the surface of the alloy had the same atomic radius as copper, corresponding to a number density of 1.93×10^{15} atoms/cm². The most serious problem corresponds to the condition in which a significant fraction of the sputtered atoms originate in the second and third atomic layers, i.e., sputtering by high energy heavy particles [21]. The situation for self-sputtering by Cu⁺ incident on a lithium overlayer one atom thick on a copper substrate vs. that of Cu⁺ incident on pure copper as calculated by TRIM is shown in Figure 6. For the pure copper, the self-sputtering yield exceeds unity and a runaway condition occurs if the Cu⁺ kinetic energy exceeds 340 eV. For the lithium overlayer, the condition $S_{Cu} = 1$

does not occur until the incident copper ion has a kinetic energy of 1500 eV. The self-sputtering problem is, therefore, considerably reduced. For light ion sputtering, a lithium overlayer reduces the expected copper erosion by a factor of 6, e.g., for 200 eV He^+ bombardment.

SUMMARY

It has been experimentally demonstrated that at temperatures appropriate for copper alloys used as a high heat flux component in a fusion reactor (300-400°C), Cu-2.6 at.% Li is thermally stable over an extended period of time and is capable of reproducibly maintaining an overlayer consisting of nearly pure lithium. Up to at least this temperature range, it is found that unlike the purely thermal case sputtering at rates comparable to those anticipated for a fusion reactor results in increasing surface concentration of lithium with increasing temperature. Qualitative features of the experimental results are explained by computer simulations which indicate that radiation-induced segregation plays a key role in maintaining the lithium overlayer. It is predicted that, depending on the projectile mass and energy, erosion of the copper should be significantly reduced compared with pure copper. The ability to maintain the lithium overlayer would appear to be limited only by depletion of the bulk lithium inventory by means of preferential sputtering but not by evaporative loss. The loss of material would, however, be limited in a reactor environment because a portion of the sputtered lithium is sputtered as secondary ions which would be returned to the emitting surface as a result of the sheath potential [22]. This effect also serves to increase the resulting surface lithium concentration although it is not as necessary for this purpose as it is at lower temperatures.

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Figure Captions

1. Peak-peak signal for the Li(KLL), Cu(LMM) and Cu(MNN) Auger transitions (arbitrary units). The data represent 6 scans between room temperature and 430°C over a period of three weeks without ion bombardment.
2. (a) Distribution of lithium (black atoms) characteristic of a dilute highly segregating alloy. The lithium constitutes most of the first atomic layer but has the bulk concentration in the second and subsequent layers.
 (b) Distribution of lithium under the influence of sputtering. Preferential sputtering depletes the surface concentration while cascade mixing and radiation-induced segregation increase the subsurface concentration.
3. Lithium Auger signal (arbitrary units) vs. fluence (flux x time) for Cu-2.6 at.% Li at 140°C. 3 keV Ar⁺, $\phi = 5.5 \times 10^{12} \text{ cm}^{-2} \text{ sec}$. The straight line portion corresponds to $\sigma_d^{\text{eff}} = 5.5 \times 10^{-17} \text{ cm}^2$.
4. Li(KLL)/Cu(MNN) Auger signal ratio vs. fluence for Cu-2.6 at.% Li at 230°C (∇), 260°C (Δ), 290°C ($\square$), and 320°C ($\circ$) 1.5 keV Ar⁺, $\phi = 2.1 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$. The 230°C data corresponds to $\sigma_d^{\text{eff}} = 5.9 \times 10^{-20} \text{ cm}^2$.
5. Calculated lithium concentration for the first several atomic layers vs. time for 3 keV Ar⁺ bombardment of Cu -2.6 at% Li. $\phi = 3.1 \times 10^{13} \text{ ions/cm}^2\text{-sec}$. The open circles indicate the first layer concentration assuming a sputtering yield equal to the calculated value of 3.5. The dashed line represents the bulk concentration.

6. Calculation of the expected lithium/copper Auger signal ratio vs. elapsed sputtering time at 140°C and 400°C. The boundary conditions assumed for these calculations are different from those assumed in the previous figure. See Ref. 17 for further discussion.
7. Calculated copper sputtering yield vs. kinetic energy for Cu^+ bombardment of pure Cu (○) and copper covered with a single atomic layer of lithium (△) (Fig. 2A). The intersection of the curves and the dashed line occurs at the kinetic energy at which a runaway self-sputtering cascade will occur.

A

B

Krauss et al Fig 4

Krauss et al Fig 6