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MODIFICATION OF ALLOY SURFACE COMPOSITION BY SEGREGATION PROCESSES AS A MEANS OF IMPURITY CONTROL IN FUSION DEVICES*

A. R. Krauss and D. M. Gruen
Chemistry Division
Argonne National Laboratory, Argonne, Illinois 60439

and

A. B. DeWald
Department of Nuclear Engineering
Georgia Institute of Technology
Atlanta, Georgia

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Abstract

The bulk properties required of materials to be used in fusion devices--tensile strength, swelling resistance, thermal conductivity, low induced activity, and high melting point are not generally compatible with the required surface properties of low Z and low chemical reactivity with hydrogen. Coatings have been suggested as a means of providing the necessary surface properties while preserving the requisite substrate properties. The coatings however, introduce new problems in terms of maintenance, thermal conductivity and mechanical integrity.

We are investigating the use of surface segregation in alloys as a means of producing low Z coatings which are self-sustaining in a reactor environment, present no thermal barrier to the substrate, and avoid mechanical problems associated with the interface region. Several candidate materials have emerged from our calculations, including alloys of copper, vanadium and

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tunsten. The segregation calculations, light and heavy ion sputtering properties and thermodynamic properties of these materials are presented. Calculations indicate that as little as one atomic layer of low Z material significantly reduces the substrate erosion for both light and heavy ion sputtering.

Experimental data on the degree of surface segregation and the rate at which the low Z component migrates to the surface are presented using dilute alloys of lithium in copper as a reference system. The long term stability of the overlayer is limited primarily by the rate at which radiation-enhanced diffusion can replace the eroded surface material. The radiation-enhanced process proceeds much more quickly than the purely thermodynamic process and depends on the damage profile, which in turn depends on the mass and energy spectrum of the incident radiation.

Introduction

The production of self-sustaining low Z coatings by means of segregation in binary alloys has been suggested by several authors [1-2]. The effectiveness of such an approach depends on a number of criteria including: (1) the degree of segregation of the low Z component, (2) the degree to which the low Z layer reduces the erosion of the higher Z substrate material, (3) the amount of low Z material introduced into the plasma, (4) the rate of segregation, and (5) the long term stability of the low Z layer in a reactor environment. These criteria are evaluated for three binary alloy systems and experimental data are presented for one of them.

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The degree of segregation actually occurring in a material in a fusion device environment is the result of a number of possibly competitive processes. Our experiments on the segregation of low Z alloy components in a relatively refractory higher Z matrix [3-4] indicate that the dominant mechanisms are Gibbsian (thermodynamic equilibrium) segregation and radiation-enhanced diffusion. The effect of the latter process in Cu-Li and Al-Li alloys appears principally to increase the diffusion rate associated with Gibbsian segregation. We therefore calculate the Gibbsian segregation as a first measure of likely candidate materials. More complete calculations are currently in progress using a model due to Lam [5] which includes the effects of Gibbsian segregation, radiation-enhanced diffusion, radiation-induced segregation, recoil mixing and preferential sputtering.

The surface concentration of the low Z alloy component at thermodynamic equilibrium is calculated by means of the Miedema model of binary alloys [6-7]. Results are shown in Figure 1 for W - 4 at% Be, V - 4 at% Al, and Cu - 4 at% Li. The values shown are the calculated concentration of the low Z component in the first atomic layer, based on the assumption that enrichment occurs only in the uppermost atomic layer. At the anticipated operating temperatures for each solvent metal in a fusion device environment, all three alloys indicate a very high degree of solute segregation.

The anticipated sputter-induced erosion can be calculated using a modified version of the TRIM computer code [9]. The modified program simulates the sputtering of a material in which the composition varies from one atomic layer to another. In the context of the Miedema model results for a very dilute alloy, it is assumed that the low Z component resides entirely in the first atomic layer. Figures 2-3 show the relative suppression in sputter-induced erosion of the high Z component of a material in which the

uppermost atomic layer contains varying amounts of the low Z constituent of the alloy. For 3 keV Ar^+ bombardment, the erosion of the high Z component is reduced by a factor of 2.45 for Cu-Li and 5.1 for V-Al. For low energy, light ion bombardment even less erosion of the high Z component occurs. The calculated erosion of V covered by a single atomic layer of Al is reduced by more than an order of magnitude, relative to that of bare vanadium for 200 eV He^+ bombardment. The erosion of the low Z alloy component in most cases approximates that of the pure high Z metal. We have in effect reduced the atomic number of the impurities while leaving the flux essentially unaltered. For the copper-lithium alloy, it should be noted that the work function of copper is almost the same as that of tungsten. Consequently it is to be expected that the ion fraction of lithium desorbed from a hot copper surface is nearly as high as lithium desorbed or sputtered from a hot tungsten surface [8]. A significant fraction of the sputtered lithium is therefore expected to occur in the form of secondary ions. As a result of the sheath potential at the limiter, and the toroidal magnetic field, secondary ions have a very low probability of entering the plasma [9-10]. Therefore the effective Li influx may be much lower than that indicated by Figure 2.

In a radiation environment it is not to be expected that solute enrichment will be restricted to the uppermost monolayer. In addition, the competition between various processes results in a dynamic equilibrium in which the surface and near-surface composition may differ markedly from the composition corresponding to thermodynamic equilibrium. Experiments have been carried out on Cu - 2.6 at% Li to determine the actual degree of Li segregation encountered during ion bombardment, the extent of the reduction of solvent erosion by sputtering, segregation rates, and factors determining the long term stability of the lithium surface layer.

Experimental

Copper-lithium alloy with a composition close to that of the compound Cu_4Li was prepared by wetting the copper with liquid lithium at elevated temperature in an inert atmosphere [4]. This material was subsequently mixed with pure copper and arc melted. Atomic absorption analysis indicated very low impurity concentrations, with an oxygen level less than 0.01 %. The pellet was then sliced and the slice was pressed between polished dies to form the sample. After degreasing, the sample was placed in a stainless steel ultra high vacuum system and the surface composition was monitored by Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) while the sample temperature and ion beam current density were varied. Long term stability of the ion beam current was achieved by feedback regulation of the internal pressure in the ionization region of a differentially pumped 5 kV ion gun. Detection stability for periods in excess of two weeks at a time was achieved by the use of pulse counting and computer-controlled data acquisition methods.

The lithium concentration at the surface of the sample was determined from the ratio of the peak-to-peak height of the 43 eV lithium Auger line to that of the 60 eV copper Auger line. Because of the low kinetic energy of these two lines, the data represent a sampling depth of less than 5 Å. TRIM calculations show that for the experimental conditions, in excess of 93% of the sputtered atoms were initially within 5 Å of the surface. The SIMS data therefore sample approximately the same depth as the Auger data. It was ascertained that the lithium secondary ion signal increased linearly with the lithium surface concentration as measured by AES over a concentration range of 5-80%. It was therefore assumed that the secondary ion yield remained

constant and that the secondary ion signal represented the sputtering rate over this range of surface concentration.

Results

After an initial room temperature sputter-cleaning to remove carbon and oxygen, no lithium Auger signal was discernible for the sample shown in Figure 4. SIMS, which has much greater sensitivity for alkali metals than does AES, did however detect a constant lithium signal. Upon turning on the sample heater (A) an immediate increase in the lithium secondary ion yield was observed. The Li^+ yield stabilized as soon as the temperature stabilized, at 132 C. The copper secondary ion signal exhibited a complementary behavior, decreasing as the lithium yield increased. Concurrently, a lithium signal appeared in the Auger spectrum, growing to a level corresponding to 62% of the surface composition.

Increasing the current density from 0.15 to 0.67 $\mu\text{A}/\text{cm}^2$ at the start of Figure 5 resulted in a decrease in the lithium secondary ion yield and a corresponding increase in the copper yield. Successive temperature increases indicated at A, B, and C in the Figure each resulted in rapid increase in the Li^+ yield and a corresponding decrease in the Cu^+ yield. After an extended period of sputtering at elevated temperature, the lithium overlayer became depleted and protection of the copper substrate decreased. This condition corresponds to a depletion of lithium in the near sub-surface region and not in the bulk lithium concentration. It is shown elsewhere [3,4] that radiation-enhanced diffusion produces a lithium-rich sub-surface region, extending to a depth roughly equal to the damage profile. This sub-surface region acts as a reservoir of lithium which can quickly come to the surface to

replace sputtered material. When the reservoir is depleted the equilibrium concentration of lithium at the surface decreases.

Upon turning the ion beam off, the lithium rich surface is restored. As shown in Figure 6, several hours are required at 134 C to restore the overlayer. When the ion beam is turned back on, it again requires several hours to deplete the surface, although material is then being removed from the surface at a rate of approximately twenty seconds per monolayer. Consequently it is concluded that the rate at which lithium diffuses to the surface is several orders of magnitude higher when the sample is undergoing ion bombardment.

It is well known that lithium is thermally desorbed from a hot tungsten surface principally as Li^+ . Since copper and tungsten have nearly the same work function, it is expected that a similarly high ion fraction will be encountered for the desorption of lithium from copper. It has been demonstrated [11] that the application of a negative electrostatic bias to a sputtered sample effectively suppresses the emission of positive secondary ions, thereby reducing the erosion of species which are sputtered predominantly as secondary ions.

Correspondingly less material is then required from the sub-surface reservoir to maintain the lithium surface layer.

Discussion

Experimentally it was found that for 2.6% Li in Cu, initial rapid segregation of lithium to the surface occurred in all samples studied. The minimum temperature at which significant segregation occurred varied from sample to sample but in no case exceeded 130 C. Further temperature increases

up to 230 C resulted in progressively greater lithium enrichment of the surface. The observed initial risetime in the surface lithium concentration was essentially the same as the temperature risetime of the sample heater. The actual segregation time therefore does not exceed 10-100 seconds. Depending on the sample and temperature, maximum lithium surface concentration measurements ranged from 62% to 97%. It should be noted that at the high end of this range, there is some uncertainty arising from the fact that the Auger sampling depth exceeds one atomic layer. If the first and second layers have, as expected, significantly different composition, the measured value will be a weighted average over several layers rather than a true indication of first layer composition. As the lithium concentration at the surface increased, the erosion of copper decreased. For 80% measured surface lithium (Figure 5) the copper secondary ion yield decreased by a factor of 3 relative to that of an essentially pure copper surface. This shielding factor is comparable with the value of 2.45 calculated by TRIM for a 100% lithium monolayer on a pure copper substrate undergoing 3 keV Ar^+ bombardment.

Related experiments in our laboratory and computer simulations [12] indicate that the material segregating to the surface does not come uniformly from the bulk, but rather originates in the near sub-surface region. Irradiation results in the production of a damaged layer in which solute migration occurs much more rapidly than in the undamaged region. The damaged region then acts as a reservoir for the replenishment of lithium sputtered from the surface. When this region is depleted, the replenishment rate is decreased and during irradiation, the surface concentration of lithium decreases. If the ion beam is turned off, the recovery time of the lithium overlayer is much greater after a prolonged period of sputtering.

Summary

For three metals of interest for fusion applications, there are dilute (1-4%) alloys with low Z metals in which it is expected that the equilibrium surface concentration of the low Z component exceeds 90% at temperatures expected for reactor operation. In the absence of radiation effects the enrichment is expected to be confined to the uppermost monolayer. For a material consisting of a high Z substrate covered by a single layer of low Z atoms, significant reduction in high Z erosion is expected for both light ion and self-sputtering. For 200 eV He^+ incident on Al/V, the V erosion predicted by TRIM is 8% that of bare vanadium. For 3 keV Ar^+ incident on Li/Cu the expected Cu erosion is 40% that of pure Cu. The light metal erosion rate ranges from somewhat less than, to about twice that of the bare high Z material. For CuLi the low Z erosion rate is significantly reduced by the application of a negative bias to the sample. The TRIM results have been experimentally continued for a lithium overlayer formed at the surface of an alloy containing 2.6 at % Li in Cu.

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FIGURE CAPTIONS

1. Calculated first layer concentration (atom %) of the low Z component of three binary alloys versus temperature. The bulk composition of all three alloys is taken as 4 at% and the calculation is done in the Miedema model.
2. TRIM calculation of the lithium and copper partial sputtering yields for a material consisting of a partial overlayer of lithium on a copper substrate. All data are normalized to the sputtering yield of bare copper.
3. TRIM calculation of the aluminum and vanadium partial sputtering yields for a material consisting of a partial overlayer of aluminum on a vanadium substrate. All data are normalized to the sputtering yield of bare vanadium.
4. Plot of lithium Auger signal and Li^+ and Cu^+ SIMS signals vs time. The sample was initially at room temperature and no Auger signal was visible. The sample heater was turned on at A, and the temperature reached 130 C in about one hour. 3 keV Ar^+ , 0.11 uA/cm^2 .
5. Plot of lithium and copper secondary ion signals vs time. 3 keV Ar^+ current density was increased to 0.67 uA/cm^2 at the start of the Figure. The heater current was increased at times A, B, and C.
6. Plot of the surface lithium concentration as measured by AES vs time for several ion beam current densities, with and without sample bias. $T=134 \text{ C}$.

SECONDARY ION YIELD (arbitrary units)

NORMALIZED SPUTTERING YIELD

FIRST LAYER Li ATOM FRACTION

ATOM FRACTION Li IN FIRST LAYER