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CURRENT STATE OF DEVELOPMENT AND EXPECTED PERFORMANCE OF COPPER-LITHIUM
ALLOYS AS AN IMPURITY CONTROL SYSTEM IN FUSION APPLICATIONS*

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ABSTRACT

A new approach to impurity control involves the development of materials displaying both strong surface segregation of a low-Z component and high secondary ion fractions in the sputtering of that component. Key issues that have been studied with particular reference to copper-lithium alloys relate to the completeness of the overlayer, its rate of formation in a reactor environment, lowering of substrate sputtering and self-sputtering yields, durability of the overlayer, and depletion of the bulk alloy in the low-Z component. Other factors that must be considered in the materials selection process relate to response to disruptions, heat transfer, thermal stress, fabricability, radiation damage, activation, and tritium permeation. Copper-lithium alloys have been evaluated as a surface material for the impurity control system of the INTOR reactor. Both the medium-edge temperature limiter regime and the low-edge temperature divertor regime were examined. The analysis used TRIM code data to predict sputtering coefficients for copper-lithium with a 1.5 monolayer coverage of lithium. The REDEP code was used to evaluate the erosion performance for INTOR. Other properties such as fabrication and thermal performance were also briefly assessed. It was found from the standpoint of erosion that copper-lithium is a very good candidate material for the medium-edge temperature regime and also works well in the low-edge temperature regime. For the medium-edge temperature regime, the use of copper-lithium results in an almost negligible erosion rate over the entire surface.

INTRODUCTION

Impurity control is becoming increasingly important in magnetic confinement fusion machines as devices operate with pulse lengths on the order of seconds and make use, for

example, of large area Faraday shields for ICRF antennas immersed in the plasma edge. A large number of properties are important for materials selection involving impurity control systems such as limiters, divertor, plates and beam dumps.¹

The candidate materials considered for plasma side use where impurity generation occurs may be divided into low-Z, medium-Z, and high-Z materials. At low plasma edge temperatures (<50 eV), several materials can be used, but high-Z materials such as W are predicted to have the greatest lifetimes. At higher edge temperatures (100-300 eV), both medium and high-Z materials are unacceptable due to excessive self-sputtering. The permissible plasma side materials are, therefore, confined to those whose self-sputtering coefficients do not exceed unity, thus limiting the choice of materials to atomic weights approximately that of SiC unless the edge temperature can be kept below 50 eV. Because candidate heat sink materials are copper or transition metal alloys, most suggestions for plasma side materials in high heat flux applications have involved low-Z coatings such as TiC or Be. Recent experience in TFTR with TiC coated poco-graphite limiters has shown, however, that severe problems can be associated with this approach to impurity control.²

The current lack of suitable plasma side materials encourages one to seek out alternative approaches that may provide more satisfactory solutions to this important problem area. One such approach to impurity control has involved an investigation of alloy systems which spontaneously form low-Z overlayers as a consequence of exposure to the fusion reactor environment.³⁻⁵ Several candidate systems for the production of such self-sustaining low-Z overlayers have been identified and are being investigated from both a theoretical and experimental point of view.

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Alloys under investigation include Cu-Li, V-Al, W-Re, and Fe-Al. While in all these cases the low-Z component in the bulk is relatively dilute, typically less than 10 at.%, its equilibrium surface concentration can be expected to be greater than 90% under the conditions obtained in a fusion reactor.

The key idea in the approach to impurity control outlined above is that surface segregation, which is thermodynamically driven by Gibbsian adsorption and kinetically enhanced in a radiation environment, can provide a self-regenerating low-Z surface by diffusion from the bulk.⁵ In principle, Gibbsian adsorption gives enrichment only for the very first layer of atoms with bulk alloy concentrations reestablished within one or two atomic layers from the surface. Although concentration profiles can be expected to be strongly modified in the presence of charged particle and neutron radiation fields, it is necessary to establish the sputtering behavior of the material for a purely Gibbsian adsorption concentration profile. To be applicable in an actual machine, this approach to impurity control must provide in the first instance for a reduction in the sputtering yield of the medium-Z alloy component by about an order of magnitude which can be achieved with a low-Z overlayer which is one monolayer in thickness. Theoretical and experimental work on reductions in substrate sputtering yields as a result of monolayer coverages will be referenced here.

For surface segregation to be a practical "coating" mechanism in fusion machine applications, the low-Z monolayers must be self-sustaining as well as protective. To be self-sustaining, surface segregation kinetics must be rapid enough to replenish material sputtered from the surface. There are two mechanisms which could bring this about. First, radiation-enhanced diffusion speeds up the process of surface segregation by several orders of magnitude. Second, if the sputtered flux consists primarily of secondary ions, a small negative potential on the target (~20 V), such as provided by the plasma sheath potential, is sufficient to return the ions to the surface, thus reducing the sputtering yield.

It is desirable, therefore, that sputtered atoms originate in the very first layer of surface atoms, that the surface ionization coefficient is high in order to have large secondary ion fractions, and that the low-Z component of the alloy segregates very completely at the surface and does so rapidly in a radiation field. This paper discusses progress made up to now in developing self-sustaining surface segregating low-Z layers for fusion applications with particular reference to the Cu-Li system.

BEHAVIOR OF COPPER-LITHIUM ALLOYS UNDER ION BOMBARDMENT

The binary Cu-Li phase diagram was established by Klamm and Volavsek⁶ and found to have a solid solution range from 0-20 at.% Li. On the basis of Cu-cell volume expansion data as a function of Li content, it was concluded that Li is present in the solid solutions in a partially ionic state, leading to the expectation that Li has a low activity in the alloy. This conclusion is borne out, not only in the chemical behavior of the alloys (nonreactivity with water, for example), but also in the fact that in our preparations of Cu-Li alloys, which involved a thermal reaction step followed by arc melting,^{7,8} very little lithium is lost during repeated meltings of alloys containing up to ~15 at.% Li. Sputtering properties of the alloys have been extensively investigated by us experimentally, and it has been found that at sputter-induced erosion rates on the order of 1 second per monolayer, and temperatures appropriate to the use of copper as a limiter material, an alloy containing as little as 2.6 at.% Li forms an overlayer consisting primarily of lithium.⁴ The lithium overlayer is stable during extended irradiation at high temperature, and the sample exhibits negligible reduction in bulk lithium concentration after prolonged sputtering at temperatures up to 430°C.⁹ In these experiments, the sheath potential at a limiter surface has been simulated by applying a bias voltage to the sample and monitoring the surface composition during sputtering by means of Auger spectroscopy.¹⁰ For a temperature range of 140°C to 320°C, spanning the expected operating temperature of a copper limiter in a fusion reactor, a significant fraction of the lithium sputtered from the copper substrate is in the form of secondary ions which for a 20-30 eV or greater sheath potential would be returned to the limiter surface at a point within ~100 μ m of the point of origin¹¹ and thus make no contribution to the net erosion. Experimentally, we have shown that a 22 V bias essentially completely suppresses the depletion of the lithium overlayer.^{8,12}

In accord with experimental results,⁴ TRIM code calculations on copper and lithium sputtering yields from a matrix characterized by a high degree of surface segregation indicate that for a single atomic overlayer of lithium, and absent a negative potential, the copper erosion is reduced by a factor of 4-6 relative to that of pure copper, depending on the mass and energy of the incident particle.⁹ While analysis of the near-surface lithium concentration by Auger electron spectroscopy leads to the conclusion that more than one monolayer of lithium is present, physical arguments based on the observed high ion fraction of the sputtered lithium and the stability of the lithium overlayer at temperatures in excess of 400°C⁹ dictate that the effective thickness of the

lithium overlayer does not exceed 2 atomic layers.

A considerable body of both experimental¹³ and calculational evidence now shows that sputtered atoms originate almost entirely with the first 1-2 atomic layers. Consequently, an overlayer of lithium 1-2 atomic layers thick is expected to provide substantial reduction in erosion of the substrate material. This topic has been reviewed recently by Gruen, Krauss, and Pellin.¹⁴

Calculated yields for the self-sputtering of copper from a pure copper surface and from copper covered with 1.0 and 1.5 atomic layers of lithium are shown in Fig. 1. For comparison, the self-sputtering yield of tungsten is also shown. For impact energies in excess of 1 keV, the sputtering yield of tungsten exceeds unity, corresponding to the generation of a self-sputtering cascade region. For tungsten, an impact energy of 1 keV corresponds to an edge temperature of ~100 eV. For copper with a single lithium overlayer, the predicted kinetic energy corresponding to unity self-sputtering yield is 400 eV higher than for tungsten. If the lithium overlayer is as much as 1.5 monolayers thick, the self-sputtering window for Cu-Li is 3400 eV wide.

PERFORMANCE EVALUATION OF COPPER-LITHIUM ALLOYS IN FUSION REACTOR APPLICATIONS

Using the sputtering and reflection coefficients found from the TRIM code, the REDEP computer code was used recently¹⁵ to compute the erosion of a limiter and divertor coated with Cu-Li for INTOR applications.¹⁶ The results of this and other studies allow one to compare leading candidate surface materials for a variety of key issues (see Table I).

Although sputtering behavior is a very important consideration, there are other factors which affect the choice of a plasma side material. Besides sputtering erosion, the factors involved in materials selection are: response to disruptions, heat transfer and thermal stress, fabrication, radiation damage, activation, and tritium permeation. The Cu-Li alloys are limited in operation to plasma edge temperatures ≤ 200 eV due to self-sputtering considerations. Only low-Z elements like Be and C, whose self-sputtering coefficients never exceed unity, can be used at higher edge temperatures.

The Cu-Li alloys appear to have favorable characteristics with respect to thermal stress considerations and tritium permeation. The high thermal conductivity of low alloy content copper alloys results in reduced thermal stresses and the capability to accommodate high heat fluxes. Thermal stresses associated with property mismatches at the interface of the plasma side material and heat sink material should be

reduced or eliminated since Cu-Li would either be bonded to another copper alloy with similar properties, or it may be possible to use Cu-Li as both the plasma side and structural material. The very low solubility of hydrogen in copper results in low tritium permeation rates.

The concerns of Cu-Li alloys involve disruption response and activation. If large amounts of energy are deposited on the surface during disruptions, the melt layer that forms could be thick, and eddy current forces that occur during disruptions could result in the loss of the melt layer. The actual amount of erosion is uncertain, however, since the disruption conditions cannot be accurately specified at this time. Copper is known to become highly activated during irradiation, and in fact, is the poorest of the candidate materials with respect to activation.

The fabrication and irradiation properties of Cu-Li alloys are largely unknown, and experimental work is needed in these areas.

CONCLUSION

Based on the present performance analysis, a copper lithium alloy appears to have good potential as an impurity control material for fusion applications. As shown, the sputtering properties of a self-sustaining layer of lithium on copper of only 1.5 atomic layers thick would allow the material to be used as a tokamak limiter or divertor with plasma edge temperatures in the range of 0 - 200 eV, a range unmatched by any other material. The self-sustaining overlayer is maintained by favorable thermodynamic driving forces and radiation-enhanced diffusion kinetics. Since the lithium component tends to be sputtered as a charged ion, which quickly returns to the surface, there is apparently little lithium lost in any event. While there are some drawbacks to the use of copper-lithium and several areas of uncertainties, this is also true of the other candidate materials. Indeed, since there are few viable candidate materials for impurity control, the addition of even one to the list is of major significance, in our opinion. Other alloys exhibiting similar sputtering properties as Cu-Li but with different bulk properties may also be possible, and these are currently being explored.

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Table 1. Performance Comparison of Cu-Li With Several Leading Candidate Surface Materials

Key Issue	Desirable Behavior	Cu-Li	Be	W	C
Self-sputtering threshold energy	no limit	3.4 keV	no limit	1 keV	no limit
Plasma edge temperature limit	no limit	200 eV	no limit	50 eV	no limit
Net erosion behavior for medium edge temperature limiter regime	0	<0.3 cm/yr	>5 cm/yr	not useable due to self-sputtering	>5 cm/yr (physical sputtering only)
Net erosion behavior for low edge temperature divertor regime	0	0	10 cm/yr	0	10 cm/yr
Plasma contamination behavior	acceptable	acceptable	acceptable	acceptable	acceptable
Disruptions	no vaporization or melting, low electromagnetic forces	possibly large melt layer thickness & large magnetic forces	possibly large melt layer thickness	high threshold for melting, possibly <u>NO</u> melting or vaporization	very good-low vaporization, no melting
Heat transfer & thermal stresses	high thermal conductivity, low elastic modulus close match in properties between plasma side and heat sink materials	has potential for very low thermal stresses when bonded to copper heat sink or when used as a monolithic structure	possible high thermal stresses because of property mismatch with heat sink	possible high thermal stresses because of property mismatch with heat sink	low thermal stresses but possible problems because of property mismatch with heat sink
Fabrication	low cost, fabricable in thicknesses ~ 1 cm, weldable or brazeable, machinable	unknown in large sizes	can be formed by powder metallurgy, brazeable, expensive	available in sizes to 2 cm thick, not weldable but brazeable, difficult to machine, expensive	readily available but potential problems with bonding
Radiation damage	little or no effect of neutron damage on bulk properties to ~ 50 dpa low swelling & creep	unknown	potentially poor due to high helium generation rates	potentially poor due to radiation hardening & embrittlement	poor radiation response - cannot be used $>2\text{MW}\cdot\text{yr}/\text{m}^2$
Activation	low afterheat, no long term decay products	poor	good	high activation-short term, good-long term	good
Tritium permeation	should provide effective barrier for permeation to coolant, should have low inventory in material	good	good	good	potentially high tritium inventories

TRIM results for the calculated self-sputter yields of $\text{Cu}^+ \rightarrow \text{Cu}$, $\text{W}^+ \rightarrow \text{W}$, $\text{Cu}^+ \rightarrow \text{Cu}$ with 1 atomic layer of Li, $\text{Cu}^+ \rightarrow \text{Cu}$ with 1.5 atomic layers of Li. Yields are for normal incidence.