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RECENT RESULTS ON THE PREPARATION AND PROPERTIES OF Li-CONTAINING Cu ALLOYS*

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Introduction

It has been suggested that erosion of fusion materials by sputtering, and generation of plasma impurities can be greatly reduced by using materials selected to maximize their secondary-ion fraction [1]. One approach proposed for maximizing the secondary-ion fraction is to maintain an alkali-metal overlayer on selected materials. By this means, secondary-ion fractions exceeding 90% might be achieved [1]. In order to avoid the thermal, mechanical, and replenishment problems associated with coatings or claddings, alloy systems have been proposed that would produce self-sustaining secondary-ion emitting overlayers in a fusion irradiation environment via surface segregation [2,3].

Initial studies, focused on lithium-copper alloys, have shown that self-sustaining secondary-ion emitting lithium overlayers form on predominantly copper substrates. These overlayers have been shown to reduce significantly the sputtering-induced erosion of the substrate [4-7]. The detailed behavior of lithium overlayer formation and its maintenance by surface segregation under ion bombardment conditions can be expected to be strongly correlated with the basic physico-chemical properties of the Cu-Li binary system. Unfortunately, there exists only a very sparse data base regarding this system. Until recently, there have been only three papers

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published relating to the Cu-Li phase diagram [8-10]. In Ref. 8, only the liquidus curve in the Cu-Li system was determined. Klemm and Volavsek [9] describe the solid solution of Li in copper. By reacting lithium with copper powder at temperatures from about 300°C to 800°C, they determined that the solid solubility extends up to a composition limit of about 20 at.% Li (or Cu_4Li). Old and Travena [10], on the other hand, reacted liquid Li with solid copper from 200°C to 600°C and found only a "face-centered cubic intermediate phase" whose composition is near Cu_4Li . They further conclude that "the solubility of lithium in pure copper is low." Although the description of the nonsolubility of lithium in copper by Old and Travena appears to be a direct contradiction with the description of the lithium-copper system by Klemm and Volavsek as a solid solution, the x-ray diffraction data given in both papers is completely concordant. These two sets of authors disagree however, on the amount of Li found in their different preparations. While Old and Travena consistently find about 20 at.% Li in their analyzed preparations, Klemm and Volavsek found concentrations which varied from about 8 at.% Li to about 19 at.% Li. This data is apparently what leads Klemm and Volavsek to interpret the system as a solid-solution of Li in Cu. The failure to observe any Li concentration gradient at the copper interface, is probably what leads Old and Travena to conclude that the solubility of Li in Cu is low. Our experience, in the light of this apparent contradiction, will be discussed later.

Experimental

An appropriate amount of Cu OFHC rod is machined as a straight-walled, flat-bottomed crucible whose inside diameter is 5/8". A Cu OFHC press fit cover of about 1/8" thickness is machined to seal the Cu crucible. After

cleaning in 20-25% HNO_3 solution and washing with distilled water and acetone, the Cu crucible and cover are taken into a He-filled glovebox. An appropriate amount of Li, which includes a 10-20% excess for allowance of Li losses, is added to the crucible. We have found it convenient to add the Li in the form of Li-filled copper tubing (0.60" OD) obtained from Foote Mineral Company. In this case, an appropriate length of Li-filled copper tubing is cut in the dry box and slipped into the pure copper crucible. The crucible top is then pressed into place in the dry box. The crucible may now be safely removed from the dry box. Ambient air appears not to penetrate this cold-sealed crucible cover. In earlier experiments, the Cu-Li alloy was produced by arc-melting the crucible.

In order to increase the amount of material produced per batch, the following procedure was adopted. The Li-containing copper crucible is placed inside a boron nitride (BN) crucible, used to contain the Cu-Li melt. The BN crucible is itself placed in a quartz tube whose ID is about 1-3/4". The quartz tube is evacuated with a mechanical pump and backfilled with UHP argon. The entire assembly is placed in a vertical position in a resistance-heated furnace at about 350°C for about 16 hours. This preheat treatment has been found substantially to reduce the amount of Li lost during the subsequent higher temperature treatments. The quartz tube is removed from the furnace and the furnace temperature is then raised to about 1100°C. The quartz tube assembly is lowered into the furnace and the temperature monitored until the melting point of Cu is again reached at the heating coils. The sample is maintained in the liquid state for about 20 mins and subsequently cooled by removing it from the furnace to the ambient air. The cooling process, although relatively rapid, was much slower than

for the arc-melted samples. After removal from the crucible, the sample is inverted and remelted. Some annealing treatments were also investigated.

Reactions with oxygen were performed by weighing cut turnings or 3/8" diameter disks of some of the above prepared Cu-Li alloys and placing them in an alumina crucible. The crucible containing the Cu-Li alloy was then placed in a stainless steel tube, closed at one end and fitted with a valve at the other end. The stainless steel tube was evacuated to $\sim 10^{-3}$ Torr and backfilled with a known pressure of oxygen. The sample was then placed in a furnace and heated for about 16 hours at 515-530°C.

Disks of various thickness were cut from the 1" diameter boule with a low-speed diamond cutting wheel. These were polished using various grades of diamond powder. Lithium analyses were performed by atomic absorption measurements after dissolving the samples in nitric acid solutions. Optical microscopic observations have been made with a Bausch & Lomb microzoom microscope.

Results

Several rods of 1" diameter have been prepared and analyzed. These results are given in Table I. A lengthwise section was taken from one of these rods (#14). The lithium concentration was determined at various positions along the length of the slice as shown in Curve A of Fig. 1. The rod was then inverted and annealed for 24 hours at 850°C and again sliced and analyzed as shown in Curve B of Fig. 1. Further annealing for 16 hours at 950°C resulted in a relatively uniform Li concentration profile as shown in Curve C of Fig. 1.

A 3/8" disk of about 8 at.% Li in copper was reacted with gaseous oxygen at 520°C for 24 hours. Examination of the surface of the disk after

reaction revealed a reddish-orange surface with patches of yellowish-orange to orange excrescences on the surface. After being exposed to air for one week most of the excrescences had turned black. A series of reactions of copper turnings containing about 18 at.% Li with different amounts of oxygen revealed gradually darkening colors (from orange to deep red to black) as the amount of gaseous oxygen added was increased.

Discussion

We will refer to the Cu-Li phase diagram shown in Fig. 2 in our discussion of the preparation of homogeneous Cu-Li alloys. Fig. 2 has been redrawn using the data given in Ref. 9. Recent thermodynamic calculations of the Cu-Li system have been performed by A. D. Pelton [11]. His results indicate the presence of a metastable liquid-liquid immiscibility gap with an envelope that peaks near the liquidus curve at about 40-45 at.% Li. Whether or not this metastable immiscibility gap exists, it does not appreciably affect the discussion which follows.

As can be observed from Fig. 2, cooling a sample with less than 20 at.% Li from the liquid to the solid phase involves traversing a two-phase region of solid plus liquid. As explained in an earlier paper [12], the density difference between the solid which first precipitates and the liquid which remains, is the most likely cause of the lithium concentration gradients observed in ingots which have been subjected to only one melt [see Curve A in Fig. 1]. In some cases, this concentration gradient could be smoothed by inverting the sample and remelting (see e.g., Samples 12, 13, and 15 in Table I). However, for larger preparations, such as Samples 18, 19, and 20, even this remelting procedure failed to give uniform Li concentrations. In these cases, it appears that an annealing treatment in the two-phase region

of the phase diagram can produce a uniform Li concentration (see Curve C in Fig. 1). Annealing treatments in or near the solidus phase boundary appear merely to reduce the Li concentration without markedly affecting the concentration profile (see Curve B in Fig. 1).

With one exception, all polished Cu-Li samples appeared to consist of at least two phases under low resolution microscopic examination. The minority phase, whose volume fraction ranged from about 1-25%, appeared as micron-sized dark areas under coaxial illumination. In general, there was a positive correlation between the chemically analyzed Li concentration and the volume fraction of the minority phase. As noted previously [12], the minority phase is most likely a lithium enriched material originating from liquid trapped during the solidification process. After annealing at 850°C, the top half of Sample 14 appeared to have a homogeneous microstructure, i.e., there was no visual evidence for the formation of a second phase. The second phase starts to appear ~ 0.5 inch from the top of the ingot, at a Li concentration of 6-8 at.% Li. Assuming equilibrium conditions, that would mean that the solid solubility of Li in Cu is limited to about 6-8 at.% Li. This situation puts us between the limits of solubility proposed by Klemm and Volavsek (20 at.% Li) and by Old and Travena (<0.1 at.% Li [13]). We note, however, that we have no information as to whether these solid solutions are thermodynamically stable or merely metastable phases.

If we assume the majority phase in some of our samples contains about 8 at.% Li, then it is of interest to calculate the Li concentration required in the minority phase in order to achieve a mass balance with the chemically analyzed Li concentration. The results of such calculations are shown in Table II for a pre-arc melted and a furnace melted sample of about the same lithium concentration. It appears that the minority phase in the furnace

melted sample has a much higher Li concentration than that of the arc-melted sample. This is most likely associated with the thermal history of each sample.

At present, we do not have enough information to speculate extensively on the nature of the products obtained from the reaction of our Cu-Li alloys with oxygen. It is of interest, however, to note that the reaction may be stopped at a partially oxidized phase which is air sensitive (as noted by the change in color from orange to black upon extended exposure to the ambient air) and probably contains both copper and lithium (because partially oxidized pure Cu does not exhibit the aforementioned color change upon a similar air exposure).

As a result of the above discussion, we see that, depending on the thermal processing of the alloy, there may be varying amounts of free lithium in the solid. This free lithium affects the erosion/redeposition behavior of the binary alloy in a fusion environment. Some of the samples prepared both by arc-melting and in the vacuum furnace were subjected to plasma sputtering, both in the PISCES high flux device at UCLA and in a lower flux device at Argonne. For the 12 at.% Li samples prepared in the electric furnace, heating in a helium plasma resulted in the formation of Li droplets on the surface, resulting in substantial evaporation of neutral lithium although the copper erosion was suppressed to the point that Cu emission lines were no longer visible in the plasma. The 12% arc-melted samples and the 6% furnace-melted samples did not exhibit this behavior. In these samples, the formation of the lithium overlayer during sputtering took longer and does not appear to have exceeded ~ one monolayer. The effect of this monolayer on the erosion of the copper substrate is discussed in detail elsewhere [14]. It is sufficient here to say that for these samples, little

loss of lithium and a reduction of copper erosion of 2-3x were observed, as measured both by weight loss and plasma emission spectroscopy. This reduction in erosion is in good agreement with earlier predictions [4-6].

Conclusions

Homogeneous solid solutions of Li in copper have been prepared containing up to 6-8 at.% Li. However, the possible metastable nature of these materials has not yet been fully investigated. The existence of a unique intermetallic compound near the composition Cu_4Li is currently being investigated by single crystal x-ray diffraction and powder neutron diffraction techniques.

The copper-lithium binary alloy has demonstrated potential as a means of forming a self-sustaining coating for the reduction of sputtering-induced erosion in fusion applications. The initial performance under high flux conditions is strongly dependent on the lithium content and method of preparation.

Table I. Summary of Furnace Melted Cu-Li Samples

Sample#	Initial Li(at.%)	Melting Temp.	Melting Time(min.)	Analysis At.% Li			Comments
10	10	1100°C	15	B:6.2	M:7.6		preheated pre arc-melted
12	5	1110°C	30				preheated
12*	5	1110°C	20	B:4.1	M:4.2	T:4.1	~130g preheated
13	10	1110°C	30				
13*	10	1100°C	20	B:10.3		T:9.1	~130g
14	10	1100°C	22	B:2.3		T:17.3	~136g preheated
15	5	1110°C	33				preheated
15*	5	1110°C	20	B:5.3		T:5.2	~130g
18*	5	1090°C	~30/29	B:3.0		T:5.3	~245g
19*	10	1060°C	30/45	B:8.9		T:12.0	~250g
20*	15	1050°C	30/35	B:5.7		T:19.5	~244g

B = bottom piece

T = top piece

M = middle piece

* = remelted sample

Table II. Calculated Minority Phase Li Concentrations

Sample #	Vol. fraction of minority phase (%)	Chemically analyzed Li concentration (at.%)	Calc. Li concentration in minority phase (at.%)*
11**	22.5	12.5	28
26	3	12.0	141

*This concentration has been calculated to give a mass balance with the chemically analyzed Li concentration, assuming that the majority phase contains 8 at.% Li (see text).

**Pre-arc melted sample.

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Figure Captions

Fig. 1 - Curve A: Li concentration profile of Sample 14. Curve B: Lithium concentration profile of Sample 14 annealed at 850°C. (Since this sample was inverted; the actual concentration profile has been inverted to allow for an easier comparison with Curve A.) Curve C: Lithium concentration profile of Sample 14 annealed at 950°C. The solid lines serve only as guides to the eye.

Fig. 2 - Cu-Li phase diagram. Redrawn from data in Ref [9].

Fig. 1

Fig. 2