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**MATERIALS CONSIDERATIONS IN LIQUID METAL ION SOURCE DEVELOPMENT**

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Abstract - Successful development of a liquid metal ion source depends upon the satisfactory confluence of several critical design considerations. At least nine desirable properties of the alloy and substrate exist which cannot be fully and simultaneously satisfied in a given contact system. A compromise must usually be made based upon the most important source characteristics. We review these properties, with emphasis on the material and thermodynamic behavior of liquid metal alloy surfaces.

**I - INTRODUCTION**

Liquid metal ion sources (LMIS) of high melting nonmetals may be achieved by selection of a low melting eutectic alloy and a suitable substrate material. The choice of the alloy and substrate is based on a number of considerations. The alloy must be electrically conductive, have a low vapor pressure at the melting point, and possess low viscosity in order to prevent the formation of jets in the beam. The substrate must allow for good wetting without excessive reaction with the alloy. In this paper we identify several key features of the liquid alloy and substrate which allow for successful development of LMIS. Despite the numerous and often conflicting requirements, it is possible to achieve long-lived sources for a variety of technologically important ions.

**II - REQUIREMENTS FOR THE IDEAL LIQUID METAL ION SOURCE**

1. A Low Melting Temperature. The first desirable property of the alloy is that it possess a low melting point. Low melting temperatures are required to minimize reaction between alloy and substrate, and are essential to suppress reaction in many well-wetted contact systems of liquid alloys and refractory metal substrates. High melting materials may be made compatible by formation of binary and ternary eutectic compositions which lower the melting temperature. The best solution is to choose a shallow eutectic that is low-melting or a low melting compound containing the element of interest. A deep eutectic is less favorable because a slight digression from the eutectic composition (which may occur by interdiffusion between alloy and substrate) begins precipitation of second phase material. A congruently-melting compound, by contrast, remains liquid during such digressions. Further, compound formation frequently acts to lower the vapor pressure of highly volatile species through liquid interactions within the compound. On the other hand, deep eutectics usually possess lower melting temperatures than compounds, so often a compromise must be made between low melting points and broad stoichiometries over which the alloy remains liquid.

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2. Low Volatility at the Melting Temperature. The second desirable property of the liquid alloy is that it possess low volatility at the melting point. Low volatility is necessary to conserve the liquid film supply and promote long life. Elemental boron and arsenic, for example, cannot be used for LMIS because both of these elements have high vapor pressures at their melting points and would volatilize completely if operated at this temperature for any significant period of time. A general rule of thumb is that component partial pressures greater than  $10^{-7}$  torr are unacceptable. Present evidence from studies of several liquid alloys suggest that component vapor pressures may be lowered by choosing combinations which possess a low (i.e., highly negative) Gibbs free energy of formation. Such combinations have sufficient stability to lower the thermodynamic activity of the ionizing component, and hence, the component vapor pressure above the alloy. The best solution is to select alloy compositions that are congruently vaporizing at the melting point. This is because preferential vaporization of the alloy components eventually alter the initial stoichiometry and cause changes in the melting temperature.

3. High Relative Bulk Concentration of Ion Species of Interest. The third desirable property of the alloy is that it possess a high relative bulk concentration of the intended ionizing element. It is the bulk, and not the surface, concentration of the intended element that is important because the steady state emission characteristics of LMIS reflect the bulk stoichiometry of the material (see Table I) for LMIS where little alloy/substrate interaction occurs and which operate under conditions of congruent field evaporation. Further, assuming the field evaporation mechanism of ion formation to be valid, the current of ion species  $k$  is linearly dependent upon the fractional bulk concentration of atom  $k$  /1/. Best yields of, say,  $B^+$  or  $As^+$  in a LMIS of B and As are therefore obtained by choosing an alloy combination having the highest mole fraction of B or As compatible with low melting. Surface segregation of low surface tension alloy components in the liquid /2/ does not appear to contribute to the beam stoichiometry.

4. Low Surface Free Energy and Good Wetting. Fourth, it is desirable for the alloy to possess a low surface free energy. Low surface tension materials promote wetting of the alloy to the substrate. Good wetting, defined as a contact angle considerably less than 90 degrees, is necessary to facilitate liquid flow from the reservoir to the apex tip where emission occurs. The governing relation is Young's equation:

$$\cos C = (T_{sv} - T_{sl}) / T_{lv}$$

where  $T_{sv}$ ,  $T_{sl}$ , and  $T_{lv}$  are the solid-vapor, solid-liquid, and liquid-vapor surface tensions respectively and  $C$  is the contact angle. Young's equation shows that the best wetting is realized when the liquid alloy has the lowest possible surface free energy. Otherwise stated, wetting is a consequence of the relative magnitudes of cohesion and adhesion in a contact system. If the adhesive forces between alloy and substrate are greater than the cohesive forces of the alloy and substrate separately, then wetting is likely to occur. Our studies indicate that this simple model of wetting is complicated by surface segregation of low-level impurities in the liquid alloys which inhibit reaction between alloy and substrate /3/. Utilizing surface coatings composed of materials reactive to the impurities allows wetting to occur by tying up the impurities at the interface.

5. Low Solubility of Alloy in Substrate. Fifth, it is important that wetting occur without excessive attack of the substrate. The rate and extent of diffusion and reaction of alloy components into the substrate material must be minimal. Our studies have confirmed that this mechanism is the major lifetime-limiting mechanism for contact systems composed of liquid metal alloys of B wetted to refractory metal substrates. A representative example is shown in Figure 1. In this study, the molten surface of a PtB eutectic wetted to an Re substrate was monitored over time by Auger spectroscopy. Excessive reaction between alloy and substrate was observed to occur within minutes after contact, and the alloy required successively higher temperatures to maintain it in the molten state. Auger spectra during this period

showed monotonically decreasing surface concentrations of B with corresponding increases in Pt. The system eventually suffered catastrophic breakdown after a few hours. Auger spectra of the corroded surface after breakdown are shown in Figure 1. In addition to depleted surface concentrations of B, the surface shows relatively small amounts of Re. A high resolution Auger analysis of a fractured cross-section of the failed contact system is shown in Figure 2. A central region that is primarily Re and Pt is surrounded by a second region which has large amounts of B (the alloy had wet both sides of the Re). It is clear that both B and Pt have diffused into the substrate, and that Pt appears to be preferentially attacking the Re. We conclude that it is difficult to inhibit reaction at the melting temperatures of most contact systems composed of boride metal alloys and refractory metals. Diffusion of alloy components into the substrate alters its electrical resistivity, leading to a situation where the circuit power must be constantly monitored to prevent radical changes in temperature for resistively heated source configurations.

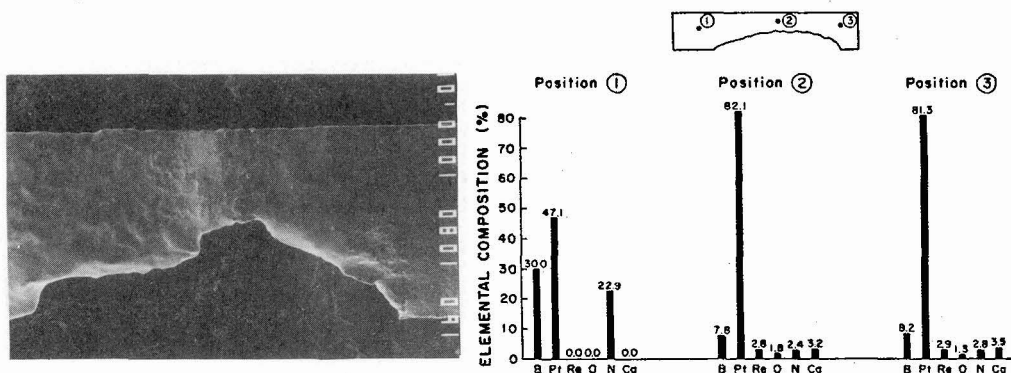


Fig. 1 - Auger surface elemental composition for the Pt<sub>72</sub>B<sub>28</sub> on Re alloy at 300 K following catastrophic failure.

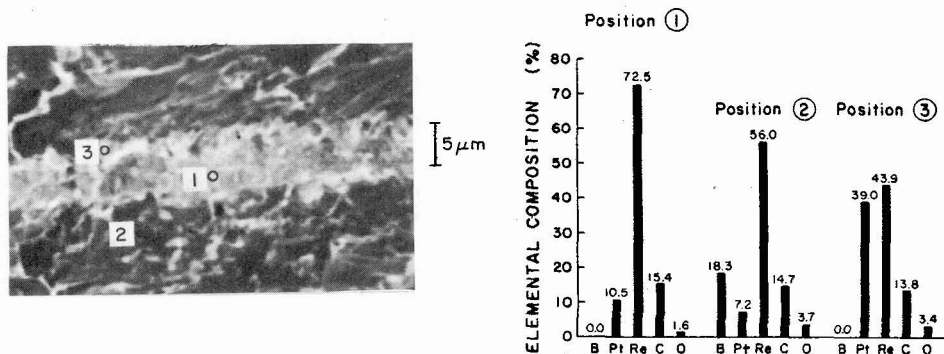


Fig. 2 - Auger surface elemental composition of three positions within a fractured cross-section of the failed Pt<sub>72</sub>B<sub>28</sub> on Re system above at 300 K.

**6. Low Solubility of Substrate in Alloy.** The sixth desirable property of the contact system is that the extent of dissolution of the substrate into the alloy be minimal. In the case of a eutectic mixture on a refractory metal substrate, dissolution of the substrate into the alloy changes the composition of the eutectic and acts to increase the melting point of the liquid alloy. The emitter then shuts off. To remelt the alloy, an increase in circuit power is necessary, but this increases the rate of dissolution and results in a runaway condition which terminates with catastrophic breakdown of the emitter. Further, we have observed a

number of cases where the dissolving metal forms metal borides in the liquid alloy and suppresses the ratio of B in the beam. To correct this problem, selection of an inert substrate is necessary, but this is usually incompatible with good wetting. Wetting occurs by lowering the total energy of the contact system during chemical bond formation, so the liquid alloy must interact with the substrate to some extent. The dual requirements of good wetting and low rates of the chemical reaction are particularly challenging in light of the mutual exclusivity of these properties. It may be that the best solution is to have no substrate at all by development of a consumable electrode with localized heating of the apex region. It is questionable, however, whether such a configuration would be adequate for focused beam applications.

7. Favorable Mechanical, Electrical, and Vacuum Properties. Seventh, it is desirable for the contact system to possess favorable mechanical, electrical, and vacuum properties. The substrate material must be electrically conductive for resistively heated needle sources, and be readily machined or etched into sharp tips. The structure must have sufficient mechanical strength to tolerate electric fields of the order of tenths of volts per angstrom. If the substrate is too brittle, as is the case for many fine glassy needles, it may not survive wetting and assembly operations. The coefficient of thermal expansion of the substrate and its ability to withstand temperatures near 1000 K must be adequate to prevent thermal drift in the focusing column. The substrate must be easy to clean in order to elicit consistent wetting by the alloy. For example, it is well-known that oxide formation which forms on exposure of metallic substrates to atmosphere can dramatically affect the contact angle /4/. Auger studies we have performed on many commercially produced refractories such as W and Re showed significant concentrations of surface impurities even after high temperature thermal annealing. Finally, the LMIS should be able to function effectively in less than ultra-high vacuum conditions.

8. Congruent Ion Formation. Eighth, the existence of congruent ion formation is an important requirement for a LMIS. Congruent ion formation means that the stoichiometry of the beam reflects the stoichiometry of the liquid alloy producing the ions. A noncongruent ion forming LMIS will not operate for the following reasons: (1) a highly noncongruent ion beam will lead to local concentration gradients near the emitter apex causing local solidification of the LMIS; (2) a moderately noncongruent ion beam will gradually alter the source reservoir composition and ultimately result in (1); (3) concurrent with (1) and (2), a noncongruent ion forming LMIS source may exhibit a beam stoichiometry unacceptably low in the ion species of interest.

It is clear that a stable, long lived LMIS must exhibit congruent or near congruent ion formation. Assuming a field evaporation mechanism for ion formation, the activation barrier for field evaporation  $Q(F)$  may be written as:

$$Q_i(F) = I_i - W + H_i - f(F)$$

where  $I_i$  is the first ionization potential of the  $i$ th evaporating species,  $W$  is the surface work function,  $H_i$  is the vaporization energy of the  $i$ th evaporating species, and  $f(F)$  depends on the details of the evaporation model /5,6/. For the case of a binary alloy of components A and B operating as a LMIS, it may be shown /7/ that the expression  $Q_A - Q_B = 0$  provides a measure of the congruency of ion formation. If one assumes that both alloy components experience the same work function and that  $f_A(F) \sim f_B(A)$ , which is approximately true for the image hump model, then the requirement that

$$I_B - I_A + H_B - H_A = 0$$

must be satisfied for congruent ion formation. This expression places a fundamental requirement on the ionization and vaporization energies of the alloy components

TABLE I

Alloy and Beam Compositions for Various Alloys at 20  $\mu$ A Total Current

Alloy Composition/ Substrate	Beam Composition
Pd. <sub>73</sub> B. <sub>27</sub> /Si-C	Pd. <sub>77</sub> B. <sub>17</sub> Si. <sub>06</sub>
Pt. <sub>72</sub> B. <sub>28</sub> /Re	Pt. <sub>89</sub> B. <sub>11</sub>
Au. <sub>87</sub> Si. <sub>13</sub> /W*	Au. <sub>89</sub> B. <sub>11</sub>
Y. <sub>62</sub> Ni. <sub>22</sub> B. <sub>15</sub> /Re	Y. <sub>69</sub> Ni. <sub>308</sub> B. <sub>002</sub>

\*Indicates alloy with minimal substrate/  
alloy interdiffusion and near congruent  
ion formation.

TABLE II

Summary of Heats of Vaporization  
(at 1300 K) H and Ionization  
Potentials I for Various Elements

Element	H (eV)	I (eV)	H + I (eV)
Be	3.45	9.32	12.77
Au	3.37	9.18	12.55
B	5.7	8.26	12.96
Ni	4.21	7.60	11.81
Pd	3.66	8.30	11.96
Pt	5.54	8.88	14.42
Si	4.57	8.12	12.69
Y	3.91	6.5	10.41

In Table II are listed the values of I + H for various elements where H is the heat of vaporization at 1300 K of the pure elements. The energetics of the field evaporation mechanism require that H should be taken from the alloy and not from the pure elements. However, as a first approximation, we can estimate the compatibility of various alloy combinations with respect to congruent ion formation based on the Table II values. On this basis, the model predictions for various combinations of the difference in the Q-values must be satisfied. Those alloy combinations indicated by \* in Table III give values of  $Q_A - Q_B$  nearest to zero and therefore might be expected to show near congruent ion formation. On this basis, the only promising alloy combination for a source of B is the PtB alloy system. As a source of Be and Si, the AuSiBe is predicted to be a promising alloy combination.

Several of the Table III alloy combinations have been investigated for their potential as LMIS. The results of these investigations are given in Tables I and IV. Table I compares the stoichiometries of the beam with that of the alloy. The predictions of the field evaporation model are generally followed. For example, the YNiB alloy does not provide any B in the beam as expected. On the other hand, the PtB alloy is both stable and near stoichiometry. The somewhat lower ratio of B/Pt in the beam compared to the original alloy is due to loss of B by diffusion into the Re substrate.

The PdB and NiB alloy are not expected to be good sources of B. Although the B/Pd ratio in the beam does not differ from that of the alloy as much as the YNiB alloy, it has very little  $B^+$  in the beam as shown in Table IV. Most of the B in the beam is tied up as  $PdB^+$ . Since we have no values for H or I for PdB, the model cannot be used to evaluate this possibility. Nevertheless, the favorable formation of  $PdB^+$ , while it can help to maintain congruent field evaporation and a smooth running source, is of little use in providing a large fraction of  $B^+$  in the beam.

The AuSi alloy forms Au and Si congruently in the beam as predicted by the model. Thus, with the limited results available at this time, it appears that the field evaporation model using the values of H of the pure elements, rather than the more appropriate values of H from the respective alloys, gives a first order basis for selection of compatible alloy combinations for LMIS.

### 9. Favorable Electron Optical Characteristics

Assuming it has been possible to satisfy the material and congruency requirements listed above, it is still possible for the LMIS to fail by way of inadequate electron optical properties. For focused beam and implantation applications, it is

TABLE III

Model Predictions for Various Alloy Combinations

Alloy (AB)	$Q_B - Q_A$ (ev)
BNi	-2.15
BPd	-2.00
BPt	0.46
BeAu*	-0.22
SiAu*	-0.14
AuSiBe*	
BeAu	-0.22
BeSi	-0.08
SiAu	-0.14
YNiB	
BNi	-2.15
BY	-3.55
NiY	-1.40

\*Near congruent ion formation expected

TABLE IV

% Abundance of Various Elements in the Beam at 20 microamps for a Pd<sub>72</sub>B<sub>28</sub> LMIS on Si/Carbon (T = 1165 K)

		%	
Pd <sup>+</sup>		66.9	
PdB <sup>+</sup>		16.2	
Pd <sup>++</sup>		6.4	
B <sup>+</sup>	Total Pd	3.7	77.4
Si <sup>++</sup>		3.7	
Pd <sub>2</sub> B <sup>+</sup>	Total B	1.7	16.5
Si <sup>+</sup>		1.2	
Pd <sub>2</sub> B <sup>+</sup>	Total Si	.3	6.0
BO <sup>+</sup>		.2	
PdSi <sup>+</sup>		.2	
Si <sub>2</sub> <sup>+</sup>		.17	
B <sup>++</sup>		.01	

necessary for the source to have a small virtual source size and high angular intensity. Further, the relative intensities of the various ion species must be favorable and exhibit low energy spreads.

### III - Conclusions

In view of the numerous and often conflicting requirements for liquid alloy ion sources, it is remarkable that sources may be developed which satisfy many of these requirements to a high degree.

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