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The surface of liquid dilute metal alloys in vacuum

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Abstract. We report work-function measurements and Auger spectroscopy of liquid gallium–aluminium alloys which indicate that the surfaces of liquid dilute alloys can have an instability in vacuum less than ultra-high that is quite distinct from normal surface oxidation. The solute (aluminium) continuously diffuses to the surface where it oxidises to form an insoluble oxide. Even in very dilute liquid alloys the surface eventually becomes covered in a layer of the oxidised solute, so the surface properties are unlike those of either the solute metal or its oxide. This may explain some anomalies that have been obtained in the surface properties of liquid alloys.

1. Introduction

We have been studying the behaviour of liquid metal alloys in vacuum because we have found low-melting-point liquid metals, such as mercury, gallium and indium, useful in the study of the contact charging of insulators by metals (El-Kazzaz and Rose-Innes 1987). In an extension of this work we proposed to use liquid alloys of these metals in order to provide a range of liquid metals† of different work functions. This paper reports some unexpected properties of these liquid metal alloys. Most of the results reported in this paper concern liquid alloys of gallium, because our previous experiments had shown gallium (melting point 30 °C) to be a particularly useful contactor in contact charging experiments.

2. Experimental details

2.1. Specimens

The gallium used was specified as being of 99.9999% purity. The very dilute alloys referred to in section 3 were made by mixing previously diluted gallium alloys with appropriate amounts of pure gallium.

† To avoid tedious repetition, we shall use the general term ‘metal’ to cover both pure metals and alloys.

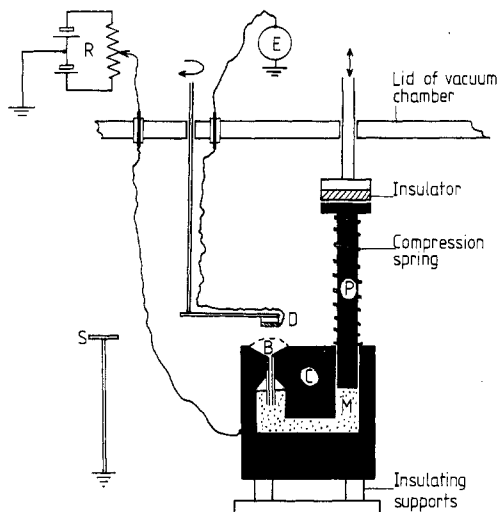


Figure 1. The apparatus.

2.2. Apparatus

All experiments, unless otherwise stated, were carried out in a vacuum of about 10^{-5} Torr.

The liquid alloys were manipulated in vacuum by the method (Lederman 1981) we have used in previous experiments (El-Kazzaz and Rose-Innes 1987), and the essential features of the apparatus are shown in figure 1. The liquid metal M is normally held in a heated graphite crucible C (graphite is insoluble in gallium). The temperature of the crucible is maintained (typically at 50°C) by an electric heater and thermistor thermometer connected into a servo-circuit. When a measurement is to be made the plunger P is depressed, forcing the liquid up through the narrow 1 mm tube to form a blob, B, which is the specimen, on top of the crucible. This procedure gives a specimen with a fresh bright, shiny surface. When the measurement is finished the liquid is withdrawn into the crucible by raising the plunger.

The work function of the liquid metal specimen B is measured by a variant of the Kelvin method. An insulated metal disc (D, figure 1) is attached to a rotatable arm so that it can be positioned either over the liquid metal specimen B or over an earthed stainless steel plate S. The disc is connected to one input terminal of an electrometer voltmeter E, the other input terminal of which is earthed. An adjustable DC voltage V is applied between the insulated crucible (i.e. effectively to the liquid metal specimen) and earth by means of the potentiometer R. V is adjusted until there is no net deflection of the electrometer when the disc is swung from the liquid metal to the reference plate, in which case Vq (q is the electronic charge) equals the amount by which the work function of the specimen differs from that of the stainless steel reference plate. (To save tedious repetition we shall in this paper use the expression 'relative work function' to mean the work function of the specimen relative to that of our stainless steel reference.)

The disc D is cut from the same sheet as the reference plate S. The fact that D and S are the same material ensures that any difference in capacity when D is over B and when it is over S does not affect the determination of the work function of B relative to S.

The apparatus was tested by placing a stainless steel disc, cut from the same sheet as the reference plate, where the specimen B normally sits. We observed that, as expected,

when the applied voltage V was set to zero, there was no net deflection of the electrometer when D was swung from B to S .

3. Initial experiments

In order to avoid damaging the insulator in the contact-charging experiments, we need to restrict ourselves to alloys with a melting point less than about 160°C . However, phase diagrams of binary alloys (see, for example, Smithells 1976) show that the melting point usually rises very rapidly with increasing concentration of solute, so the range of liquid alloys available with a melting point below 160°C is rather limited. One suitable alloy is gallium–aluminium which remains liquid below 160°C up to a concentration of about 22 at.% aluminium.

When small amounts of aluminium were dissolved in gallium we found that the relative work function of the liquid alloy and the contact charge it deposited on corundum were indeed different from those of pure liquid gallium. However, to our surprise, the substantial change in the contact charging and work function was independent of the concentration of aluminium even down to low concentration; see table 1.

Table 1. Measured work function, relative to that of stainless steel, of pure liquid gallium and liquid gallium–aluminium alloys 15 seconds after exposure (further exposure up to 90 minutes produces no significant change in these values).

Aluminium content (at. %)	Work function relative to that of stainless steel (eV)
0	-0.42 ± 0.02 at atmospheric pressure
0	-0.29 ± 0.03 at 10^{-5} Torr
1.3	-0.90 ± 0.02
2.6	-0.90 ± 0.04
5.3	-0.82 ± 0.02
10.8	-0.90 ± 0.02

} at 10^{-5} Torr

Because there must be *some* minimum concentration of solute which changes the properties of the liquid metal, we next prepared even more dilute alloys. We found that the relative work function of these decreased with time, all eventually reaching the same limiting value of about -0.90 eV (figure 2).

Finally, it can be seen from table 1 and figure 2 that the relative work function of pure gallium was -0.29 eV when measured in a vacuum of 10^{-5} Torr and -0.42 eV when measured in the laboratory atmosphere. In both cases the work function did not vary significantly with time.

4. Discussion of preliminary results

We thought that an explanation for the behaviour described in the previous section might be as follows. In a liquid alloy the solute atoms are, unlike those in a solid alloy,

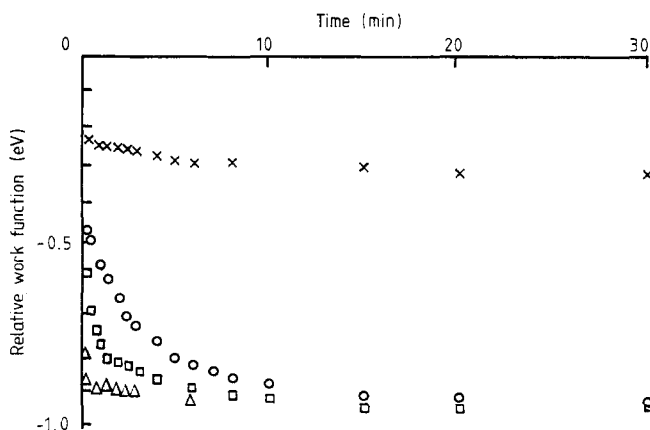


Figure 2. Variation with time of relative work function of very dilute liquid gallium–aluminium alloys at a pressure of 10^{-5} Torr. Δ : 0.26 at.% Al; \square : 0.010 at.% Al; \circ : 0.0052 at.% Al; \times : pure gallium.

mobile and can in time migrate to the surface. In a vacuum of 10^{-5} Torr the bombardment of the surface by residual gas atoms is sufficiently intense, about 10^{13} collisions $\text{mm}^{-2} \text{s}^{-1}$, to give a high probability of oxidising solute atoms arriving at the surface. In a time depending on the concentration of the solute, the surface will become covered in a layer of insoluble oxidised solute, so the work function of the surface will always tend to the same value, i.e. that of the oxidised solute. This explanation is supported by the fact that the -0.90 eV relative work function to which the liquid gallium–aluminium alloys tend is nearly the same as what we measure for the surface of solid aluminium (-0.88 ± 0.02 eV) which, of course, is covered by an aluminium oxide layer.

5. Confirmatory surface analysis experiments

We tested our hypothesis for the work-function changes of our dilute alloys by examining their surface composition by Auger spectroscopy which reveals the surface composition averaged over a depth of about 6 nm. The metals were introduced into the spectrometer in solid form and then melted after the pressure had been reduced to 10^{-9} Torr.

Figure 3(a) shows the differentiated Auger spectrum of a sample of pure gallium whose surface after melting had been etched by argon ion bombardment to produce a fresh surface, simulating that produced in the work-function measurements by forcing the liquid metal through the narrow tube. There is a strong gallium peak and a weak oxygen peak suggesting a metal surface with only a little oxide on it. The liquid gallium was then exposed to an air pressure of 10^{-5} Torr for four minutes (2400 L) and the Auger spectrum taken again. The exposure was found to have made no discernible difference to the spectrum, which is consistent with our observation that the work function of a fresh liquid gallium surface changes very little in a vacuum of 10^{-5} Torr (figure 2). Subsequent exposure of the liquid gallium to the laboratory atmosphere resulted in a great increase in the oxygen peak, and subtraction of the first spectrum from the second showed that a component of the gallium peak had shifted by -6 eV, a chemical shift characteristic of oxidised gallium. These results seem consistent with our interpretation

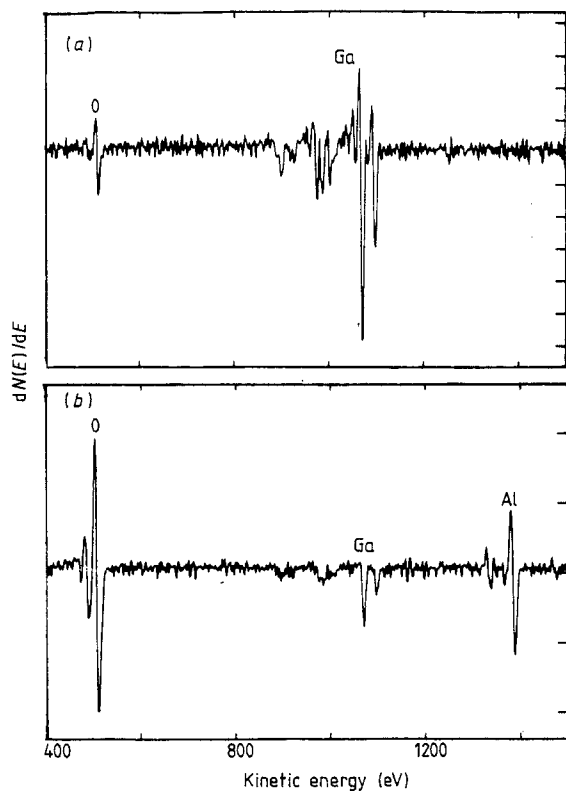


Figure 3. Auger spectra (differentiated, N = number of counts, E = energy). (a) Liquid gallium whose surface has been ion etched. (b) Liquid gallium—0.26 at. % aluminium alloy exposed to 10^{-5} Torr for one minute.

that a liquid gallium surface oxidises only extremely slowly (i.e. in a time long compared to the duration of our experiments) in a vacuum of 10^{-5} Torr. (It must be remembered that atmospheric pressure is about 10^8 times greater than 10^{-5} Torr, so an oxidation completed in, say, one second at atmospheric pressure could take about three years at 10^{-5} Torr!) These results also seem consistent with our observation (section 3) that the relative work function of liquid gallium is different when measured in vacuum and when measured in air, but that it is independent of time in both cases (presumably in air the gallium surface had fully oxidised before we had time to make the first measurement).

We next examined the Auger spectra of the surfaces of our gallium–aluminium alloys. A specimen of solid Ga–0.26 at. % Al was the first to be analysed. A small area ($\sim 10 \text{ mm}^2$) of its surface was abraded with abrasive paper, and the unabraded and abraded surfaces were examined in the spectrometer. The spectrometer cannot detect less than about 1% of aluminium in gallium; nevertheless the Auger spectrum of the unabraded surface showed aluminium peaks, characteristic of oxidised aluminium, and also oxygen peaks of comparable intensity to the gallium peak. However, the spectrum of the abraded area revealed much reduced aluminium and oxygen peaks and an increased gallium peak. This suggests that, during preparation of the specimen, there had been segregation of the aluminium to the surface, where it had oxidised.

The specimen was then melted in the vacuum chamber and after about one minute's exposure to $\sim 10^{-5}$ Torr pressure (600 L) the Auger spectrum on the abraded area, which was still clearly visible, was recorded. We found that the aluminium and oxygen peaks had greatly increased and the gallium peak greatly decreased (figure 3(b)). This suggests

that in the liquid state the aluminium solute had come to the surface where it had oxidised to form a surface layer of aluminium oxide.

The differentiated gallium peak in figure 3(b) has a greatly reduced peak-to-trough ratio compared to that in figure 3(a). This results from electron scattering reducing the change in gradient on the low-kinetic-energy side of the peak, and indicates that a large proportion of the gallium is below, rather than at, the surface (Tougaard 1986, Langeron *et al* 1984). This is further evidence for the enrichment of aluminium at the surface.

6. Discussion and conclusions

Both the work-function result, i.e. that even minute quantities of aluminium dissolved in liquid gallium can change the work function from that of gallium to that of aluminium oxide, and the subsequent Auger spectra measurements are consistent with the following interpretation. Although at the temperature (50 °C) at which the experiments were carried out aluminium is soluble in gallium, in the liquid alloy the solute atoms are mobile and aluminium atoms will constantly be arriving at the surface. In a vacuum of 10^{-5} Torr some of these will be oxidised to form aluminium oxide which is insoluble in the liquid gallium, and so a surface layer of aluminium oxide will be built up. This layer will form even in a very dilute alloy because there is a continuing supply of aluminium atoms to the surface, though, of course, in more dilute solutions the surface layer takes longer to form (see figure 2). The fact that the relative work function for our alloys asymptotically approaches -0.90 eV suggests a complete coverage of the surface by aluminium oxide which will occur long before all the Al has left the bulk liquid. (For our most dilute specimen, if all the Al went to the surface and became oxidised, the resulting aluminium oxide layer would be about $2 \mu\text{m}$ thick—which seems improbable. For our more concentrated alloys the aluminium oxide layer would be even thicker.) The gradual change of relative work function from the initial to the final value could be due either to increasing coverage of the surface by aluminium oxide film, or build-up of a continuous film to a limiting thickness. We must emphasise that this situation is quite different from that of dilute *solid* solutions where the solute atoms are much less mobile within the bulk and any oxidation of the surface would be almost entirely that of the host metal. However, some segregation of solute atoms to the surface as a result of their oxidation has been observed in solid Ni–Zr alloys (Walz *et al* 1989) but in this case, the increase in solute (Zr) concentration at the surface amounted to only about 30% whereas in our case, the increase is of many orders of magnitude. It is also different from the thermodynamically stable situation where the free energy of the solute atoms may be lower near the surface, resulting in an increased concentration at the surface. Our mechanism is a dynamic one in which the *oxidation* of solute atoms arriving at the surface to form an insoluble oxide coating plays an essential role.

The effect of this dynamic surface process is that dilute alloys of aluminium in gallium are initially unstable in vacua that are less than ultra-high; even in very dilute alloys a surface layer of oxidised solute grows at the expense of the aluminium in solution until a stable condition is reached where the surface is covered by aluminium oxide.

Although our measurements have been confined to solutions of aluminium in gallium, there seems no reason why some other liquid alloys should not suffer the same instability in vacuum. This may explain some of the anomalies that have been observed in measurements of the surface properties, such as work function and contact charging, of liquid alloys (Harper 1967).

References

- El-Kazzaz A M and Rose-Innes A C 1987 *J. Phys. D: Appl. Phys.* **20** 1616
Harper W R 1967 *Contact and Frictional Electrification* (London: Oxford University Press) p 318
Langeron J, P, Minel L, Vignes J L, Bouquet S, Pellerin F, Lorang G, Aillourd P and Le Héricy J 1984 *Surf. Sci.* **138** 610
Lederman A 1981 *Solid State Technol.* **24** 123
Smithells C J 1976 *Metals Reference Book* (London: Butterworths) p 403
Tougaard S 1986 *Surf. Interface Anal.* **8** 257
Walz B, Oelhafen P and Güntherodt H-J 1989 *Appl. Surf. Sci.* **37** 337