

Surface and grain boundary wetting of Fe based solids by molten Pb and Pb-Bi eutectic

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Surface and grain boundary wetting and penetration of pure Fe and a martensitic steel by Pb and Pb-Bi eutectic alloys were studied by the sessile drop and dispensed drop techniques at different temperatures (400–900°C) and times (up to 30 h). By using two different atmospheres—high vacuum and a He-H₂ gas—and different heat treatments, wetting was studied for both oxidized and deoxidized solid substrates.

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1. Introduction

The interfaces between low melting point liquid metals such as Pb, Sn, Bi etc. and high melting point metals and alloys play an important role in different processes of practical interest such as soldering in microelectronics, hot-dip metallic coating of steel or heat transfer by liquid metals in nuclear reactors. Increased interest has been shown recently in liquid metal (LM)—solid metal (SM) systems due to active international efforts to develop new safer nuclear reactors. In some of these applications (heat exchangers using liquid metals), an important factor for the lifetime of the solid is grain boundary wetting and penetration by the LM. Both surface wetting and grain boundary penetration depend critically on the surface chemistry of the solid. For instance, oxide layers on metallic solids are known to act as barriers to surface wetting [1].

In the present study, surface and grain boundary wetting and penetration of Fe and a martensitic steel by Pb and Pb-Bi eutectic alloys were investigated using the sessile drop and dispensed drop techniques, varying the temperature (400–900°C) and the time (up to 30 h) in conditions in which the surface oxide layer could be removed from the solid substrates.

2. Experimental procedure

Two polycrystalline substrates were used: high purity iron (99.99%) and the martensitic stainless steel T91, which contains 8.98% Cr, 0.96% Mo, 0.39% Mn, 0.35% Si, 0.19% V, 0.13% Ni and 0.09% C. After polishing with diamond paste up to 1 μm granularity, the average surface roughness R_a of the substrates was a few nm. XPS analysis revealed that with this preparation the steel and iron surfaces were covered by an oxide layer about two nanometers thick. High purity (99.999%) Pb and Pb-55.2%Bi eutectic (total amount

of impurities less than 10 ppm) were used for the experiment.

Wetting was studied by the sessile drop technique as well as its variant, the “dispensed drop” technique. The sessile drop experiment involved placing a sample of Pb or Pb-Bi on an iron or steel substrate in the isothermal zone of the furnace. The substrate itself was placed on an alumina plate. For the high vacuum experiment, in order to limit pollution of the furnace by evaporation of Pb or Bi during temperature rise, the sample on the steel substrate was placed under a quartz cap with polished bottom edges. In order to evacuate the air in the cap through the micron-size capillaries formed between the quartz edges and alumina plate, the furnace chamber was pumped for 12 h before heating.

The dispensed drop experiment involved heating the fusible metal separately in an alumina crucible. Once the experimental temperature was reached, the liquid was extruded from the crucible, then the whole capillary introducer and the alloy droplet descended so as to initiate contact between the lower surface of the droplet and the substrate. Thereafter, complete transfer of the drop to the substrate took place and spreading continued in the classical sessile drop configuration. The height of droplets generated by this method is close to one mm.

Experiments were performed in a metal furnace under high vacuum (2×10^{-6} Pa at room temperature) or in three types of static atmospheres at $P \sim 1$ atm: (i) technical purity helium (<3 ppm H₂O, <2 ppm O₂), (ii) helium purified by passing it through a bed of Zr-Al getter before introduction into the furnace and (iii) He-8 vol.%H₂ (<0.4 ppm H₂O, <0.1 ppm O₂) purified by passing it through a cartridge with activated carbon cooled with liquid nitrogen.

After cooling, selected samples were cut perpendicular to the former solid-liquid interface, ground and polished with alumina suspension up to 0.3 μm. SEM was used to determine the shape of the grain boundary grooves developed at the solid/liquid interface.

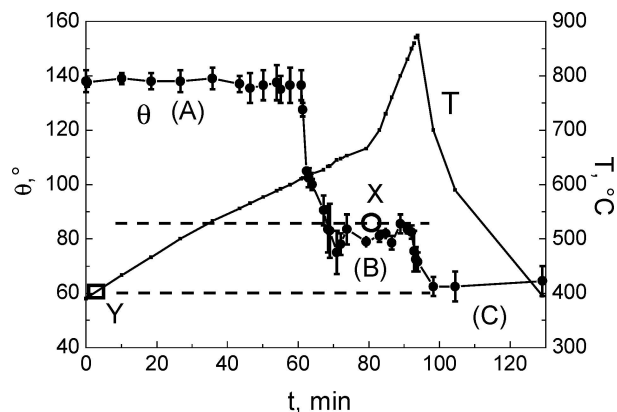


Figure 1 Contact angle of a sessile drop versus time during a temperature cycle for molten Pb-Bi on T91 steel substrate in high vacuum. The point designed by a circle was obtained by depositing a drop after heat treatment of substrate at 790°C and the point designed by a square by depositing a drop at 400°C after heat treatment at 850°C.

3. Results and discussions

3.1. Surface wetting

As reported in the previous section, at room temperature the stainless steel surface was covered by an oxide layer a few nanometers thick. It is well known from brazing technology [2] that stainless steels can be deoxidized by heating at high temperatures (typically 900°C and more) under high vacuum, which favours the elimination of volatile oxides (CO) formed by reduction of Cr_2O_3 by C contained in the steel.

Fig. 1 shows the change with time in the contact angle of a Pb-Bi drop on a T91 steel substrate during a continuous rise in temperature up to 800°C in a sessile drop experiment performed in high vacuum. All the contact angles are advancing ones as they were obtained during an increase in the drop base diameter. The results are very similar to those obtained previously for pure Pb on a stainless steel with a composition close to the composition of T91 [3]. By analogy with [3], we attribute the contact angle at low temperatures (domain A) to oxidation of the liquid metal. The contact angle at intermediate temperatures (domain B) is for deoxidized Pb-Bi alloy on oxidized steel, and only the contact angles at $T > 830^\circ\text{C}$ (domain C) are for deoxidized Pb-Bi on a deoxidized steel surface. When the dispensed drop method is used, the oxide skin on the liquid metal is broken during drop extrusion through the capillary. According to our interpretation of the three wetting domains, the breaking of the oxide skin on the alloy would suppress the large non-wetting contact angles observed in domain A and in high vacuum experiments would lead to contact angles that would depend only on the prior heat treatment of the steel. This is confirmed by the results in Fig. 1: after heat treatment of steel at 850°C in vacuum, the contact angle measured at a lower temperature is 60°, very close to the contact angle of domain C. After heat treatment of the substrate in vacuum at 790°C, i.e. at a temperature lower than the temperature needed to deoxidize the steel, the contact angle of a Pb-Bi drop on steel at a lower temperature is 85°, which is typical of domain B.

Note that unlike the decomposition of the oxide layer on the steel surface, which was achieved only in high

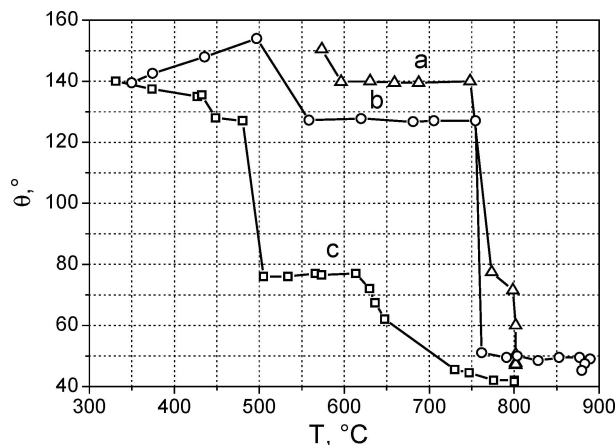


Figure 2 Contact angle of Pb on pure iron versus temperature in commercial He (a), purified He (b) and He-H₂ (c). Continuous heating with 1000°C/h (a, b) and 200°C/h (c).

vacuum, the oxide layer on the pure iron surface was also removed by heating under inert or reducing gas atmospheres. This is clearly shown by the curves in Fig. 2 obtained with pure Pb during a continuous increase of T in different gas atmospheres. Whatever the gas, at $T > 800^\circ\text{C}$ the contact angles are typical of low miscibility metallic systems [1]. The measured θ values of 40–50° are in good agreement with the values found for the same system by Popel *et al.* [4] (40° at 370°C in H₂) and by Gomez *et al.* [5] (53° at 750°C in Ar-H₂). In Fig. 2 the high obtuse contact angles at low temperatures are for oxidized Pb while the intermediate temperature plateau, corresponding to deoxidized Pb on oxidized iron, is clearly seen in the case of He-H₂ gas and still distinguishable in the case of He. To measure the Pb contact angle on iron at low temperature (400°C) in the absence of oxide films, several dispensed-drop experiments were performed after *in situ* heat treatment of the substrate in He-H₂ or in high vacuum at 850°C. Contact angles in the range 45–50° were found, which are very close to the values measured at high temperatures.

Wetting of pure iron by Pb-Bi eutectic was very similar to wetting by pure Pb. The contact angle of deoxidized Pb-Bi alloy on deoxidized Fe at 800°C was $50 \pm 5^\circ$. Note that the same contact angle (53°) was reported for pure Bi on iron at 910°C in H₂ atmosphere [6]. At 500°C in H₂ a contact angle much higher than 90° was found in [6], which clearly corresponds to wetting of oxidized surfaces.

The similar θ values measured on clean iron surfaces for clean Pb and Pb-Bi droplets are due to the resemblance of interactions of Pb and Bi with iron. Neither of the metals forms intermetallics with iron, and the solubility of iron in liquid Pb-Bi is very close to the solubility in liquid Pb (30 ppm and 7 ppm at 700°C correspondingly [7]).

3.2. Grain boundary wetting

SEM examination of the Pb (or Pb-Bi)- deoxidized iron (or steel) interfaces held at 400°C for several hours did not reveal any reactivity and the interface appeared

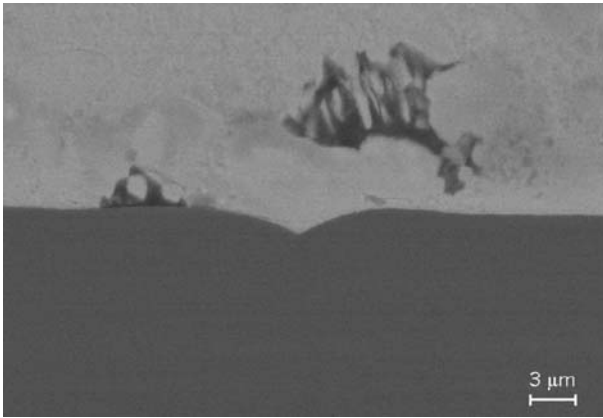


Figure 3 SEM micrography of a Pb-Bi/solid Fe GB groove after 20 h at 800°C.

flat at the scale of 0.1 micron. For this reason the next experiments were performed at 700 and 800°C. Before contact, the substrate surface was deoxidized by heat treatment in high vacuum at 850°C. Then the droplet was deposited *in situ* on the substrate and He-H₂ gas was introduced in the furnace in order to limit metal evaporation during the subsequent long-time holding.

Grain boundary (noted in the following GB) grooves formed on the intersection of GB planes with the solid-liquid interface were observed with SEM on sections normal to the interface. Similar GB groove shapes were obtained with Pb and Pb-Bi on pure iron. Most of the grooves are convex and smooth with no facets on the groove walls, which testifies to weak anisotropy of solid/liquid interfacial energy (Fig. 3). Neither of the liquids wetted the GBs, the dihedral angle lying between 85° to 150°. The most frequently observed angle is in both cases 120–130° (Fig. 4b). The only significant difference is in the groove depth: grooves formed in contact with Pb-Bi eutectic are deeper than that in the Pb/Fe system (Fig. 5).

According to Mullins [8] grooving is driven by differences in curvature at the SL interface leading to a transfer of solid atoms from regions of high curvature near the groove root to regions of small curvature far from the root. If the grooving kinetics are limited by volume diffusion of solid atoms through the liquid, the grooves deepen and widen with time according to a $t^{1/3}$ law (the time exponent is $\frac{1}{2}$ when groove growth is controlled by the dissolution—reprecipitation process

at the interface and $\frac{1}{4}$ when the limiting step is interfacial diffusion):

$$w/5 = d \cdot tg \frac{\phi}{2} = 1.01(At)^{1/3}, \quad (1)$$

where A is a rate constant, ϕ is dihedral angle, w is the width and d the depth of the groove. The rate constant is a function of the equilibrium concentration of solid in liquid C_0 , interfacial energy σ_{sl} , molar volume of solid V_m and the diffusion coefficient of solid atoms in liquid phase D :

$$A = \frac{C_0 \sigma_{sl} V_m^2 D}{RT}. \quad (2)$$

Experimentally, groove widths are difficult to measure accurately on metallographic sections. Groove depths can be measured much more accurately but they present a wide distribution of grooves due to differences in GB energies in polycrystalline specimens caused by misorientation effects, as shown in [9]. However from Equations 1 and 2 it follows that the product $d \cdot tg \frac{\phi}{2}$, called “reduced width” w^* in [9], is not a function of GB energy and should be constant for a given sample. This is confirmed by the distribution of w^* values exhibiting a sharp maximum in contrast with the distribution of depths (Fig. 4).

In Fig. 5, reduced width w^* values measured in the Pb/Fe system are plotted versus the cubic root of time. Data for 2 h taken from [10] fit well to our experimental points. The straight line in Fig. 5 indicates that grooving kinetics is limited by volume diffusion, in agreement with previous studies [10, 11].

As mentioned above, the grooves formed in contact with Pb-Bi eutectic are significantly deeper than in the Pb/Fe system (Fig. 5). Indeed the experimental value of the grooving rate constant A_{exp} for Pb-Bi eutectic at 800°C was found to be $(1.7 \pm 0.6) \times 10^{-22} \text{ m}^3/\text{s}$, five times higher than the value $(3 \pm 1) \times 10^{-23}$ found for Pb/Fe. Examination of Equation 2 indicates that this difference is mainly caused by the difference, by a factor 4.6 [7, 12], in the values of C_0 . Taking for molten Pb-Bi/solid Fe $\sigma_{sl} \cong 0.5\text{--}1 \text{ J/m}^2$ [15], the diffusion coefficient evaluated from A_{exp} lies between $2 \times 10^{-9} \text{ m}^2/\text{s}$ and $4 \times 10^{-9} \text{ m}^2/\text{s}$, in good agreement with the experimental value $D = 2.9 \times 10^{-9} \text{ m}^2/\text{s}$ [13]. This agreement confirms that even if convection

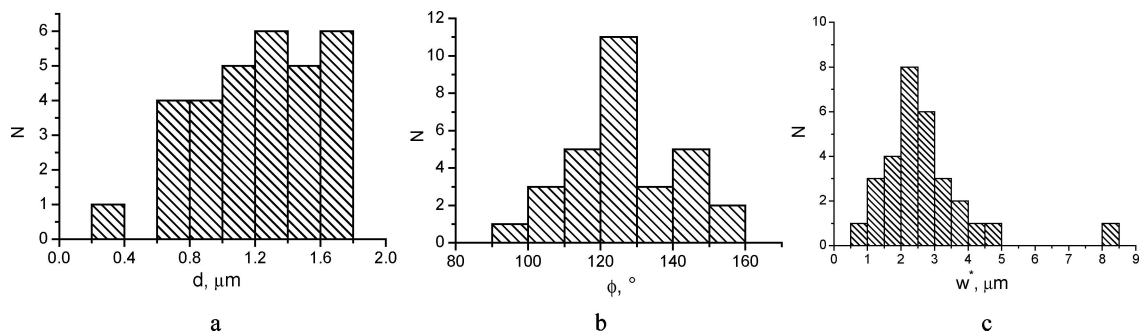


Figure 4 Pb-Bi/Fe system after 20 h of contact at 800°C. Distribution histograms for GB groove depth d , dihedral angle ϕ and reduced width $w^* = dtg(\phi/2)$ (c).

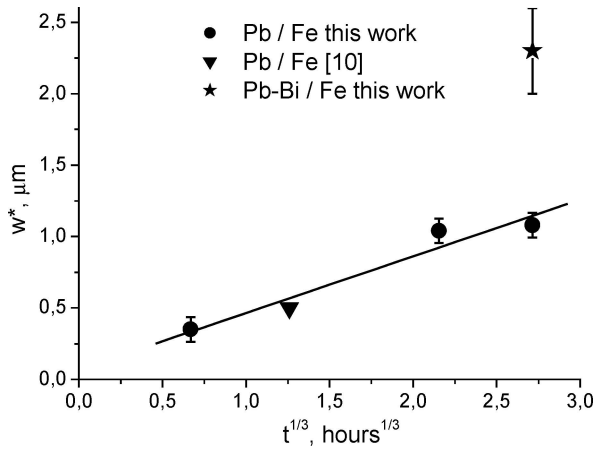


Figure 5 Reduced groove depth w^* versus cubic root of time in Pb/Fe and Pb-Bi/Fe at 800°C.

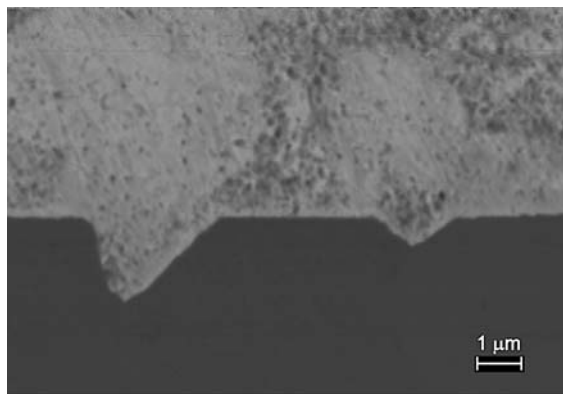


Figure 6 SEM micrography of GB grooves formed on liquid Pb-Bi/T91 steel interface at 700°C after 30 h.

can affect the mass transport in the liquid near the grooves, this effect is weak and transport is essentially diffusive.

GB grooving experiments in the Pb-Bi/stainless steel system, performed in He-H₂ atmosphere after achieving intimate contact of the liquid alloy with the steel substrate, showed that a limited number of grooves are non-faceted with dihedral angles higher than 90°. However the majority of grooves at 700–800°C are faceted and do not present the characteristic maxima resulting from redeposition of solid material on the flat solid-liquid interfaces on both sides of the grooves (Fig. 6). Moreover, the distributions of groove depths show widening with time, as can be clearly seen for the 30 h holding time (Fig. 7). This is an indication of a high difference in grooving rate for different GB grooves. We attribute the drastic change in GB groove morphology compared with the Pb-Bi/Fe system to the presence in the steel of a significant amount of chromium and to its interaction with oxygen. Chromium oxides are much more stable than iron oxides. Thus reoxidation of the substrate at the interface can occur even under He-H₂ atmosphere, as evidenced by the change in colour of the steel free surface after the experiment. An oxide layer at the interface could significantly decrease the dissolution rate and cause changes in the GB grooving mechanism from volume diffusion controlled (Pb-Bi/Fe) to interface controlled [14].

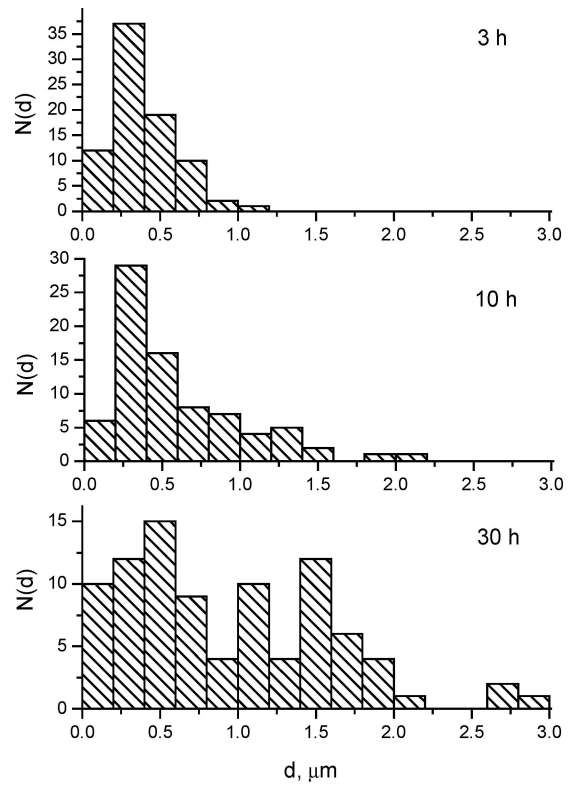


Figure 7 Distribution histograms of groove depths after 3, 10 and 30 hours exposure of T91 steel to Pb-Bi melt at 700°C.

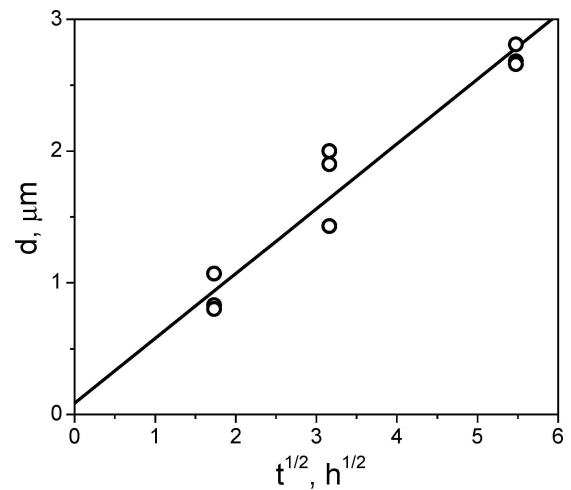


Figure 8 Groove depth vs. square root of time for Pb-Bi/FeCr system at 700°C. For each time the three deepest grooves are given.

Given the absence of a maximum on the histogram for $t = 30$ h in Fig. 7, it is difficult to interpret the grooving kinetics in this system quantitatively. Nevertheless, for semiquantitative analysis of the grooving kinetics, the depths of the 3 deepest grooves were plotted vs. exposure time (Fig. 8). Maximum penetration depth increased according to a $t^{1/2}$ law. Such a kinetic law is in agreement with a mechanism that assumes the process at the interface to be the limiting factor of GB grooving [8].

4. Conclusions

As expected for liquid metal on solid metal systems, Pb and Pb-Bi eutectic wet deoxidized surfaces of Fe

(contact angles in the range 40–50°) and martensitic steel (contact angles 60–65°). The effect on these contact angles of temperature between 400 and 900°C is very weak. A less expected result was that the contact angles of Pb and Pb-Bi liquid on thin oxide layers formed on Fe and steel substrates in low P(O₂) environments were close to or lower than 90°. Such oxide layers are therefore not really protective: the liquid can penetrate defects in the oxide film (pores, microcracks. . .) and establish direct contact with the solid.

The grain boundaries of Fe and martensitic steel are not wetted by Pb and Pb-Bi alloys, the dihedral contact angle being in the range 100–130°. The groove deepening rate is controlled by volume diffusion in the molten metal in the case of Fe, while in the case of steel the controlling step seems to be the process at the solid/liquid interface.

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