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Wetting of W by liquid Pb and PbLi alloys and surface interactions

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Abstract

Wetting of W by Pb and Pb–17 at.%Li in the range 400–900 °C is studied by the dispensed drop technique. Experiments are performed using different furnace atmospheres (high vacuum, reducing gas) and different heat treatments to achieve W deoxidation. A simple pairwise model is used to explain the relation between surface interaction, which is responsible for wetting, and bulk interactions determining miscibility.

1. Introduction

The main requirement for containers materials used for liquid metals is negligible reactivity. In the case of metals with low or moderate melting point such as Sn, Pb, Ag or Au, this condition is satisfied by several non-metallic materials such as iono-covalent oxides (alumina, magnesia, etc.) and graphite. With these ceramics, non-wetting (i.e. a contact angle $\theta > 90°$) is observed [1,2]. This is interesting in many applications (crucibles, moulds), in which a mechanically weak interface is needed in order to obtain easy detachment of the solidified metal during cooling. In contrast, wetting is needed in some applications, for instance for the flow of metallic films. The requirements of negligible reactivity and good wetting can both be satisfied using the refractory d-metals W, Mo or Ta as substrate materials. Indeed it is well established that wetting can be observed in liquid metal/solid metal systems, in principle even in the case of non-immiscible couples [2]. It should be noted that the extent of wetting varies widely among these systems, from $\theta = 10°$ to $\theta = 80°$, though the reasons for this variation are not known.

In the present investigation, wetting and interfacial interactions are studied for Pb/W and Pb–Li/W couples. Together with other refractory materials, tungsten is a candidate for fusion reactor blankets [3]. In this application, the refractory solid could work in contact with liquid Pb or Pb–Li eutectic alloy.

Pb/W is one of the most immiscible metallic couples, as indicated by the very high value of partial enthalpy of mixing of W in molten Pb

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($\Delta H_{W(Pb)} = 166$ kJ/mol [4]). W–Li interactions are even weaker than W–Pb ($\Delta H_{W(Li)} = 203$ kJ/mol). Standard thermodynamic calculations performed using these values indicate that the solubility of W in liquid Pb and PbLi in the 400–900 °C temperature range is much lower than 1 ppm.

As wetting in metallic systems is extremely sensitive to pollution by oxygen, two different furnace atmospheres, high vacuum and He–H_2, and various heat treatments were used in the present study to achieve W deoxidation.

2. Experimental set-up

Tungsten substrates were prepared from sintered polycrystalline ingot (99.96%, Plansee). The main impurities were Mo (100 ppm), P (50 ppm), Fe (30 ppm), C (30 ppm) and O (30 ppm). Just before introduction into the furnace, the W plates were polished up to 1 μm diamond paste. The average surface roughness R_a of the substrates was less than 10 nm. XPS analysis of the W surface just after polishing revealed the presence of a thin, nanometric oxide layer corresponding to the oxide WO_3. High-purity Pb (99.999%) and Pb–17 at.%Li eutectic alloy (Metaux Speciaux, total amount of impurities less than 50 ppm) were used for the experiments.

Wetting was studied by the 'dispensed drop' modification of the classic sessile drop technique. The experiment involved heating the fusible metal separately in an alumina crucible. Once the experimental temperature was reached, a drop was extruded from the crucible and transferred to the substrate. Afterwards spreading continued in the classic sessile drop configuration. The main advantages of this method over the classic sessile drop technique is that it leads to the formation of clean droplets as the oxide layer often covering liquid metal surfaces is disrupted during extrusion [5]. Also it allows a wetting experiment to be performed at a given temperature after heat treatment of the substrate at a higher temperature.

The time-dependent change in the linear dimensions of the drop (base radius and height) and contact angle θ are filmed by a video camera (25 frames per second) connected to a computer enabling automatic image analysis to be performed. This device is used to obtain the characteristic dimensions of the drop (base radius R and contact angle θ) with an accuracy of ±2° for θ and ±2% for R. Experiments were performed in a metal-walled furnace under high vacuum (2×10^{-6} Pa at room temperature) or in a static atmosphere of He–8 vol.%H_2 gas (impurities < 0.4 ppm H_2O, <0.1 ppm O_2) further purified by passing it through a cartridge with activated carbon cooled with liquid nitrogen. After cooling, selected samples were cut perpendicular to the interface, ground and polished up to 0.3 μm alumina suspension. A scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDXS) was used to examine the solid/liquid interface as well as the substrate surface chemistry.

3. Results and discussion

3.1. Wetting by Pb

Due to the high vapour pressure of Pb, wetting experiments in high vacuum were performed only at 400 °C. In the first experiment the temperature was raised directly to 400 °C, then a Pb drop was deposited on W without any additional heat treatment. The contact angle rapidly stabilised (Fig. 1) and remained constant for a few thousand seconds (note that this information does not appear in Fig. 1). The high, non-wetting contact angle $\theta = 106° \pm 2°$, which is close to (but somewhat lower than) the contact angles of non-reactive metals on iono-covalent oxides [2], indicates that the W surface is not metallic but still oxidised. For instance when the contact angle of Pb was measured in the same conditions on an α-alumina mono-crystalline substrate, the value found (107° ± 3°) (Fig. 1) was very close to that on W. When the dispensed drop experiment at 400 °C was performed with a W substrate preheated to 930 °C in high vacuum,

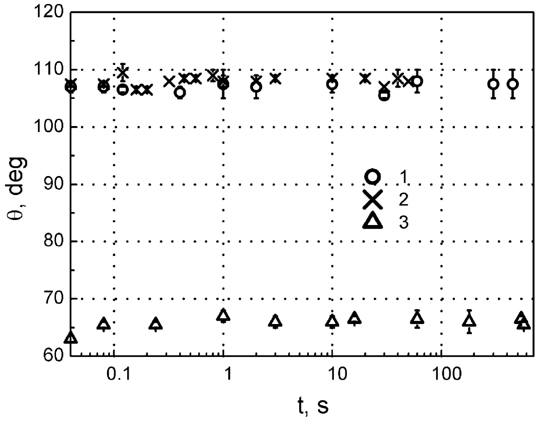

Fig. 1. Contact angle versus time for liquid Pb in high vacuum at 400 °C on various substrates: (1) W, (2) sapphire and (3) heat-treated W.

a contact angle of 66° was observed and remained constant throughout the entire experiment (2000 s). For two other droplets processed using the same conditions, the equilibrium contact angles were 70° and 66°, respectively. The average value over the three droplets is $\theta = 67° \pm 2°$. This wetting contact angle indicates that the prior treatment at 930 °C in high vacuum produced complete or partial deoxidation of the W surface. Decreasing the heat treatment temperature from 930 °C to 870 °C produced a slight increase in the contact angle at 400 °C (average value over three droplets $\theta = 69° \pm 2°$ versus $\theta = 67° \pm 2°$).

In order to study the effect of a reducing atmosphere on wetting, a Pb drop was deposited on a W plate under high vacuum at 400 °C. The vacuum was then replaced by a He–H_2 mixture and the change in the contact angle with time was determined during the temperature rise (Fig. 2). A sharp non-wetting to wetting transition occurred at 570 °C. Afterwards the contact angle continued to decrease gradually to 63° at 800 °C. Even lower contact angles were observed at 900 °C but these were only apparent ones, caused by the evaporation of Pb as indicated by the decrease in drop volume. A second experiment carried out under He–H_2 by depositing a drop directly at 800 °C led to a steady contact angle $\theta = 60° \pm 3°$. When a dispensed drop experiment was performed at 400 °C in He–H_2 with a W substrate preheated to 900 °C in the same gas mixture, the contact angle $\theta = 59° \pm 2°$ was very close to the contact angles attained at 800 °C. The value $\theta = 59°$ is the lowest contact angle observed in this study for Pb on W at 400 °C. This value will be taken as the upper limit of the contact angle of Pb on a clean W surface (Table 1).

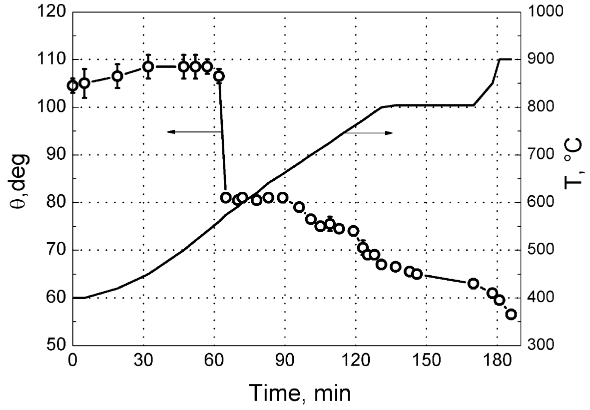

Fig. 2. Contact angle of Pb on W during temperature rise to 900 °C in He–H_2.

The sharp decrease in θ observed at 570 °C strongly suggests that at this temperature the surface chemistry of W changed suddenly. If we accept that the contact angles close to 110° observed at low temperatures (Fig. 2) are on WO_3 (in accordance with XPS analyses of W at room temperature) and that the contact angles close to 60° measured at 800 °C are on metallic or nearly metallic W surfaces, the sharp change in surface chemistry at 570 °C may correspond to a change from WO_3 to WO_2. As for the gradual decrease in θ from 80° to 60°, occurring between 670 °C and 800 °C, it indicates that during this stage the W surface would be 'composite', partly metallic and partly oxidised (Fig. 3). For such a surface the observed contact angle θ is given by Cassie's equation [6] $\cos\theta = \alpha\cos\theta_{ox} + (1-\alpha)\cos\theta_m$ as a function of the contact angle of the liquid on the metal, θ_m, and on the oxide, θ_{ox}, and of the coverage α of the surface by the oxide. Accordingly, the contact angles observed between 670 °C and 800 °C (Fig. 2) would reflect the change with temperature of coverage α. This interpretation of sharp and gradual wetting transitions can also be applied to other metallic substrates presenting different oxidation states such as Fe [7,8].

Table 1
Contact angles at 400 °C of Pb and Pb–17 at.%Li on oxidised W (noted W_{ox}) and heat-treated W (noted W_{ht})

	θ (°)		$\frac{\Delta W_a}{W_a} \times 100\%$
	Pb	Pb–Li	
W_{ox}	106 ± 2	87 ± 2	45
W_{ht}	59 ± 2	49 ± 2	9
Al_2O_3	107 ± 3	95 ± 3	30

All results were obtained in high vacuum except for Pb on W_{ht} (He–H_2). ΔW_a is the increase in work of adhesion of Pb caused by Li.

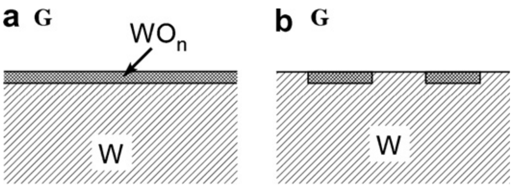

Fig. 3. Schematic representation of W surface in contact with a reducing gas G during (a) a sharp decrease in θ (in this case only the value of n in WO_n changes) and (b) a gradual decrease in θ (the total oxidised area decreases).

3.2. Wetting by Pb–Li

As it was argued in [5,9], the addition of 17 at.% of Li to Pb has no effect on the surface tension σ_{LV} of molten Pb. Moreover Li can hardly lower the solid W–liquid Pb interfacial energy as Li interactions with W are even weaker than Pb–W interactions (see Section 1). Therefore, in the absence of any pollution of the W surface by oxygen, Li can hardly improve the wetting of W by Pb. However Li can affect the wetting of oxidised W. Indeed, the affinity of Li for oxygen is much higher than that of Pb, as attested by the values at 400 °C of standard Gibbs energy of formation (per oxygen gram · atom) of Li_2O (−512 kJ) and PbO (−152 kJ). According to the model described in [10], Li would improve wetting by chemisorption at Pb/oxide interfaces. This model prediction was confirmed by a dispensed drop experiment performed with a PbLi alloy on a single α-Al_2O_3 crystal in high vacuum (as Li forms with hydrogen stable hydrides, all experiments with PbLi were performed in high vacuum). As seen in Table 1, Li leads to a significant decrease in θ, corresponding to a 30% increase in the work of adhesion W_a (equal to $\sigma_{LV}(1+\cos\theta)$). The addition of Li to Pb causes a significant improvement in the wetting of oxidised W, corresponding to a 45% increase in W_a. When heat-treated W is used, the effect of Li on W_a is still significant but rather limited (Table 1).

Table 2
Contact angles of four Pb–Li drops at 400 °C in high vacuum on W_{ht}

Drop	t (s)	θ (°)
1	600	51 ± 2
2	1350	47 ± 2
3	1950	55 ± 2
4	2340	63 ± 2

t is the holding time for W_{ht} at 400 °C before dropping.

It is important to notice that the θ values measured at 400 °C on W heated previously at 900 °C remain constant for only a limited time (typically 30 min). In the case of higher holding times at 400 °C, some pollution of the W surface by oxygen occurs. This is shown by the results obtained in the same experiment with four droplets by varying the deposition time (Table 2). Long deposition times provoke a limited but significant increase in θ. Even higher contact angles are expected to form at longer times.

3.3. Reactivity

In agreement with the thermodynamic calculations (see Section 1), SEM examination of Pb/W and PbLi/W interfaces after short experiments (less than 1 h) at 400–800 °C does not reveal any reactivity and the interface appears flat at the scale of 0.1 μm (Fig. 4). However, examination of the W free surface near the solid W/liquid PbLi/vapour triple line shows that some reactivity exists at this particular area whatever the type of W, with or without heat treatment. Semi-quantitative EDAX analysis

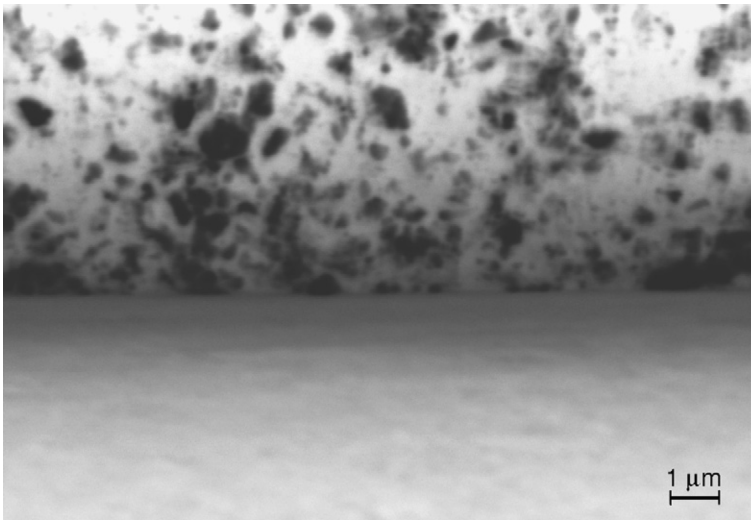

Fig. 4. SEM micrograph of a Pb (top)/W (bottom) cross-section (70 min at 800 °C in He–H_2).

of oxygen at the tungsten surface reveals an increase in oxygen concentration near the triple line (Fig. 5). Such oxygen segregation was not observed with pure Pb. The main source of oxygen is the furnace

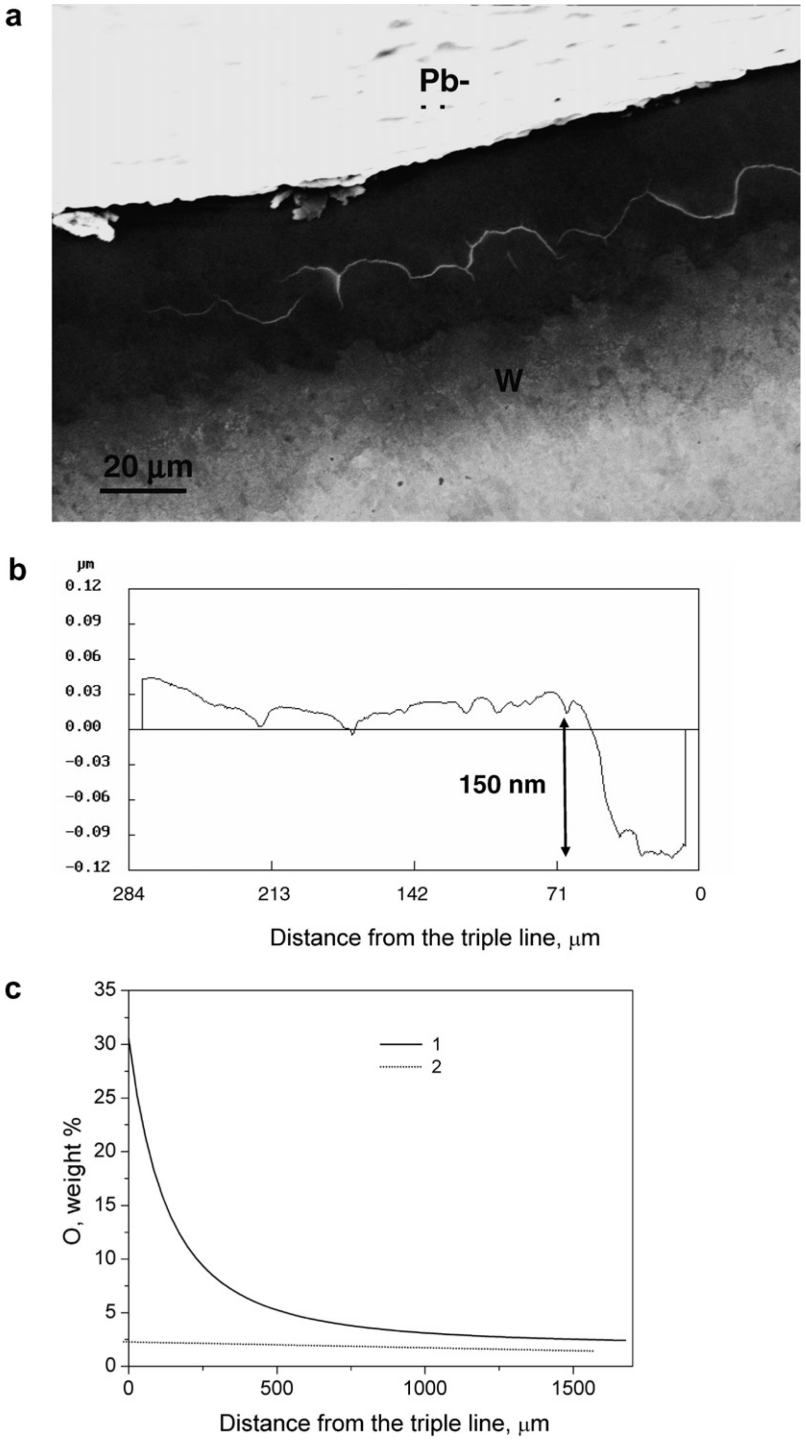

Fig. 5. (a) SEM micrograph of W surface near a PbLi drop observed from above (48 min at 400 °C). (b) High-resolution profilometry of this area is shown. (c) Concentration of oxygen on W surface as a function of the distance from the triple line for PbLi (1) and Pb (2) droplets.

atmosphere. This oxygen adsorbs at the W surface and, afterwards, migrates by rapid surface diffusion towards the PbLi droplet, attracted by the high affinity of Li for oxygen. The oxide layer may be Li_2O or, more likely, a mixed Li–W oxide (the $Li_2O–WO_3$ oxide was reported in [11]). A careful examination of the W surface in the vicinity of the triple line by means of a high-resolution profilometer revealed a depression 150 nm deep and 50 μm wide (Fig. 5(b)). The reason for this depression is not clear. A possible explanation is that it results from stress produced during thickening of the oxide layer, resulting in detachment and rupture of the layer. Whatever the origin of this depression, the above observations clearly demonstrate significant corrosion of W close to the triple line, occurring even after short experiments at 400 °C. This corrosion is initiated by the interactions between Li contained in the droplet and oxygen present as an impurity in the furnace atmosphere.

3.4. Surface interactions versus bulk interactions

In this study wetting contact angles in the range 50–60° were achieved for Pb/W and Pb–Li/W systems. This good wetting, which attests to the development of strong hetero-atomic bonds at the interface, may appear contradictory with the immiscibility of Pb and Li with W, reflected by the very high values of partial enthalpy of mixing of W in molten Pb and Li. This (apparent) paradox will be discussed below using a pairwise, nearest-neighbour model allowing a simple expression to be established for the contact angle of a liquid B on a solid A as a function of bond energies ε of pairs AB and BB [2]:

$$\cos\theta = \frac{W_a}{\sigma_{LV}} - 1 = 2\frac{\varepsilon_{AB}}{\varepsilon_{BB}} - 1. \tag{1}$$

In the framework of this model, the partial enthalpy of mixing at infinite dilution of A in B, $\Delta H_{A(B)}$, divided by the Avogadro number N_{Av} and by the coordination number Z, is given by

$$\frac{\Delta H_{A(B)}}{N_{Av}Z} = \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}. \tag{2}$$

From Eqs. (1) and (2) one can see that the contact angle is determined by *the ratio* of only *two bond energies* while the enthalpy of mixing (and thus, the miscibility of A and B) depends on a *linear combination of three bond energies.* A semi-quantitative evaluation of θ can be made for the Pb/W couple using the value $\Delta H_{W(Pb)} = 166$ kJ/mol estimated in [4] and the evaporation enthalpies ΔH_e of pure Pb and W, taken from [12]. These quantities are related to the bond energies by

$$\Delta H_e^{Pb} = -\frac{1}{2} Z N_{Av} \varepsilon_{PbPb} = -\frac{1}{2}\varepsilon^*_{PbPb}, \tag{3a}$$

$$\Delta H_e^{W} = -\frac{1}{2} Z N_{Av} \varepsilon_{WW} = -\frac{1}{2}\varepsilon^*_{WW}. \tag{3b}$$

The values of different molar bond energies ε^*, calculated through Eqs. (1)–(3), are reported in Table 3. It can be seen that the PbW bond is strong and even much stronger than the PbPb bond, leading to $\cos\theta \gg 1$, i.e. to 'more than perfect' wetting of W by Pb. It can be easily verified that this simple model leads to the same prediction for any AB couple consisting of a low melting point metal B (implying a low $|\varepsilon_{BB}|$ value) and a refractory metal A (high $|\varepsilon_{AA}|$).

The above model thus helps to explain why good wetting can be observed in metallic AB systems even in the absence of any miscibility between A and B. Note that the model predicts 'more than perfect' wetting of A by B (implying $\theta = 0$) while the experimental results for Pb/W and for other metallic couples [2] indicate wetting, but only partial ($0 < \theta < 90°$). Actually, the model calculations are for an ideally clean W surface free from any adsorption or pollution. In wetting experiments, the W surface can be modified by two types of elements:

(i) Impurities such as oxygen and carbon. Concerning oxygen, even the lowest θ value achieved in the present study has not been proven to be for a W surface completely free from oxygen. As for carbon, its effect on W surface energy in $He–H_2$ is unlikely because carbon can react with hydrogen, forming volatile hydrocarbons. However carbon segregation on a W surface in high vacuum cannot be excluded.

(ii) Atoms of Pb or Li adsorbed on the W surface. It is a well-established fact that the surface energy of high melting point metals is reduced

Table 3
Molar bond energies ε^* for different pairs calculated from Eqs. (2) and (3) taking $\Delta H_{Pb(W)} = 166$ kJ/mol, $\Delta H_{ev}^{Pb} = 178$ kJ/mol and $\Delta H_{ev}^{W} = 821$ kJ/mol

Bond	ε^* (kJ/mol)
Pb–Pb	−355
W–W	−1640
Pb–W	−830

several tens of per cent by the adsorption of atoms of low melting point metals [13]. Note that while the effect of impurities on wetting depends on the quality of materials and on the furnace atmosphere, the second effect is an intrinsic feature of any B/A couple. This effect alone can explain why wetting is certainly good but never perfect in non-reactive metal B on metal A systems.

4. Conclusions

The contact angle of Pb on W in reducing gas varies between 110°, a value typical of oxidised W observed at temperatures close to Pb melting point, and 60°, a value corresponding to a metallic or nearly metallic W surface, observed at 800 °C. The decrease in θ from 110° to 60° occurs in two different ways, namely by a sharp decrease occurring at constant temperature, attributed to a change in the chemistry of the surface oxide, and by a gradual decrease, explained by the reduction in the W area covered by the oxide with temperature and time. The good wetting observed for Pb and PbLi on deoxidised W testifies to the establishment of strong hetero-atomic interactions at the solid–liquid interface, which contrasts with the very weak Pb–W and Li–W interactions developed in the bulk liquid. This behaviour, which is general for low melting point metals on refractory metals, was successfully explained using a simple pairwise model. Finally, when an element with high affinity for oxygen, such as Li, is added to Pb, the wetting of oxidised W is strongly improved while the wetting of deoxidised W is affected only slightly. Moreover, through its strong interactions with oxygen, Li leads to corrosion of W at the triple line, which is significant even in experiments with low temperatures (400 °C) and short times (less than 1 h).

References

[1] Y. Naidich, in: D.A. Cadenhead, J.F. Danielli (Eds.), Progress in Surface and Membrane Science, vol. 14, Academic Press, New York, 1981, p. 353.

[2] N. Eustathopoulos, M. Nicholas, B. Drevet, Wettability at High Temperatures, Elsevier, Oxford, 1999.

[3] S. Zinkle, N. Ghoniem, Fusion Eng. Design 51&52 (2000) 55.

[4] A. Niessen, F. De Boer, R. Boom, P. De Châtel, W. Mattens, A. Miedema, CALPHAD 7 (1983) 51.

[5] P. Protsenko, A. Terlain, M. Jeymond, N. Eustathopoulos, J. Nucl. Mater. 307–311P2 (2003) 1396.

[6] A. Cassie, Discuss. Faraday Soc. 3 (1948) 11.

[7] P. Protsenko, N. Eustathopoulos, J. Mater. Sci. 40 (2005) 2383.

[8] B. McGurran, M. Nicholas, Brazing and Soldering 8 (1985) 43.

[9] P. Protsenko, Surface and Grain Boundary Wetting of Solid Metals by Fusible Metallic Melts, PhD thesis, Moscow State University, 2002.

[10] J.G. Li, L. Coudurier, N. Eustathopoulos, J. Mater. Sci. 24 (1989) 1109.

[11] E.K. Kazenas, I.O. Samoylova, Metals 5 (2000) 44, in Russian.

[12] R. Hultgren et al., Selected Values of the Thermodynamic Properties of the Elements, ASM, Ohio, USA, 1973.

[13] E. Hodkin, M. Nicholas, D. Poule, J. Less-Common Met. 20 (1970) 93.