

The effect of thermodynamic properties of Me–Ti (Me = In, Sn, Ga, Au, and Ge) melts on the wetting of the CaF₂ substrate

S. Barzilai · M. Lomberg · M. Aizenshtein ·
N. Froumin · N. Frage

Received: 15 June 2009 / Accepted: 30 October 2009 / Published online: 17 November 2009
© Springer Science+Business Media, LLC 2009

Abstract The effect of Ti additions on the wetting behavior of CaF₂ by non-reactive liquid metals (In, Sn, Ga, Au, Ge) was investigated. Pure metals do not wet CaF₂ while minor additions of Ti improve wetting. Small changes of the contact angle were observed in the CaF₂/Au–Ti and CaF₂/Ge–Ti systems, which are characterized by strong Me–Ti interaction in the melt, while considerable decrease of contact angle was obtained in the CaF₂/In–Ti, CaF₂/Sn–Ti and CaF₂/Ga–Ti systems, which display a relatively weak Me–Ti interaction. According to a thermodynamic analysis and experiential observations, Ti does not react with the substrate to form condensed phases at the metal/CaF₂ interface. Therefore, it was assumed that the mechanism of the wetting improvement is attributed to the Ti segregation at the interface. The results of the XPS analysis confirm a Ti enrichment of the region close to the interface, moreover, according to the high resolution XPS spectrum, obtained from this region, the position of the In4d peak has a chemical shift, which is typical for In–Ti intermetallic compounds. The XPS analysis does not provide sufficient evidence for the formation of the intermetallic interfacial layer at elevated temperature. Thus, further investigations have to be designed and conducted in order to clarify this issue.

Introduction

The wetting mechanism of ceramic substrates, e.g., oxides, carbides, borides, and nitrides by liquid metals that contain active elements is closely linked to the chemical reactions that take place at the interface between the melt and the substrate. As a result of these interactions, an interfacial layer, which consists on the active element and the non-metallic component of the substrate (oxygen, carbon, nitrogen, or boron), may be formed and promote wetting [1–8]. Nevertheless, it was observed experimentally for extremely thermodynamically stable alkaline earth fluorides [9–15], that even though no new phases are detected at the metal/ceramic interface, the presence of an active element such as Ti, significantly affects the wetting behavior. In our previous communication [13], on the basis of experimental results and ab-initio DFT calculation, it was suggested that a preferential Ti adsorption from the Me–Ti drop takes place at the interface, reduces the interfacial energy, and improves wetting. Moreover, it should be noted that the wetting behavior varies significantly for different Me–Ti systems [16].

In the present study, the results of a systematic investigation of the wetting behavior in the CaF₂/Me–Ti melts (Me = In, Sn, Ga, Au, Ge) systems are presented. In order to estimate the degree of Ti adsorption at the interface for various CaF₂/(Me–Ti) systems, we applied the Langmuir–McLean segregation model.

Experimental

The CaF₂ substrates were prepared by powder metallurgy techniques. CaF₂ powder (99.9% purity) was isostatically

S. Barzilai · M. Lomberg · N. Froumin · N. Frage (✉)
Department of Materials Engineering, Ben-Gurion University,
P.O. Box 653, Beer-Sheva 84105, Israel
e-mail: nfrage@bgu.ac.il

S. Barzilai · M. Aizenshtein
NRC-Negev, P.O. Box 9001, Beer-Sheva 84190, Israel

hot pressed (1273 K 100 MPa). The relative density of the compacted samples was 99%. The samples of 15 mm diameter were sliced to 3 mm width and polished down to the 1 μm diamond paste level. Before the wetting experiments, the samples were ultrasonically cleaned in acetone and ethanol. Wetting experiments were performed by the sessile drop method in dynamic vacuum ($1\text{--}4 \times 10^{-3}$ Pa) in the 1123–1373 K range. The metals used were 99.99% purity. Contact angles were measured directly from the magnified profile images of the molten metal drop. The composition of metal/ceramic interfaces was studied using SEM (Jeol GSM 5600) equipped with an EDS analyzer. The interfacial region beneath the In–Ti drop was analyzed by X-ray Photoelectron Spectroscopy (XPS) accompanied with Ar-sputtering depth profile using the ESCALAB 250 system. In order to analyze the interfacial region, the samples with solidified drop were heated on a heating plate up to 170 $^{\circ}\text{C}$ under dry Nitrogen atmosphere. The main volume of the drop was mechanically removed after the drop was melted. Very thin adhered to the substrate metallic layer was analyzed by high resolution XPS technique with lateral resolution of about 20 μm .

Results

Wetting experiments

The spreading kinetics for the $\text{CaF}_2/(\text{Me})$ and $\text{CaF}_2/(\text{Me-Ti})$ systems are presented in Fig. 1. The experimental results indicate that for 1123–1373 K temperature range (Table 1), pure liquid metals do not wet CaF_2 ($\theta \approx 110\text{--}130^{\circ}$) and the contact angles remain constant (Fig. 1a) with time. The addition of 2 at.% Ti to the melt leads to improved wetting and its effect depends on the nature of Me (Fig. 1b). The improved wetting is more significant for the In–Ti melt, while only minor changes take place for the Ge–Ti and Au–Ti melts.

Interface characterization

No evidence of new phase formation at the interface was detected by SEM analysis in the $\text{CaF}_2/(\text{Me-Ti})$ systems. The results of the XPS depth profile analysis are presented in Fig. 2a. It has to be pointed out that the sputtering rate is about 0.1 nm/s and after 470 s of sputtering, the characteristic peaks of Ti, In, and CaF_2 were seen. Thus, we suggest that the region, which was analyzed in the 470–550 sec sputtering duration range, corresponds to the interface region (IR) (Fig. 2a). XPS depth profile indicates a significant Ti enrichment within the region close to the interface. In this region, the position of In4d peak displays a chemical shift of about ~ 0.5 eV from the line of pure In and rather corresponds to the position of the same peak in the In–Ti intermetallic (Fig. 2b).

Discussion

In general, addition of active elements improves wetting in ceramic/metal systems by a chemical reaction at the interface. The reaction between the melt and the substrate leads to the formation of a new interfacial layer [1–8]. However, according to the results of the thermodynamic analysis, reported in our previous study [13], no condensed phases are formed at the interface. The thermodynamic calculation is supported by SEM characterization of the interface [13].

In the absence of chemical reactions at the interface and taken into account that the surface energy of the substrate (γ_{SV}) remains constant, wetting improvement, according to Young's Equation (1) [17], may be achieved by reduction of the interfacial solid–liquid energy (γ_{SL}) or by altering of the interfacial liquid–vapor energy (γ_{LV}).

$$\cos \theta = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \quad (1)$$

Unfortunately, the values of γ_{LV} for the investigated binary Me–Ti melts were not found in the literature. At the

Fig. 1 Contact angle for various CaF_2/Me (a) and $\text{CaF}_2/(\text{Me-2at\%Ti})$ systems (b)

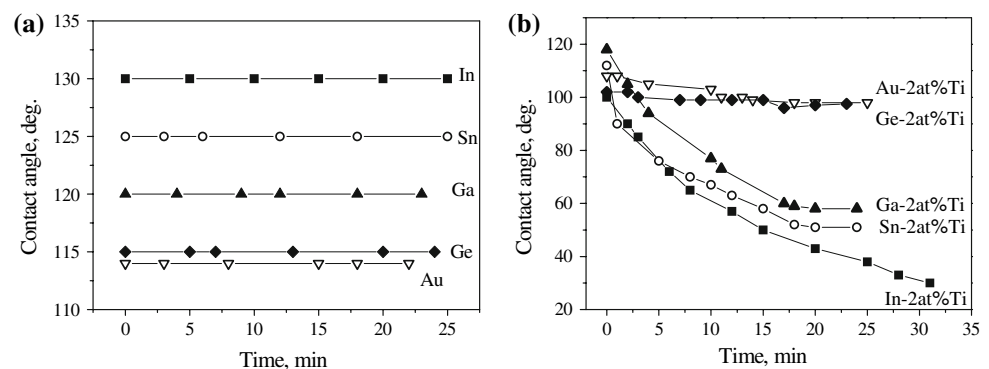
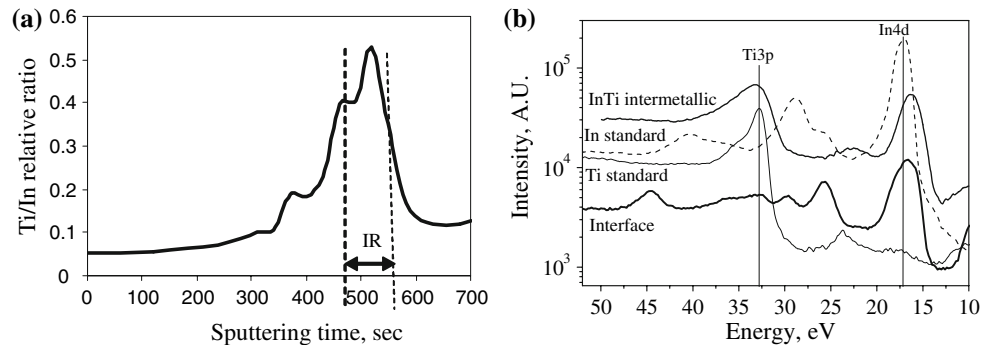


Table 1 The estimated values of the Ti atomic fraction $X^s(\text{Ti})$ at the substrate surface for various systems

CaF ₂ /Me–Ti system	T (K)	$\gamma_{\text{LV}}(\text{Me})^a$ (J/m ²)	X^b (at.%)	$\theta^{\text{Me}/\text{CaF}_2}$ (deg)	$\theta^{\text{Me–Ti}/\text{CaF}_2}$ (deg)	$X^s(\text{Ti})$
In–Ti	1123	0.49	2	130	30	0.99
Sn–Ti	1173	0.47	2	125	51	0.98
Ga–Ti	1173	0.69	2	120	58	0.99
Au–Ti	1373	1.12	2	114	98	0.85
Ge–Ti	1273	0.64	2	115	98	0.71

^a Values correspond to the temperature of the experiments [25]

Fig. 2 The results of the XPS analysis of the CaF₂/In–Ti interface: **a** Ti to In ratio as a function of sputtering time, **b** high resolution spectrum obtained from the interface region (IR) along with the standard spectrum for pure Ti, In and In–Ti intermetallic



same time, according to [18], the measured γ_{LV} value for the Cu–Ti system at 1473 K does not change up to 10 at.%Ti. Moreover, above 10 at.% γ_{LV} increases with the increase of Ti content in the melt. Thus, it is reasonable to assume that for dilute Me–Ti alloys dissolved Ti has only minor effect on the γ_{LV} value. So, the effect of Ti on wetting is related to changes of the solid–liquid interfacial energy due to Ti adsorption at the interface [19].

Based on the previous assumption and the experimental observations it may be concluded that the wetting behavior (Fig. 1) is connected to the thermodynamic properties of the Me–Ti melts that determine the level of the adsorption and, eventually, the wetting behavior. For dilute Me–Ti alloys, the values of $\Delta H^{\text{mix}}(\text{Ti})$ are -6.4 , -52.8 , -74.6 , -98.0 , and -124.0 kJ/mol for the In–Ti, Sn–Ti, Ga–Ti, Au–Ti and Ge–Ti melts, respectively [20, 21]. The difference in the $\Delta H^{\text{mix}}(\text{Ti})$ values reflects the difference in the Me–Ti bonding in the melts and determines the level of Ti adsorption at the interface. For high negative value of $\Delta H^{\text{mix}}(\text{Ti})$, Ti dissolved in the melt is strongly bonded to the solvent atoms and its adsorption is limited. On the other hand, if Ti is only weakly bonded to Me (low $\Delta H^{\text{mix}}(\text{Ti})$ values) the degree of the adsorption is higher, and the effect of Ti on the γ_{SL} value and, thereby, on the wetting angle, is more significant. The correlation between the effect of Ti additions and the $\Delta H^{\text{mix}}(\text{Ti})$ values for various systems is presented in Fig. 3.

In order to quantify the degree of Ti adsorption, the level of coverage of the CaF₂/(Me–Ti) interface by Ti atoms was

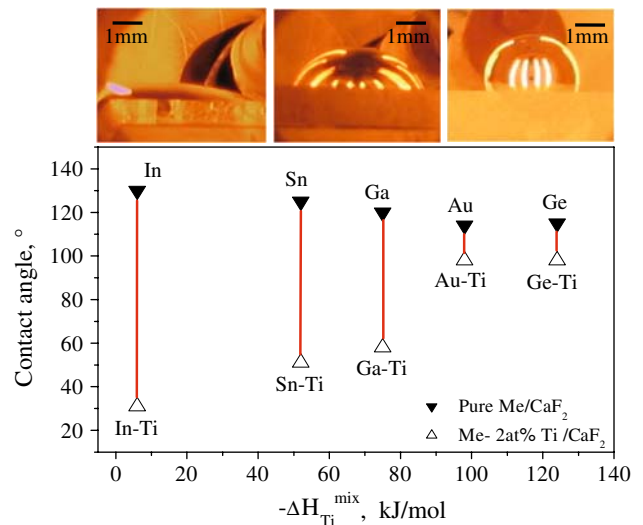


Fig. 3 The contact angle for pure Me and for Me–Ti alloys as a function of the Ti partial mixing enthalpy

estimated according to the Langmuir–McLean’s adsorption approach modified by Wynblatt et al. [22–24]. Originally, this model was developed to calculate the free energy for segregation of an active element from a dilute solution at a liquid/vapor interface using the value of γ_{LV} surface energy [22]. In the present work, this approach has been further extended in order to calculate the Ti concentration at the solid/liquid (CaF₂/Me–Ti) interface, using the γ_{SL} values, calculated according to Eq. 1, and the measured values of the contact angles.

The atomic fraction of the active element at the interface (X^s) was calculated using Eqs. 2–4.

$$X^s = \frac{KX^b}{1 - X^b + KX^b} \quad (2)$$

$$K = \frac{\exp(X^b - \Delta\gamma_{SL}/RTA) - 1}{X^b} \quad (3)$$

$$\Delta\gamma_{SL} = \gamma_{LV}^{Me}(\cos \theta^{Me} - \cos \theta^{Me-Ti}) \quad (4)$$

where X^s is the atomic fraction of Ti at the solid/liquid interface, X^b is the concentration of Ti in the alloy, K is the segregation equilibrium constant, $\Delta\gamma_{SL}$ is the change in the γ_{SL} value as a result of Ti adsorption and A is the number of sites on the substrate surface per unit area. The A value equal to 1.43×10^{-5} mol/m² was calculated using the parameters of the crystalline structure of CaF₂ compounds (see Appendix). The calculated values of the Ti atomic fraction at the solid/liquid interface X^s (Ti) are presented in Table 1. The substrate surface coverage level as a function of the ΔH^{mix} (Ti) value for various systems is shown in Fig. 4.

According to Fig. 4 the systems may be divided into two groups. The first group relates to the Ge–Ti and Au–Ti melts, which display a strong inter-atomic interaction and a low level of Ti coverage; the second one includes the In–Ti, Sn–Ti, and Ga–Ti melts with a relatively weak inter-atomic interaction and display a coverage level close to 100%. The results of the calculation are in a good agreement with our assumption related to the adsorption mechanism for wetting improvement in the systems with different thermodynamic properties. In spite of this conclusion, two issues have to be considered. First, is it suitable to apply the simple Langmuir–McLean's adsorption approach in the cases of high level of coverage? The second issue has to be addressed to the possibility of the formation of an extremely thin layer of

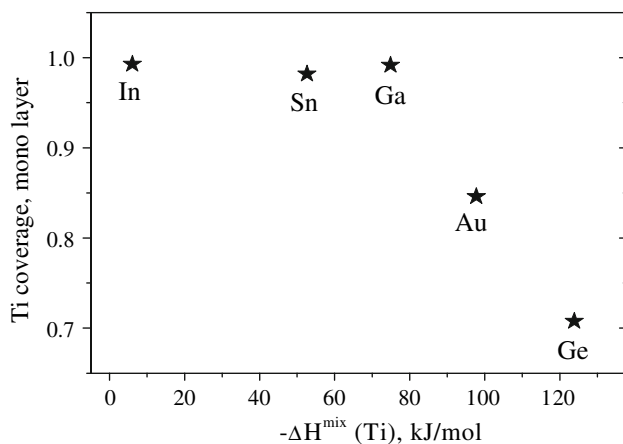


Fig. 4 The calculated values of the substrate surface coverage level for various systems

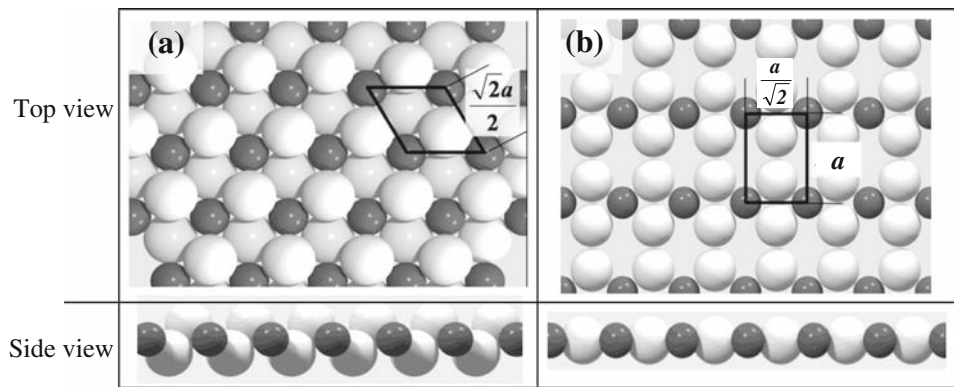
a new intermetallic phase at the interface that was not detected by conventional characterization methods applied in the present study. The presence of such interfacial layer may change dramatically the nature of the interface and may stand behind the significantly improved wetting in the systems with a weak solvent-solute interaction. It has to be noted that the nominal composition of the molten drops corresponds to the single phase (Me–Ti liquid solution) region in the Me–Ti phase diagrams. Even though, the titanium concentration at the interface is much higher than in the bulk, its activity has to be equal to that in the volume of the drop. Thus, the formation of intermetallic phase with similar thermodynamic properties as those of the regular bulk phase cannot take place. One may still assume that a two-dimensional interfacial phase, which has different thermodynamic properties may be formed. The question is: how we may detect this layer? It has to be taken into account that due changes that take place during cooling and solidification of the drop the results of the analysis obtained at room temperature do not always reflect the actual chemical and phase compositions of the interface at elevated temperature. Thus, the results of the XPS analysis (Fig. 2b) do not provide sufficient evidence for extremely thin layer formation at elevated temperature. Further investigations have to be design and conducted in order to clarify this issue.

Conclusions

The effect of Ti dissolved in liquid Me–Ti alloys on wetting of CaF₂ depends strongly on the solvent nature. Based on the thermodynamic properties of the liquid solution and a classical adsorption model, it was established that the coverage level of the substrate surface by Ti as well as the final contact angle, depends on the value of the partial mixing enthalpy ΔH^{mix} (Ti), which reflects the inter-atomic interaction within the melt. Systems with high negative ΔH^{mix} (Ti) values (Au–Ti and Ge–Ti systems) display a relatively low coverage level of the substrate surface and exhibit only minor changes of the contact angle. For systems with low ΔH^{mix} (Ti) value (In–Ti, Ga–Ti and Sn–Ti), high coverage. Thus, the effect of Ti on the wetting behavior of the CaF₂/Me–Ti systems strongly correlates with thermodynamic properties of Me–Ti liquid solutions. Further investigations have to be design and conducted in order to clarify the possibility of the formation of a two-dimensional intermetallic layer.

Acknowledgements The authors wish to thank Mr. Shimon Tamsot and to Ms. Hila Nagar for their technical assistance. This work was supported by the Israeli Council of High Education and the Israeli Atomic Energy Commission, grant 138-05.

Fig. 5 Schematic presentation of the crystallographic planes for (111) (a) and (220) (b) planes of CaF₂. Dark and bright spheres refer to Ca and F atoms, respectively, *a* is the lattice parameter of CaF₂ and it equal to 5.463 Å



Appendix. Calculation of the number of sites for Ti adsorption on CaF₂ per unit area

According to XRD analysis of polycrystalline CaF₂, the (111) and (220) planes display the highest intensity and hence are seemed to be dominant in the crystal

In a previous study [19], it was shown that for the (111) surface the preferential adsorption site of Ti atom on CaF₂ is atop of the fluorine atom. On this plane, one atom of Ti per unit cell could be adsorb (Fig. 5a) and the number of sites on this surface per unit area is: $A^{(111)} = 1.268 \times 10^{-5} \text{ mol/m}^2$ (see calculation below). Assuming that the preferential site is independent of CaF₂ orientation when considering a polycrystalline substrate, the *A* for (110) plane was calculated in the same manner. In this case there are two adsorption sites for Ti atoms per unit cell (Fig. 5b) and the number of adsorption is: $A^{(110)} = 1.575 \times 10^{-5} \text{ mol/m}^2$.

For (111):

$$S = \frac{(a)^2}{2} \sin 60 = (5.463 \text{ \AA})^2 \frac{\sqrt{3}}{4} = 1.292 \times 10^{-19} \text{ m}^2$$

$$A = \frac{n(\text{Ti})}{S \times N_a} = \frac{1}{1.292 \times 10^{-19} \times 6.02 \times 10^{23}} = 1.286 \times 10^{-5} \text{ mol/m}^2$$

For (220):

$$S = a^2 \sqrt{2} = (5.463 \text{ \AA})^2 / \sqrt{2} = 2.11 \times 10^{-19} \text{ m}^2$$

$$A = \frac{n(\text{Ti})}{S \times N_a} = \frac{2}{2.11 \times 10^{-19} \times 6.02 \times 10^{23}} = 1.575 \times 10^{-5} \text{ mol/m}^2$$

$$\bar{A} = \frac{1.286 \times 10^{-5} + 1.575 \times 10^{-5}}{2} = 1.43 \times 10^{-5} \text{ mol/m}^2$$

where *S* is the area of the two dimensional unit cell, *n* is the number of adsorption cite per unit cell, *N_a* is the Avogadro number and *A* is number of sites on the substrate surface per unit area.

References

1. Eustathopoulos N, Nicholas MG, Drevet B (1999) Wettability at high temperatures. Pergamon Materials Series, New York
2. Howe JM (1993) Int Mater Rev 38:233
3. Marin J, Olivares L, Ordonez S, Martinez V (2003) Mater Sci Forum 416:487
4. Rado C, Kalogeropoulou S, Eustathopoulos N (2000) Mater Sci Eng A 276:195
5. Froumin N, Frage N, Polak M, Dariel MP (1997) Scripta Met 37:1263
6. Mortimer DA, Nicholas M (1973) J Mater Sci 8:640. doi: 10.1007/BF00561219
7. Kharlamov AI, Loichenko SV, Nizehenko VI, Kirillova NV, Floka LI (2001) Powder Metall Met Ceram 40:65
8. Muolo ML, Ferrera E, Novakovic R, Passerone A (2003) Scripta Mater 48:191
9. Naidich YV (2000) Powder Metall Met Ceram 39:355
10. Krasovsky VP, Naidich YV (2002) Powder Metall Met Ceram 41:72
11. Naidich YV, Krasovsky VP (1998) J Mater Sci Lett 17:683
12. Krasovsky VP, Naidich YV (2001) Trans JWRI 30:61
13. Froumin N, Barzilai S, Aizenshtein M, Lomberg M, Frage N (2008) Mater Sci Eng A 495(1–2):181
14. Barzilai S, Aizenshtein M, Lomberg M, Froumin N, Frage N (2007) Solid State Sci 9:338
15. Barzilai S, Aizenshtein M, Lomberg M, Froumin N, Frage N (2008) J Alloys Compd 452:154
16. Barzilai S, Argaman N, Froumin N, Fuks D, Frage N (2009) Surf Sci 603:2096
17. Young T (1805) Phil Trans R Soc 95:65
18. Krasovskiy VP, Naidich YV, Krasovskaya NA (2003) Alloys 4:18 (in Russian)
19. Barzilai S, Argaman N, Froumin N, Fuks D, Frage N (2008) Surf Sci 602:1517
20. Zhuravlev VS, Turchanin MA (1997) Powder Metall Met Ceram 36–3(4):141
21. Kleppa OJ, Topor L (1985) Metall Trans A 16A:93
22. Howe JM (1997) Interfaces in materials. Wiley, New York
23. Wynblatt P (2000) Acta Mater 48:4439
24. Wang Z, Wynblatt P (1998) Acta Mater 46–14:4853
25. Nizhenko V, Floka L (1981) Surface tension of liquid metals and alloys handbook, vol 1. Metallurgia, Moscow (in Russian)