

## Interface reaction and wetting in the $\text{CaF}_2/\text{Me}$ systems

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### Abstract

Wetting experiments using the sessile drop method were performed in the  $\text{CaF}_2\text{--Me}$  systems (Me = Cu, Ge, Al, In and Ga). Liquid Cu, Ge, In and Ga, do not wet the  $\text{CaF}_2$  substrate and contact angles are significantly higher than  $90^\circ$ . No condensed products were found at the metal/ceramic interface. In the  $\text{CaF}_2/\text{Al}$  system, evidence of an interface interaction was detected and the contact angle is about  $92^\circ$ . It was established that the spreading behavior and the values of the apparent contact angle depend on the rate of evaporation of the molten metals, the rate of sublimation of the substrate and on the value of the work of adhesion at the interface. The experimental observations are well accounted for by a thermodynamic analysis of the ternary Ca–Me–F systems.

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### 1. Introduction

Alkaline earth fluorides are relatively stable compounds and are appropriate materials for containers of reactive melts. The Ca, Mg and Ba fluorides may be used as windows for special devices on account of their high transparency in the infrared region [1]. The sessile drop method is often used in order to investigate the interaction between solid substrates and liquid alloys. The results of these experiments are useful for developing soldering/brazing regimes that are needed for hermetic attachment of fluoride windows and for predicting the possibility of using fluorides as container materials for fusing and holding reactive metallic melts.

Despite the technological importance of these materials, the published data concerning wetting and interface interaction of alkaline earth fluorides with liquid metals is limited. Naidich et al. [2–4], reported on the wettability of alkaline earth fluorides by various liquid metals and alloys. Pure metals (Cu, Au, Ag, Ga, Sn, Pb, In and Al) were studied in the temperature range of 373–1373 K, and metal alloys (Cu–Ti, Cu–Sn–Ti, Sn–V, Cu–Sn–V) were investigated in the range of 973–1473 K. Naidich et al. showed that pure metals do not wet  $\text{CaF}_2$  and the

contact angles slightly decreased with increasing temperature. Partial wetting by molten Sn containing active elements (Ti or V) was detected at relatively low temperature (up to 1173 K), and a dewetting phenomenon was observed at higher temperatures. It was suggested that the improved wetting takes place due to the formation of liquid fluorides at the interface, while the dewetting phenomenon was attributed to their evaporation at elevated temperatures. No information regarding the metal/ceramic interface structure and composition was reported.

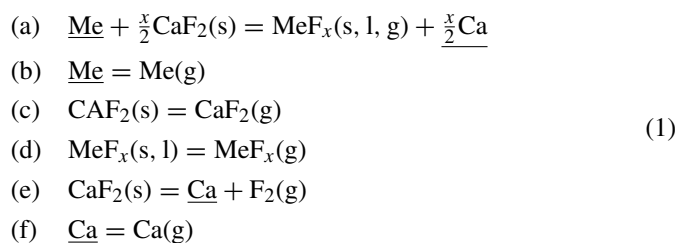
In the present study, the wetting experiments in the  $\text{CaF}_2/\text{Me}$  systems (Me = Cu, Ge, Al, In and Ga) were conducted in the temperature range of 973–1523 K, in order to investigate the effects of the chemical interaction at the interface, the sublimation of the substrate and the evaporation of the melts on the contact angle. A thermodynamic analysis of the ternary Ca–Me–F systems was performed and its results were related to the experimental observations.

### 2. Thermodynamic evaluations

The interaction between the metals and  $\text{CaF}_2$  substrate may lead to the formation of fluoride phases and to Ca dissolution in the melt, according to the chemical reaction (a). This reaction is written for various states of the fluorides (gas, liquid and solid) and for the liquid metallic phases. The reactions of the evaporation (b, c, d and f) were also considered. Reaction (e)

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corresponds to the solid substrate dissolution in the liquid metals. The equilibrium constants for Eq. (1) were calculated using the standard Gibbs energy changes (Eq. (2)) and was expressed in terms of partial pressures and the components activities.



$$K_i = \exp\left(-\frac{\Delta G_{(i)}^\circ}{RT}\right) \tag{2}$$

The underlined symbols in equations (a, b, e, f) correspond to the components in liquid solution; s, l and g denote that the component is in solid, liquid or gaseous phase. The eventual formation of condensed fluoride phases was checked by comparison of the partial pressure of each fluoride in the gaseous phase, calculated from the reaction (a), with its equilibrium vapor pressure according to the reaction (d). The standard thermodynamic characteristics of the reactions (a–f) were taken from Ref. [6].

If three phases (solid  $\text{CaF}_2$ , liquid Me–Ca solution, and gaseous phase consisting of vapor of metals and fluorides) are in equilibrium, the ternary Ca–Me–F system has two degrees of freedom. At each temperature, therefore, the composition of the gaseous phase depends on the composition of the metallic solution, namely on the activity of Ca in the melt. According to the thermodynamic analysis, the partial pressures of  $\text{MeF}_2$  and  $\text{MeF}_3$  fluorides are lower by several orders of magnitude than that for  $\text{MeF}$  and no condensed fluoride phases may be formed. The calculated partial pressures of the mono-fluorides and the vapor pressure of Ca as a function of temperature are shown in Fig. 1a and b for two different Ca activities in the melt. The horizontal line in these figures corresponds to the vacuum conditions ( $10^{-8}$  atm) in our experimental set-up for wetting investigations. As mentioned above, the interaction between  $\text{CaF}_2$  and liquid Me leads to gaseous fluorides formation and to calcium transfer from the substrate into the melt. In this study, it was suggested that if the partial pressure of the fluoride and the vapor pressure of Ca are higher than  $10^{-8}$  atm, the interaction between the

metal and the substrate would proceed under dynamic vacuum conditions. For an extremely low calcium activity in the melt ( $a_{\text{Ca}} = 10^{-8}$ , Fig. 1a), the partial pressures of the mono-fluoride phases even for relatively low temperatures are higher than the external pressure. It means that the contact of the substrate with a pure liquid Me under these conditions could lead to a partial substrate dissolution in the melt and to an increased calcium activity. The increasing activity of Ca in the melt leads to a decrease of the fluorides partial pressure in the gaseous phase according to the reaction (a). For instance, the partial pressure of GaF (Fig. 1a) at 1100 K is  $10^{-6}$  atm, thus, the interaction could take place. As a result of the interaction, the Ca activity in the melt increases and for Ca activity higher than  $10^{-4}$ , the equilibrium GaF partial pressure is already lower than the external pressure (Fig. 1b). Under these conditions, the interaction of liquid Ga with  $\text{CaF}_2$  has to stop. For higher temperatures, the partial pressures of GaF and Ca are higher than the external pressure, therefore, their evacuation will take place simultaneously and the interaction will continue.

The values of the Ca activity in the melts and the corresponding partial pressure of the Me-fluorides may be considered as the parameters, which characterize the degree of the metal/ceramic interaction. It is useful, in order to discuss the experimental results in terms of reactive wetting, to define arbitrarily an activity level of Ca above which the metal/substrate interaction may be considered as ‘reactive’. Assuming such a threshold level of Ca activity equal to  $10^{-4}$ , the systems for which the MeF partial pressure is higher than the external pressure ( $10^{-8}$  atm for our case) display a reactive behavior. The temperatures at which these conditions are fulfilled can be determined from the diagrams shown in Fig. 2. These diagrams present the equilibrium partial pressures of the Me-fluoride phases as a function of the activity of Ca in the melt. According to the calculated results, the  $\text{CaF}_2/\text{Al}$  system may be considered as reactive at temperatures higher than 970 K. For the  $\text{CaF}_2/\text{Ga}$ ,  $\text{CaF}_2/\text{In}$ ,  $\text{CaF}_2/\text{Ge}$  and  $\text{CaF}_2/\text{Cu}$  systems the threshold temperatures are 1090, 1180, 1500 and 1720 K, respectively.

### 3. Experimental procedure

The  $\text{CaF}_2$  substrates were prepared by powder metallurgy techniques.  $\text{CaF}_2$  powder (99.9% purity) was isostatically cold pressed under 240 MPa in a rubber mold. The compacted samples were sintered in an air furnace at 1273 K for

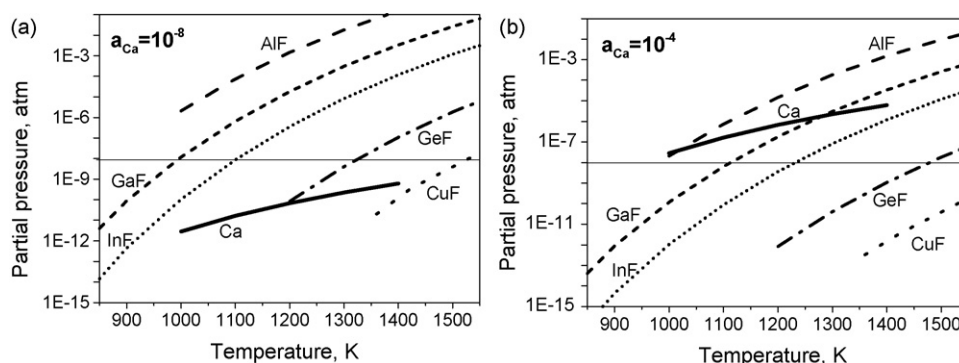


Fig. 1. Gaseous phase composition as a function of temperature for two values of Ca activity in the melt (a:  $a_{\text{Ca}} = 10^{-8}$ , b:  $a_{\text{Ca}} = 10^{-4}$ ). The horizontal line corresponds to the total pressure in the experimental set-up.

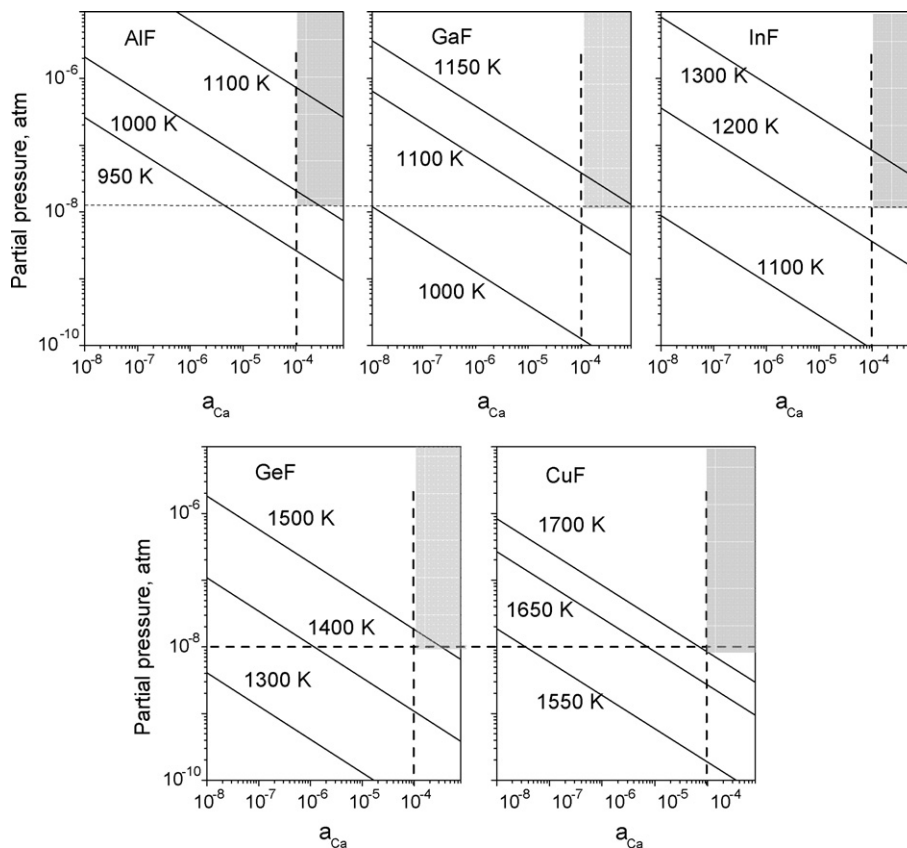


Fig. 2. Partial pressure of the fluoride phases as a function of Ca activity in the melt. The marked regions denote the conditions where the interaction between  $\text{CaF}_2$  and Me has meaningful level.

5 h. The relative density of the substrate was about 94% and contained 5.5% closed pores. The substrate was sliced to 3 mm width and polished down to the 1  $\mu\text{m}$  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 the temperature range of 973–1523 K for 20–60 min in a dynamic vacuum ( $1\text{--}4 \times 10^{-3}$  Pa). The purity of the metals was better than 99.99%. Contact angles were measured directly from the magnified profile images of the molten metal drop. At temperatures above 1500 K, intensive substrate evaporation takes place and leads to the formation of a neck-shape substrate/drop interface. In this case, an apparent contact angle was measured (Fig. 3).

The structure and the composition of metal/ceramic interfaces were studied using XRD (Philips® PW3720) and SEM (JEOL GSM 5600) equipped with an EDS analyzer.

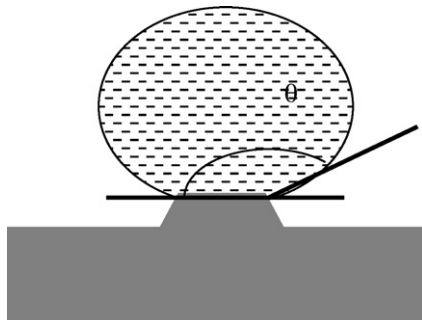


Fig. 3. Schematic illustration of the neck-shape substrate/drop interface and the apparent contact angle measurement.

## 4. Experimental results

### 4.1. Wetting results

The metals that were studied may be divided into two groups: metals with low melting temperatures (Ga and In) and with significantly higher melting temperatures (Al, Ge and Cu). The values of the contact angle for Ga and In drops at 1173 K are shown in Fig. 4a as a function of the duration of contact. The contact angles are significantly higher than  $90^\circ$  and do not change with time. The initial contact angles for these systems at 1423 K are close to  $120^\circ$ , but for Ga the contact angles decrease monotonically with contact duration (Fig. 4b). For the In drop, no change of the contact angle was observed. These results are similar to the values of the wetting angle reported by Naidich [2].

For the second group of metals, at relatively low temperature (1423 K), high values of the initial contact angles were observed (Fig. 4c). The contact angle for Cu and Ge does not change with time, while the contact angle for the  $\text{CaF}_2/\text{Al}$  system decreases rapidly from  $140^\circ$  to  $92^\circ$ . This feature is well known and is attributed to the formation of a volatile aluminum sub-oxide and de-oxidation of the drop surface during heating in vacuum at  $T > 1000$  K [5]. A unique spreading behavior (monotonically increasing contact angles with time) was detected for these systems at 1523 K (Fig. 4d).

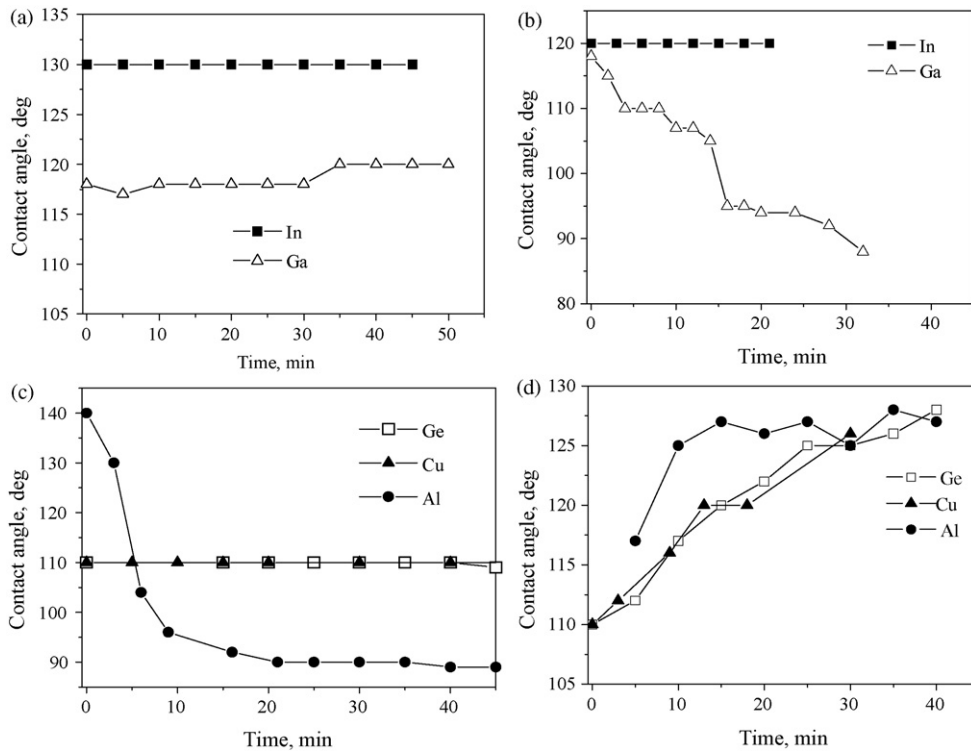


Fig. 4. Contact angle in the  $\text{CaF}_2/\text{Me}$  systems at: (a) 1173 K, (b) 1423 K, (c) 1423 K and (d) 1523 K.

The shapes of the drop/substrate interface for the  $\text{CaF}_2/\text{Ga}$  and  $\text{CaF}_2/\text{Ge}$  systems are shown in Fig. 5 as a function of contact duration. No changes of the substrate thickness and of the metal/ceramic contact area were detected in the  $\text{CaF}_2/\text{Ga}$  system, while the drop volume decreased significantly in the course of the experiment (Fig. 5a–c). In this system, the contact angle decreases as a result of the drop evaporation.

On the other hand, a reduction of the substrate thickness and only minor changes of the metal drop volume during wetting experiment were detected for the  $\text{CaF}_2/\text{Ge}$  system. The substrate sublimation leads to an increase of the apparent contact angle (Fig. 5e–f). A similar behavior was observed for the  $\text{CaF}_2/\text{Cu}$  system. For both cases, the presence of  $\text{CaF}_2$  was detected at cold parts of the vacuum chamber. Thus, the

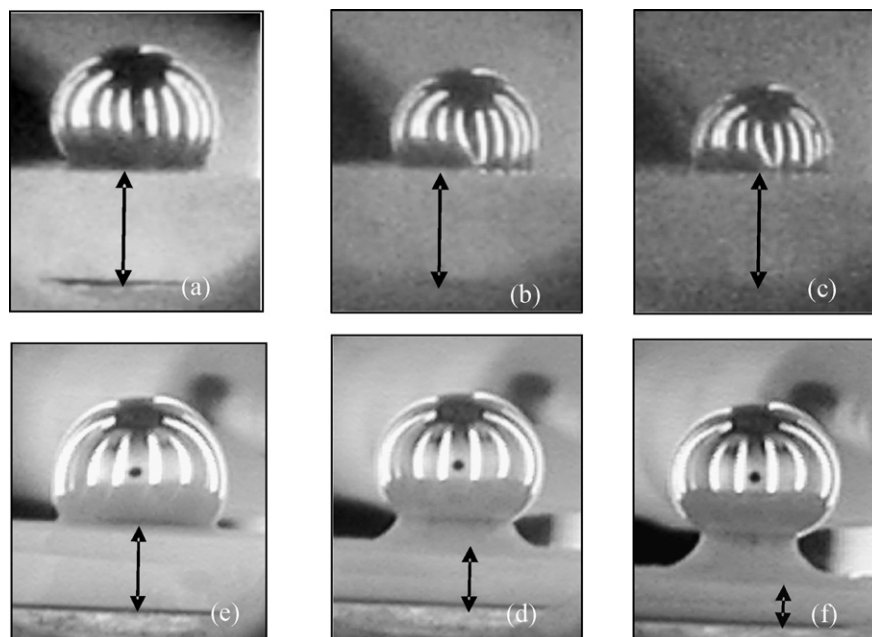


Fig. 5. Macroscopic view of the drops on the  $\text{CaF}_2$  substrate. For the  $\text{CaF}_2/\text{Ga}$  system at 1423 K after 2 min (a), 16 min (b) and 24 min (c). For the  $\text{CaF}_2/\text{Ge}$  system at 1523 K, after 10 min (e), 20 min (d) and 30 min (f). The thickness of the substrate is marked by arrows.

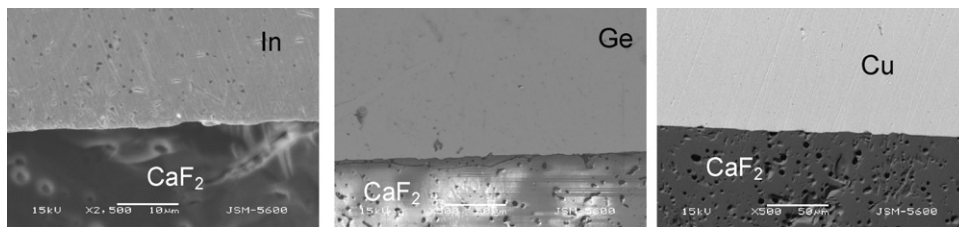


Fig. 6. SEM images of the interface in the  $\text{CaF}_2/\text{Me}$  systems after wetting experiments at 1423 K.

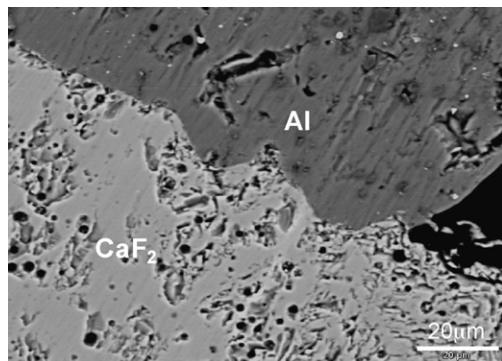


Fig. 7. SEM image of the interface between Al and  $\text{CaF}_2$  substrate after wetting experiments at 1423 K.

spreading behavior is related to the evaporation rate of the melts and the sublimation rate of the substrate and may be predicted.

#### 4.2. Interface characterization

According to SEM/EDS analysis, no evidence for the presence of new phases and of Ca in the melts was detected in the  $\text{CaF}_2/\text{Me}$  ( $\text{Me}=\text{Cu}, \text{Ge}, \text{In}$ ) systems (Fig. 6). In the  $\text{CaF}_2/\text{Al}$  system, groove formation at the metal/ceramic interface, a detectable amount of Ca (in the form of Ca containing inclusions) and a porosity within the Al drop were observed (Fig. 7). The presence of the porosity indicates the formation of AlF gas, which continuously transfers through the melt.

### 5. Discussion

The differences in the macroscopic contact angle and in the spreading kinetics for various  $\text{CaF}_2/\text{Me}$  systems (Fig. 4) may be attributed to the chemical interaction at the interface and to the rates of the metal drop evaporation and the substrate sublimation. The first factor affects mainly the initial contact angle. The second factor determines the shape of the drop/substrate interface. According to the thermodynamic analysis, only the  $\text{CaF}_2/\text{Al}$  system may be really considered as a reactive system. In this case, the lowest contact angle ( $92^\circ$ ) and evidence for interaction at the interface were observed (Fig. 7). The initial wetting angles for the Ge and Cu drops are relatively high (close to  $110^\circ$ ) and may be related to a limited degree of interaction. Surprisingly, high initial wetting angles were detected for the metals with low melting temperatures (In and Ga), even though that the  $\text{CaF}_2/\text{Ga}$  and  $\text{CaF}_2/\text{In}$  systems may be, on some extent, considered as reactive systems. It is difficult to suggest a reasonable

explanation of this feature based on the experiential results of the present study. A further investigation has to be carried out.

With regard to the spreading kinetics in the  $\text{CaF}_2/\text{Me}$  systems, a decreasing contact angle with increasing temperature is a well-known feature, generally attributed to the formation of new interface layers or to changes of surface energy of a melt [5]. The opposite wetting behavior (dewetting) is quite unique, in particular, for metal/ceramic systems. The common explanation of this dewetting behavior is related to a liquid metal film, which is unstable in contact with a solid substrate and transforms to a drop [7,8]. Another mode of dewetting was observed in the  $\text{Al}_2\text{O}_3/\text{Al}$  system [9–11]. In this system, the contact angle initially decreases due to significant evaporation of Al drop, which is strongly “pinned” to the substrate. At a certain moment, when the system is far enough from the equilibrium state, the drop “jumps up” in order to achieve its equilibrium contact angle and an apparent dewetting is observed. The differences in the spreading kinetics in the  $\text{CaF}_2/\text{Me}$  systems may be well accounted for by using the calculated vapor pressure of the metals and  $\text{CaF}_2$  (Fig. 8) assuming that these vapor pressures determine the rate of the melt evaporation and substrate sublimation. The contact angle evolution for various metals cannot be explained on the basis of vapor pressure differences only. We must also take into account that the Me drop, to some extent, is “pinned” to the substrate and the degree of “pinning” depends on the work of adhesion. The calculated values of the work of adhesion for the  $\text{CaF}_2/\text{Me}$  systems are presented in Table 1. The interface evolution may be illustrated by the schemes in Fig. 9. The spreading behavior in the systems with a high metal vapor pressure and a low value of the work of adhesion (i.e. the drop is not “pinned”

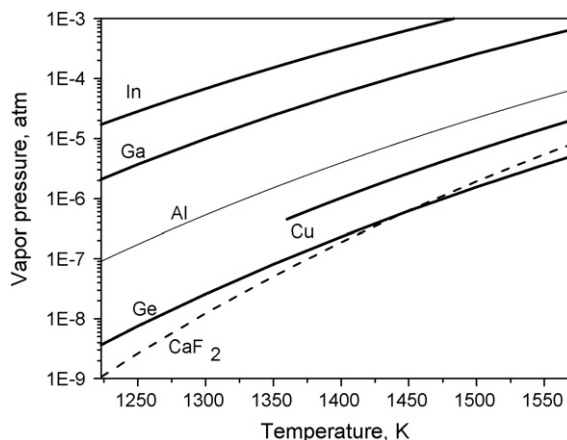


Fig. 8. Vapor pressure of pure liquid metals and  $\text{CaF}_2$  as a function of temperature.

Table 1  
Work of adhesion in the CaF<sub>2</sub>/Me systems (according to data in Fig. 4b and d)

Metal	Temperature (K)	Surface energy [5] (mJ m <sup>-2</sup> )	Initial contact angle (except for Al) (°)	Work of adhesion (mJ m <sup>-2</sup> )
Cu	1523	1350	110	887
Ge	1523	610	110	401
In	1423	560	120	280
Ga	1423	720	118	382
Al	1523	870	92	840

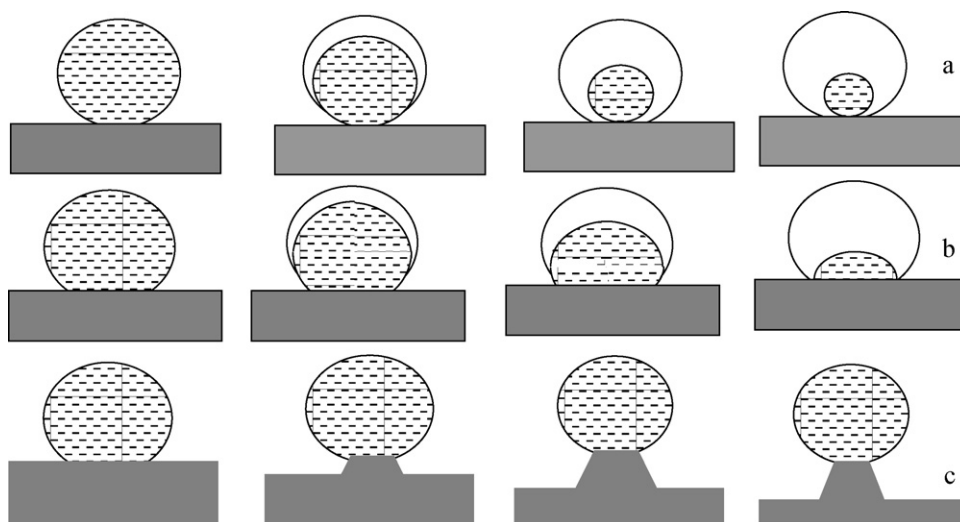


Fig. 9. The schematic draws of the contact angle evolution in the CaF<sub>2</sub>/Me systems: (a) the contact angle does not change (high vapor pressure of the metal and low work of adhesion), (b) the contact angle decreases (high metal vapor pressure and high work of adhesion) and (c) the formation of a neck-shape contact between the drop and substrate (substrate sublimation has a major role in substrate/drop interface evolution).

to the substrate) corresponds to the scheme shown in Fig. 9a. In this case, the apparent contact angle is equal to its equilibrium value and does not change. The CaF<sub>2</sub>/In system (Fig. 4b) seems to follow this scenario. For the systems with higher values of the work of adhesion and high metal vapor pressure, the interface shape evolution corresponds to Fig. 9b. In this case, the drop is “pinned” to the substrate and the contact angle decreases due to drop evaporation. These conditions are realized for CaF<sub>2</sub>/Ga in Figs. 4b and 5a–c. A neck-shape contact between the metal and the substrate is formed when the Me and the substrate have comparable vapor pressures and evaporate simultaneously. In this case, the substrate sublimation takes place only from the free surface around the drop and causes an apparent increase of the contact angle (Fig. 9c). Liquid Cu and Ge display this behavior.

In the reactive CaF<sub>2</sub>/Al system, the contact angle at 1523 K increases, while the neck-shape interface was not observed. In order to understand this behavior an additional experiment at 1573 K was carried out and a further increase of the apparent wetting angle (140°, after 5 min) was observed. This behavior may be attributed to an intensive gas transfer (Ca and fluorides) from the interface through the liquid. Even the formation of very thin gaseous layer may take place at high temperature. This layer, evidently, partially separates the drop from the substrate and provides the relatively high apparent contact angle.

## 6. Conclusion

All the investigated melts (Me = Ge, Cu, Al, Ga and In) do not wet CaF<sub>2</sub>. For liquid Ge, Cu, Ga and In the contact angle was  $\gg 90^\circ$  and no condense products at the metal/ceramic interface were detected. For the CaF<sub>2</sub>/Al system, the contact angle was  $92^\circ$  and interface interaction was detected and attributed to AlF(g) formation.

Different spreading behavior modes were observed for the various metals. The contact angle remains constant for In, decreases with time for Ga and increases for Cu, Al and Ge. The spreading behavior and the values of the apparent contact angle depend on the rates of evaporation of the metal, sublimation of the substrate and on the values of the work of adhesion at the interface. The spreading behavior of the metal drops on the CaF<sub>2</sub> substrate may be predicted by the thermodynamic analysis of the ternary Ca–Me–F systems.

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