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Wetting and infiltration of volatile fluorides by In-Ti melt

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Abstract In this study, the effect of the volatile nature of thermodynamically stable fluorides (MgF_2, CaF_2, and BaF_2) on wetting and infiltration phenomenon is discussed. Specially designed sets of experiments under different conditions of fluoride vapor evacuation were conducted. Experiments with In-Ti (~ 1 at.%) drops covered by a small cap and with artificially closed and open capillaries suggested that under restricted conditions of vapor evacuation, a thin solid layer is formed on the surface of the liquid metal, mechanically preventing both the spreading of In-Ti melt at the surface of the dense substrates and liquid penetration into the porous preforms.

Introduction

Pressureless infiltration of a porous ceramic perform by a molten metal is a promising approach for the fabrication of metal-matrix composites [1]. This process, similar to wetting phenomena, is governed by the energy gain of a system due to the substitution of ceramic- and metal-vapor interfaces by a metal-ceramic interface. Thus, in general, a good wetting between a melt and a ceramic is a prerequisite condition for spontaneous (pressureless) infiltration processes [2–6]. Nevertheless, for some systems, where good wetting is achieved as a result of chemical reactions at the interface, the free infiltration does not occur [7, 8]. This phenomenon is attributed to a blockage of the open pores by the reaction products that mechanically prevent a metal penetration.

In the previous studies [9], it was observed that In-Ti alloys display good wetting on the CaF_2 substrate, and no interfacial products were detected. The improved wetting in this system was attributed to the preferential Ti adsorption at the interface, which decreases the metal/ceramic interfacial energy [10, 11]. In spite of a contact angle of 20°, sufficient for free infiltration, the spontaneous penetration of the metal into a porous CaF_2 preform does not take place. It was suggest that this feature reflects the volatile nature of the substrate. Fluorides are thermodynamically stable compounds that have high-vapor pressure at relatively low temperatures. A comparison of the equilibrium vapor pressures of some fluorides and oxides, calculated based on the data [12] as a function of temperature is presented in Fig. 1.

The data presented clearly indicate the volatile nature of fluoride compounds in comparison with oxides. A relatively high-vapor pressure of the fluorides within the pores where the vapor evacuation is restricted may lead to its condensation on the surface of the liquid metal and the formation of a thin solid layer, which prevents the metal penetration. In order to understand this feature in depth, the infiltration of the In-1 at.% Ti alloy into porous CaF_2, MgF_2, and BaF_2 preforms and the wetting behavior under different conditions of vapor evacuation are investigated.

Experimental

Dense CaF_2 substrate (99% of relative density) polished down to the 1 μm diamond paste level and ultrasonically cleaned in acetone and ethanol was used for wetting experiments under different conditions of vapor evacuation.

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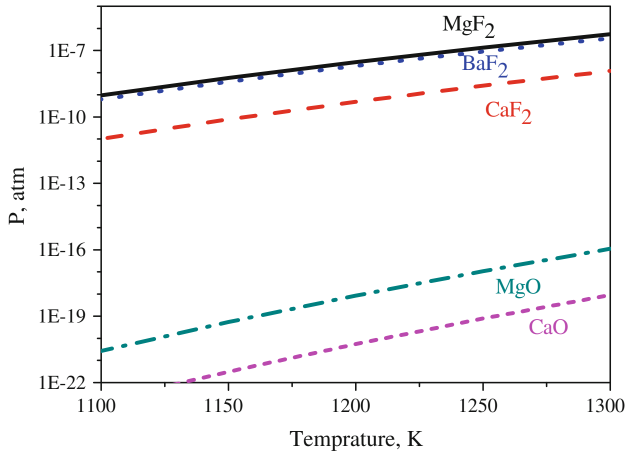


Fig. 1 The equilibrium vapor pressure of fluorides (MgF_2, CaF_2, and BaF_2) and oxides CaO, MgO as a function of temperature

The sessile drop wetting experiments were performed in a vacuum furnace (1–4 × 10^{-3} Pa) at 1123 K. In-1 at.% Ti alloy was prepared in situ during heating (purity of In and Ti was 99.99%). Along with regular sessile drop experiments, where metal drops are exposed to a dynamic vacuum, several experiments were conducted with drops covered by a small cap made from CaF_2. This cap, which has a diameter and height of about 10 mm, restricts the vapor evacuation in the vicinity of the drop. In this case, only final contact angle after cooling to room temperature may be observed.

The infiltration experiments of In-1 at.% Ti with three types of fluoride preforms (MgF_2, CaF_2, and BaF_2) were conducted under a dynamic vacuum. The preforms were prepared from 99.9% pure powders of various average particle sizes (3, 20, and 120 μm) by cold pressing and sintering in an air furnace. Open porosity of the preforms varied from 20 to 40 vol.%. The combination of various particle sizes and open porosity provides different pore sizes within preforms.

Metal/ceramic interfaces were studied using SEM (Jeol GSM 5600) equipped with an EDS analyzer. The surface of In-Ti drops was analyzed by X-ray Photoelectron Spectroscopy (XPS) with lateral resolution of about 20 μm using the ESCALAB 250 system.

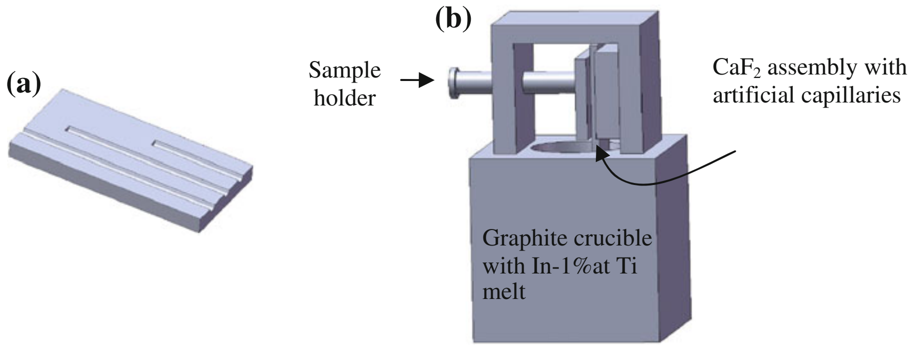
Model experiments of the liquid metal rising within open and closed artificial capillaries were also designed and conducted. The capillaries were built from two transparent CaF_2 slices attached to one another. One slice was flat and at the surface of the second one short and some long slits (~300 μm) were made (Fig. 2a). The slices were held together with a graphite sample holder (Fig. 2b). Thus, artificial capillaries, open and closed, were obtained and immersed into In-Ti alloy at 1123 K under a dynamic vacuum of 10^{-3} Pa. The levels of the raised metal within these capillaries were observed visually after cooling.

Experimental observations and discussion

The results of wetting experiments for the CaF_2/In-1 at.%Ti system were reported and discussed in our previous studies [9, 11]. It was observed that a small addition of Ti (~1 at.%) to liquid In improves wetting and a contact angle of about 20° is achieved. No evidence of new phase formation at the interface was detected by SEM analysis. The improved wetting was attributed to the preferential Ti adsorption at the interface [10, 14, 15]. A similar effect of Ti addition to pure In on the wetting behavior of the alloys was observed also for MgF_2 and BaF_2 substrates. These experimental observations are in agreement with the results reported by Naidich [13].

Surprisingly, the drops which were covered by a ceramic cap did not spread, and the final contact angle (observed after cooling) was significantly higher than 90°. This phenomenon cannot be explained by a change of the liquid–vapor surface energy, which actually decreases as a result of vapor adsorption. For the initial contact angle of about 20°, this interfacial energy decreasing should promote spreading. According to the XPS analysis performed on the surface of the solidified drops (Figs. 3 and 4a) the vapor adsorption actually takes place at the initial stage and afterward leads to the formation of a thin solid layer (~90 nm) consisting of Ca and F at the surface of the covered drop.

Fig. 2 Schematic view of a set-up for investigation of capillary rise of the melt. **a** One side of the transparent CaF_2 slice containing artificial slits (this side was attached to the flat second one with the same dimensions in order obtain artificial open and close capillaries). **b** The graphite crucible for melt and the sample holder



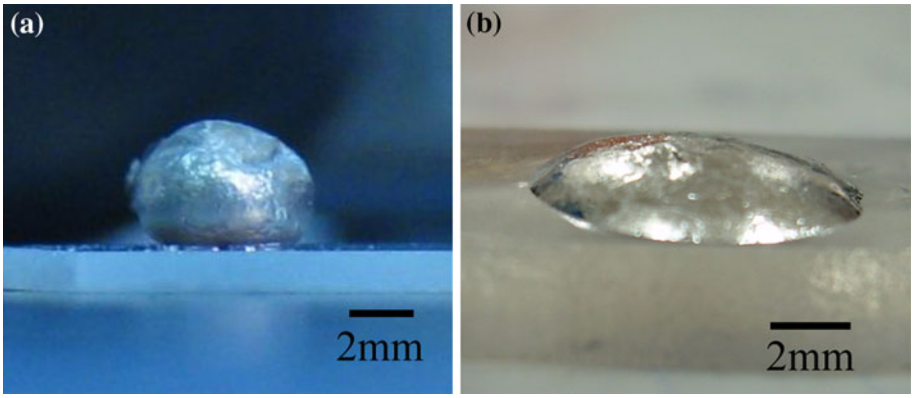


Fig. 3 Metal drops after wetting experiments under different conditions. **a** The drop was covered by a CaF_2 cap, **b** the drop was not covered

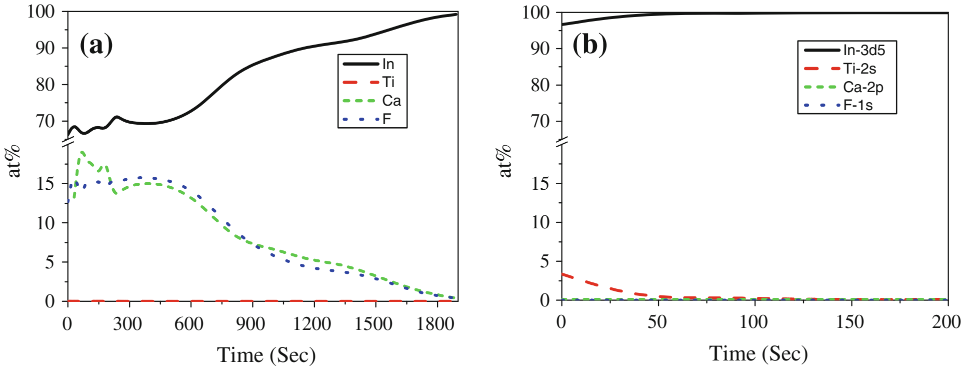


Fig. 4 XPS depth profile from the surface of the covered (**a**) and uncovered (**b**) drops

Unfortunately, due to experimental restrictions, the presence of this layer cannot be detected at the experimental temperature, but a simple calculation of the number of CaF_2 molecules (using its partial pressure 10^{-5} Pa [16], volume of the cap 0.8 cm^3 and the drop diameter of about 2 mm) shows that this number is not enough for even a mono-molecular layer formation at the drop surface as result of vapor condensation during cooling. Thus, evidently, this solid layer is formed at the experimental temperature and mechanically suppresses the spreading of the covered drops.

XPS analysis indicates that the surface of the drop exposed in a dynamic vacuum is enriched by Ti compared with its content in the bulk. This fact may be attributed to a partial Ti oxidation during cooling that always occurs. On the surface of the covered drop no presence of Ti was detected. This observation supports the suggestion that thin solid CaF_2 layer is formed at the experimental temperature and prevents Ti oxidation during cooling.

For the infiltration experiments were conducted in a dynamic vacuum and therefore low contact angles were achieved. However, In-Ti melt did not penetrate into the porous MgF_2, CaF_2, and BaF_2 preforms independently of their structure (porosity and pore size). SEM micrographs (Fig. 5) indicate relatively low contact angles and illustrate the non-infiltration phenomena.

It is clear that vapor evacuation from the porous body is significantly restricted. Thus, a thin solid layer of fluoride may be formed at the liquid surface, which is in contact with open pores, as well as at the surface of the covered drop. This layer mechanically prevents infiltration.

The results obtained with artificial capillaries confirm the suggestion. The open capillaries were completely filled, while the closed one was filled only partially (Fig. 6). It should be noted that the total pressure within the closed capillary increases from 1×10^{-3} to $2–3 \times 10^{-3}$ Pa as a result of capillary filling. It is clear that this value of the total pressure cannot be the reason for the phenomenon observed. Thus, in this case again the liquid in the open capillary was in a dynamic vacuum condition, while the evacuation of CaF_2 vapor from the closed capillary was completely constrained and a thin solid layer prevented the raising of the liquid in the capillary.

Conclusions

In-Ti ($\sim$1 at.%) drops spread on the surface of porous and dense fluoride (MgF_2, CaF_2, and BaF_2) substrates and low wetting angles sufficient for free infiltration processes were achieved. Nevertheless, spontaneous infiltration of the porous substrates by the liquid alloy does not take place. The results of the experiments, which were conducted under conditions of restricted fluoride vapor evacuation (covered drops and closed artificial capillaries), suggested

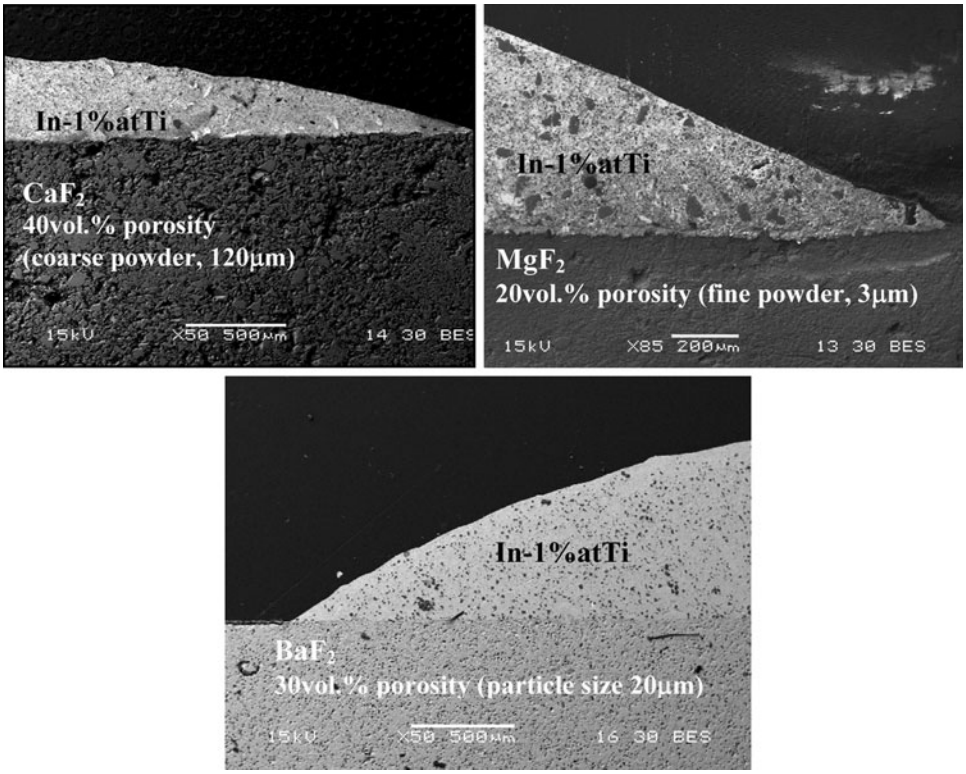


Fig. 5 SEM micrographs of the metal drops on the porous MgF$_2$, CaF$_2$, and BaF$_2$ substrates

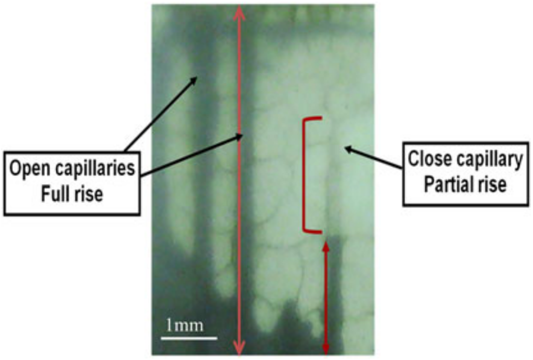


Fig. 6 Capillary melt rising in open and close capillaries

that for the substrates that display a volatile nature, a thin solid layer is formed on the surface of the liquid metal as a result of vapor condensation. This layer mechanically prevents the melt penetration into the porous body.

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