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Y_2O_3/(Cu–Me) systems (Me=Al, Ti): interface reactions and wetting

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

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Abstract Wetting behavior and interface interaction between Y_2O_3 and Cu–alloys were investigated at 1,423 K. Pure copper does not wet yttria substrate but the wettability is significantly improved by additions of Al and Ti. Different interface structures were observed in the Y_2O_3/(Cu–Al) and Y_2O_3/(Cu–Ti) systems. Relatively deep crater was detected at the interface in the first system, while Cu alloying by Ti led to formation of a flat interface with a thin reaction layer. The results of the wetting experiments and the interface features were well accounted for by thermodynamic analysis of the Y_2O_3/(Cu–Me) systems.

Introduction

Interface phenomena of metal/ceramic systems are not only of scientific interest but also of significant technological importance for variety applications. It has been established that the wettability of non-oxide ceramics by liquid metals is determined by thermodynamic characteristics of these systems, such as solubility and reactivity [1]. Rare earth oxides have high formation energy and considered as stable oxides and therefore a poor wetting by a ''non-reactive metals'' is expected. The alloying elements, which may lead to improved wetting, should react with these oxides [2]. The present study is an attempt to correlate the interface phenomena in the Y_2O_3/(Cu–Ti) and Y_2O_3/(Cu–Al) systems with thermodynamic properties of the ternary Cu–Ti–Y and Cu–Al–Y liquid solutions.

Experimental

Yttria substrates for wetting experiments with a relative density higher than 99% were prepared according to [3]. The substrate surface was polished down to 1 μm diamond paste and cleaned ultrasonically by acetone and ethanol.

Wetting experiments were performed using a sessile drop method at 1,423 K for 60 min under vacuum (10^{-3} Pa) as have been described elsewhere [4]. Cu–Al and Cu–Ti alloys were prepared in-situ by co-melting of appropriate amounts of the corresponding metals. After wetting experiments the interface was studied using scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) analyzer and X-ray diffraction (XRD).

Results

The wetting kinetics and final values of the contact angle in Y_2O_3/(Cu–Me) systems at 1,423 K are given in Fig. 1. Liquid copper does not wet yttria and the final contact angle (120°) was established after few minutes of contact. Ti and Al additions to liquid Cu improve wetting and the wetting angle less than $<90°$. was achieved at 50 at.%. Al and 10 at.% Ti (Fig. 1c, d).

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

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

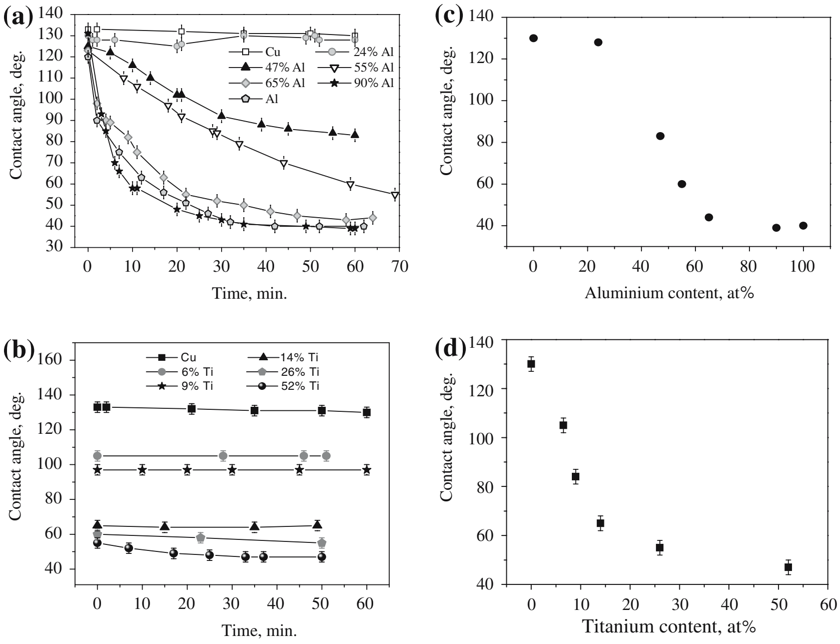

Fig. 1 The contact angles in the Y_2O_3 /(Al–Cu) and Y_2O_3 /(Ti–Cu) systems at 1,423 K: wetting kinetics—(**a**, **b**) and final values of the contact angle—(**c**, **d**)

The wetting kinetic for these contact systems are different. For Cu–Al drops, the final contact angles reached gradually (Fig. 1a) while for the Cu–Ti alloys, these angles are achieved almost immediately (Fig. 1b).

Two different types of interfaces in the Y_2O_3/(Cu–Al) and Y_2O_3/(Cu–Ti) systems were observed (Fig. 2). A strong chemical interaction between Al containing melt and yttria takes place and leads to relatively deep crater formation within the substrate.

Microscopic characterization (XRD and EDS analysis) detects that the solidified Cu–Al drop consists of Cu–Al matrix and Al_3Y inclusions. The crater within the substrate contains mainly $AlYO_3$ spinel and metallic (Cu–Al) channels (Fig. 2a).

Ti containing melts (>10 at.% Ti) also react with yttria, but only a thin interface layer (~2–4 μm) was formed (Fig. 2b).The compositions of this layer and of the solidified drop (Fig. 3) were determined by EDS analysis of a cross-sectioned sample. It was detected that interface layer near the substrate (region 1) is oxygen depleted yttria compared to yttria, which is far from the interface. The reaction product formed at the yttria/melt interface (region 2) consists of Y, Ti and O with the approximate composition of 22 at.% Y–20 at.% Ti–58 at.% O. The inclusions of the CuTi intermetallic phase, which evidently were formed in the course of cooling, were observed in the solidified drops (region 3). No yttrium presence within the drop was detected.

Discussion

The Y_2O_3/(Cu–Al) and Y_2O_3/(Cu–Ti) contact systems exhibit different wetting behavior and interface structure. The Al containing melt dissolves large amounts of Y while in the Ti containing melt, no Y dissolution was detected. These differences may be attributed to the thermodynamic properties of the ternary (Cu–Al–Y and Cu–Ti–Y) liquid metallic solutions that are in equilibrium with yttria. In order to understand the

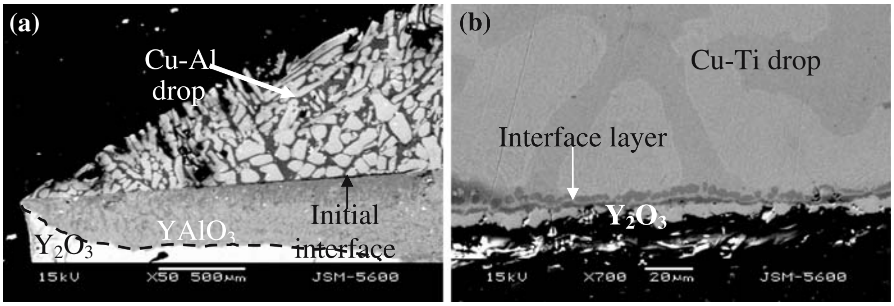

Fig. 2 Interface structure in the Y_2O_3/(Cu–47 at.% Al) (**a**) and in the Y_2O_3/(Cu–14 at.% Ti) (**b**) systems

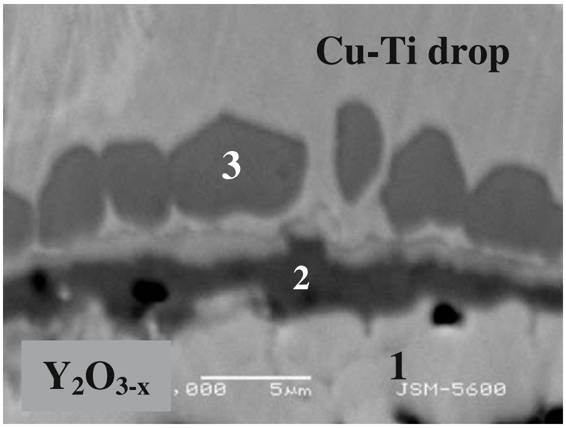

Fig. 3 SEM image and of the interface in the Y_2O_3/(Cu–14 at.% Ti). According to EDS analysis, region (1)—oxygen depleted yttria (Y_2O_{3-x}), region (2)—reaction layer with an approximate composition: 22 at% Y–20 at% Ti–58 at% O, region (3)—CuTi intermetallic precipitates. Region 2 seems to be bi-layered, however, it has a homogeneous composition, and therefore this ‘‘apparent’’ structure is attributed to the topography of the interface

differences between the systems a detailed thermodynamic analysis of the chemical interaction between Cu–Al and Cu–Ti melts with yttria was performed. As note above, the interaction of Al dissolved in liquid Cu with yttria leads to a new phase ($AlYO_3$) formation and Y transfer from the substrate to liquid solution. Thus, the equilibrium condition may be described by chemical reaction (1).

Absolute identification of the new phase formed at the Y_2O_3/(Cu–Ti) interface was impossible. Therefore, some additional considerations were taken into account in order to assume its composition. According to Zhang and Chang [5] at 1,373 K, no ternary oxides exist in Y–Ti–O system. Thus, the titanium oxide phases should be formed as a result of the interaction. There are several oxide phases in the Ti–O system and each of them is stable within a certain oxygen partial pressure range [6]. Thermodynamic analysis of the Ti–O system indicates also that the composition of a stable titanium oxide depends on the titanium activity in a metallic solution. It was established that for a relatively high titanium concentration (activity), which were investigated in the present study, the monoxide phase (TiO) is stable. Thus, the interaction may be described by Eq. 2. Underlined letters denote that Al, Ti, and Y are in liquid solutions, s and l denote solid and liquid phase

$$Y_2O_{3(s)} + \underline{Al}_{(l)} = AlYO_{3(s)} + \underline{Y}_{(l)}, \tag{1}$$

$$Y_2O_{3(s)} + 3\underline{Ti}_{(l)} = 3TiO_{(s)} + 2\underline{Y}_{(l)}. \tag{2}$$

The standard Gibbs free energies for reactions 1 and 2 ($\Delta G^0_{(1)} = 87\,\mathrm{kJ/mole}$ and $\Delta G^0_{(2)} = 268.9\,\mathrm{kJ/mole}$) were calculated for 1,423 K using thermodynamic data [7–10].

The equilibrium constants K, for these reactions may be expressed by Eqs. (3) and (4)

$$K_1 = \frac{a_Y}{a_{Al}} = \exp\left(-\frac{\Delta G^0_{(1)}}{RT}\right) = 6.5 \times 10^{-4}, \tag{3}$$

$$K_2 = \frac{a_Y^2}{a_{Ti}^3} = \exp\left(-\frac{\Delta G^0_{(1)}}{RT}\right) = 1.3 \times 10^{-10}, \tag{4}$$

where a_Y, a_{Al} and a_{Ti} are the activities of Y, Al and Ti in the melt. According to the values of the equilibrium constants, $AlYO_3$ formation in the Y_2O_3/(Cu–Al) system takes place whenever the a_Y/a_{Al} ratio is smaller than 6.5×10^{-4} and the TiO formation in the Y_2O_3/(Cu–Ti) system occurs when the activities ratio a_Y^2/a_{Ti}^3 is smaller than 1.3×10^{10}. In order to estimate the amount of Y, which may be dissolved in the Cu–Al and Cu–Ti drops, the activities ratio in the ternary solutions have to be determined as a function of Y concentration. In our previous study [11] we used the thermodynamic data [12–14] for the Cu–Al, Al–Y and Cu–Y systems and the Redlich–Kister approach [15] for the ternary Cu–Al–Y systems. Since the thermodynamic data for the Y–Ti is absent, the properties of the ternary Cu–Ti–Y system were evaluated using the first order Wagner approach for dilute solutions (5) [16].

$$\ln\gamma_i(\mathrm{Cu}) = \ln\gamma_i^0 + x_i\varepsilon_i^i(\mathrm{Cu}) + x_j\varepsilon_j^i(\mathrm{Cu}), \tag{5}$$

where *i, j*—indexes for titanium and yttrium, *x*—atomic fraction and ε—interaction coefficient. The activity coefficients $\gamma^0_{Ti}(\mathrm{Cu}) = 0.654$ and $\gamma^0_Y(\mathrm{Cu}) = 0.01$ were estimated using the thermodynamic properties of the Cu–Y and Cu–Ti systems [17, 18]. The Wagner coefficient $\varepsilon^Y_{Ti}(\mathrm{Cu})$ was evaluated according to Eq. 6, where ε_i^i (Cu) were taken as equal to $-2\ln\gamma_i^0$

$$\varepsilon_j^i(\mathrm{Cu}) = \pm\sqrt{\varepsilon_i^i(\mathrm{Cu}) \cdot \varepsilon_j^j(\mathrm{Cu})}. \tag{6}$$

According to binary Y–Ti phase diagram the repulsion tendency between Y and Ti atoms takes place, thus the positive value of ε^Y_{Ti} (Cu) = 2.8 was chosen for further calculations.

The a_Y/a_{Al} and a_Y^2/a_{Ti}^3 ratios as a function of the initial Cu content and the Y concentration in liquid solutions are shown in Fig. 4a, b. Lines 1 and 2

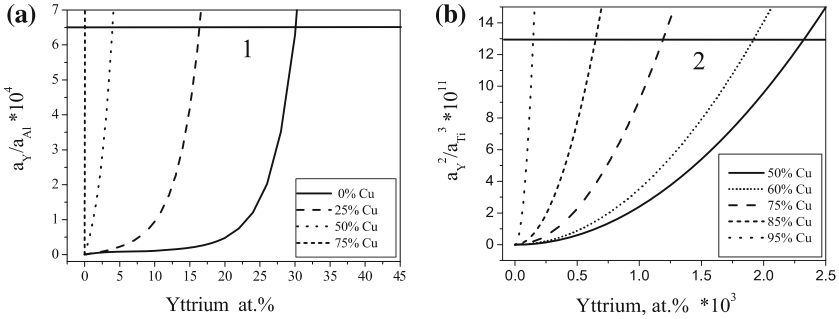

Fig. 4 Activities ratios as a function of the initial Cu content and Y concentration in the melts: (**a**)—Y_2O_3/(Cu–Al) system, (**b**)—Y_2O_3/(Cu–Ti) system

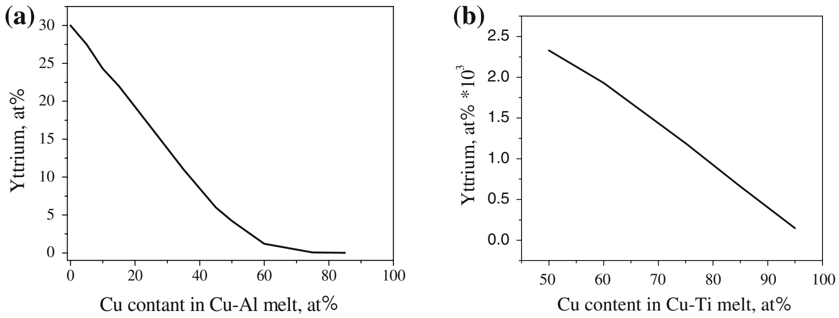

Fig. 5 Equilibrium Y content as a function of the initial Cu concentration in the melts: (**a**)—Y_2O_3/(Cu–Al) system, (**b**)—Y_2O_3/(Cu–Ti) system

correspond to the equilibrium constants for reaction (1) and (2). Each curve crosses these lines in the points, which correspond to the equilibrium Y content in the melt. For both systems, the amount of dissolved Y depends on the Cu content (Fig. 5a, b). For the Y_2O_3/(Cu–Al) system the Y content varies in 5–30 at.% concentration range, while in the Y_2O_3/(Cu–Ti) system, the Y concentrations are below 2.5×10^{-3} at.%.

These Y concentration ranges determine the amount of yttria that could be decomposed during interaction with Cu–Al or Ti melts and therefore the structure and composition of the near interface area. For the Y_2O_3/(Cu–Al) system, the equilibrium Y content in the melt is relatively high and a significant amount of yttria could be decomposed. This process is accompanied with deep crater formation and gradual decreasing macroscopic contact angle. For the Y_2O_3/(Cu–Ti) system the equilibrium concentration of Y is very low, consequently, only small amount of yttria could be decomposed. In this case, flat interface was observed and the final contact angle was achieved almost immediately.

Conclusions

The wettability in the Y_2O_3/Cu system is significantly improved by addition of Al or Ti. In the Y_2O_3/(Cu–Al) system a deep crater was formed beneath the drop and was filled by a new phase identified as $AlYO_3$. In contrast, in the Y_2O_3/(Cu–Ti) system a flat interface with very thin reaction layer was detected. The thermodynamic analysis suggests that the wetting mechanism, interface structure and the composition of the near interface area are controlled by a new phase formation and by the ability of the melt to dissolve the released yttrium.

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