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Interfacial energies and mass transport in the Ni(Al)–Al_2O_3 system: The implication of very low oxygen activities ☆

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Abstract

Adhesion and capillary-driven mass transport at ceramic–metal interfaces play a very important role in the performance and durability of materials for many applications, and the influence of the oxygen activity is a critical issue. This work systematically investigates the variation of interfacial energies and atomic transport mechanisms at metal–oxide interfaces at very low oxygen activities by bonding Ni–Al alloys and pure polycrystalline alumina under controlled conditions in sessile drop experiments. The angles and the evolution of the grain boundary grooves were analyzed by scanning electron microscopy, atomic force microscopy and focused ion beam milling to calculate the interfacial and grain boundary energies and the transport rates at the metal–Al_2O_3 interface. In parallel, high-resolution structural and chemical analysis of selected grain boundaries was performed using advanced transmission electron microscopy. Our results confirm that all the interfacial energies (metal–Al_2O_3, Al_2O_3 surface and grain boundary energy) are smaller at reduced $p(O_2)$ than those of stoichiometric interfaces. The atomic transport at the metal–Al_2O_3 interface was found to decrease initially with decreasing $p(O_2)$ but increased significantly with a further decrease in the oxygen activity.

Keywords: Metal–ceramic interfaces; Interface energy; Grain boundary energy; Grain boundary structure; Transmission electron microscopy (TEM)

1. Introduction

Adhesion and capillary-driven mass transport at ceramic–metal interfaces play a very important role in the performance and durability of materials for many applications from advanced composites to structural joints, microelectronics, solid oxide fuel cells, refractories, thermal barrier coatings, etc. However, there are still many open questions regarding the parameters that determine the capillary evolution of ceramic–metal interfaces. This is in part due to the complexity of the experimental set-ups needed to collect the high-quality experimental data required to guide and validate theoretical analysis. In this respect, recent advances in processing and characterization techniques have opened new opportunities for the analysis of high-temperature interfaces. This has resulted in novel approaches for the description of interfacial structures, including the formulation of the concept of "complexion" as the equilibrium two-dimensional state of an interface [1–4].

The fundamental thermodynamic quantity that measures interfacial bonding is the work of adhesion W_{ad}, which equals the free energy change per unit area after reversibly separating the interface to create two equilibrated free surfaces. In the case of a metal–ceramic interface we can write:

$$W_{ad} = \gamma_c + \gamma_m - \gamma_{mc'} \tag{1}$$

where γ_c is the ceramic–vapor interfacial energy or the ceramic surface energy, γ_m the metal surface energy and γ_{mc} the

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metal–ceramic interfacial energy. For metal–ceramic systems, the interfacial energies are often assessed by analyzing the wetting between a liquid metal and a solid ceramic substrate. The liquid metal forms a characteristic contact angle θ_0 on the solid ceramic. Assuming that at equilibrium the interface is flat and coplanar with the surface of the substrate, the Young equation can be used to describe a balance of forces at the triple junction in a simplified condition when the solid is perfectly rigid and insoluble, and the triple line can move only in the direction parallel to the surface of the substrate (one-dimensional approximation) [5,6]:

$$\gamma_m \cos\theta_0 = \gamma_c - \gamma_{mc}. \tag{2}$$

Mass transport at surfaces and interfaces is often evaluated by studying the evolution of grain boundary grooves on polycrystalline materials [7–24]. A grain boundary groove forms when a grain boundary intersects an interface between the solid and another phase (liquid or vapor), in order to equilibrate the interfacial forces at the triple junction (groove root). In an isotropic system this equilibrium can be written as:

$$\gamma_{gb} = 2\gamma_c \cos\left(\frac{\O_i}{2}\right), \tag{3}$$

where γ_{gb} is the grain boundary energy, and $\O_i$ is the dihedral angle at the grain boundary groove, and for the interface between a polycrystalline ceramic and a metal γ_c can be replaced with γ_{mc}.

The time evolution of the grain boundary width can be related to the rate-controlling transport mechanism. When grain boundary grooving is controlled by diffusion, the groove exhibits a characteristic maximum (hump) on each side, which would be absent if groove growth is controlled by the interfacial reaction. The groove width will vary with time as $t^{1/3}$ for volume diffusion-controlled growth, $t^{1/4}$ for interface diffusion and $t^{1/2}$ for interfacial reaction [25–27].

A metal–oxide system (M/NO_z) is intrinsically a ternary system where the oxygen activity is a fundamental variable (e.g. Ni–Al_2O_3 is actually Ni–Al–O) [28]. For a non-reactive metal–oxide couple, there is a compatibility range of oxygen partial pressures, $p(O_2)$, in which the metal and oxide phases can coexist in equilibrium (there is only one $p(O_2)$ for a metal in equilibrium with its own oxide). The lower boundary of the range is determined by the reduction of the oxide (or the formation of intermetallics such as $NiAl_x$ in the Ni–Al_2O_3 system) and the upper boundary by the oxidation of the more stable metal (or the formation of a mixed oxide, e.g. $NiAl_2O_4$). Within the compatibility range, the interfacial energies in the metal–oxide system are expected to depend on $p(O_2)$ as a result of various types of adsorption. The effect of oxygen activity on the equilibrium interfacial energies can be described using a variant of the Gibbs equation [28]:

$$\frac{d\gamma}{dlnp(O_2)} = -\left(\frac{kT}{2}\right)\left[\Gamma_O - \frac{2}{z}\Gamma_N\right], \tag{4}$$

where Γ_i refers to the excess amount of each species per unit area of interface (the interface was placed such that $\Gamma_M = 0$). This equation takes into account that in the presence of the oxide NO_z the activities of O (a_O) and N (a_N) are related:

$$a_0 a_N^z = K(T). \tag{5}$$

As a result, the difference between Γ_O and Γ_N dictates the change of γ with $p(O_2)$. Following this formulation and experimental data on contact angles and liquid metal surface energies, it has been proposed that in the range of $p(O_2)$ in which a metal and a ceramic are compatible, the interfacial energies should depend on oxygen activity [28], as depicted in Fig. 1. According to this model, a plateau region can be present if the compatibility $p(O_2)$ range is wide enough. In this plateau region all excesses are expected to be zero (a stoichiometric interface). On the other hand, the interfacial energies decrease towards the high and low ends of the compatibility range due to adsorption. For example, adsorption of oxygen on the metal surface can occur at a critical $p(O_2)$ which can be 3–8 orders lower than the equilibrium $p(O_2)$ for the oxidation of metal [28]. Conversely, adsorption of Al or the other metal or partially reduced Al–O complexes could be expected towards the lower boundary of the compatibility $p(O_2)$ range. Similarly, the energy of the grain boundaries that are in equilibrium with these interfaces is also expected to depend on the oxygen activity.

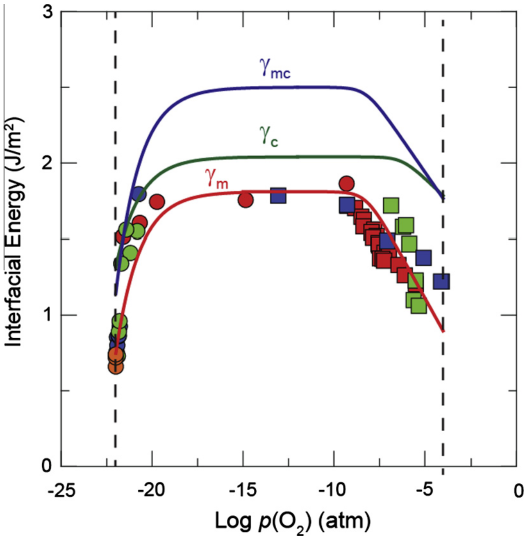

Fig. 1. Sketch illustrating the expected variation of the interfacial energies in the Ni–Al_2O_3 system in the $p(O_2)$ compatibility range (where no reaction is expected). Note that this is just illustrative to emphasize the expected effect of adsorption on the energies close to the limits of the range. As the compatibility region is relatively narrow it has been proposed that it is even possible that there is no plateau region for some of the interfaces [23]. The points correspond to experimental data for the surface tension of Ni, the low $p(O_2)$ values (circles) correspond to Ni–Al alloys assuming ideal solution. Data are taken from Refs. [36,57,59,86–89].

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