Intergranular films at metal–ceramic interfaces
Part I – interface structure and chemistry

Amir Avishai a, Christina Scheu b,1, Wayne D. Kaplan a,*

a Department of Materials Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel
b Max-Planck-Institut für Metallforschung, 70569 Stuttgart, Germany

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Abstract

In this work the structure and chemistry of intergranular films at metal–ceramic interfaces was investigated via detailed microstructural characterization of model metal–Al₂O₃ nanocomposites. We report here experimental results indicating the formation and stability of equilibrium nanometer-thick films at metal–ceramic interfaces. Thin ∼1 nm interface films were observed for two different metal–alumina systems (Ni and Cu) doped with glass-forming additives. High spatial resolution energy dispersive spectroscopy showed a difference in the chemical composition of the films at Ni–alumina and Cu–alumina interfaces. These results may have immediate ramifications on structural and functional properties of metal–ceramic interfaces.

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1. Introduction

Over the past 20 years a growing number of polycrystalline ceramic systems have been found to form amorphous equilibrium intergranular films at grain boundaries [1–4], at interfaces between dissimilar ceramic crystals [5], and at ceramic-free surfaces [6]. Microstructural features characterizing amorphous equilibrium intergranular films include a constant film thickness of the order of 1 nm, which extends along the grain boundaries or interfaces (which may reach microns in length) [1]. The film composition is often based on an oxide that includes glass network formers, such as SiO₂. These intergranular films are unique in that the total chemical content within the film is well above equilibrium segregation values, yet the films are not a three-dimensional bulk phase, and their behavior is dominated by long range forces [7]. It has been experimentally observed that the film thickness strongly depends on the composition and type of ions in the glass phase, while it weakly depends on the total amount of additives in the bulk [2,3,8]. In systems with intergranular films, low-angle grain boundaries and low-energy (“special”) grain boundaries are found to be “dry” (without a film). The films are found at high angle grain boundaries, since the total grain boundary energy (including the film) is less than the “dry” grain boundary energy [1]. This does not contradict impurity segregation to low energy grain boundaries [9–11].

Formation of a film with an equilibrium thickness suggests that a force balance exists between attractive and repulsive forces. Clarke and Shaw [1,12] modeled the force balance at ceramic grain boundaries, based on colloid-like behavior. According to their model the forces are dominated by long range attractive van der Waals forces and short range steric disjoining forces.
So far the investigation of intergranular films has focused primarily on ceramic systems. Recently, the presence of intergranular films was experimentally observed at Cu–alumina interfaces in melt-infiltrated alumina matrix composites [13]. While all of the Cu–Al₂O₃ interfaces investigated by Scheu et al. [13] contained thin amorphous films, the nature of the process used to form the composites led to the question whether the films formed at equilibrated metal–ceramic interfaces [14], or if they formed as surface films prior to infiltration with liquid Cu. Since equilibrium amorphous surface films exist [6], this is not a trivial issue. In a previous publication we reported initial experimental results supporting the presence of stable intergranular film at metal–ceramic interfaces [15]. If equilibrium films do exist at metal–ceramic interfaces, this is an important phenomenon, potentially critical to controlling both mechanical and functional properties of metal–ceramic interfaces.

In this work, we show detailed experimental results which indicate equilibrium films exist at Cu–alumina and Ni–alumina interfaces. Thin ~1 nm interface films were observed for the two different metal–alumina composite systems, containing predetermined amounts of glass-forming additives. The film thickness and chemistry were characterized in detail for both systems. The microstructural features discussed here form the basis for the calculation of Hamaker coefficients discussed in a companion paper [16].

2. Experimental methods

The processing procedure used in the present study was designed to obtain a significant number of equilibrated metal–alumina interfaces, for independent measurements of the intergranular film behavior. The metal–alumina composites served as a comparison to the samples studied by Scheu et al. [13] to establish whether equilibrium intergranular films will form under conditions in which the glass phase can stabilize. The Cu–alumina system was chosen, since the presence of intergranular films was first observed in that system [13]. Ni-alumina composites were included, to determine whether the phenomenon is limited to Cu–alumina.

2.1. Processing

Specimens for investigation were based on a polycrystalline α-Al₂O₃ composite (prepared using Sumitomo AKP 50 powder), reinforced with Ni or Cu particles. For each composite, two sets of samples were prepared, with and without glass-forming additives. SiO₂ was introduced by adding 4.2 g tetraethylorthosilicate (TEOS) into a water-based alumina (100 g) slip (70 wt.% Al₂O₃). The green alumina samples were prepared by pressure filtration, followed by firing at 900 °C for 4 h. Ca was then added by infiltrating the porous alumina preform with Ca nitrate in a water based solution (water/Ca nitrate, 4/1.5 by weight). The samples were then dried and calcined at 900 °C for 2 h. Cu or Ni was added in a similar manner to the Ca (using nitrates), and heat treated in a reducing atmosphere (Ar + 5 vol% H₂) to obtain Cu or Ni metal particles [17]. Sintering of the Cu–alumina composites was performed at 1550 °C for 4 h under argon at a total pressure of 0.013 Pa. The partial pressure of oxygen was measured to be lower than 1.3 × 10⁻⁷ Pa. The Ni–alumina composites were sintered under argon at a total pressure of 13.3 kPa at a temperature of 1500 °C for 4 h. The partial pressure of oxygen was lower than 1.3 × 10⁻¹³ Pa. For both composites heating and cooling rates of 20 °C/min were used.

2.2. Characterization

The microstructure and local chemistry of the sintered nanocomposites was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques, at room temperature. XRD measurements were used for phase identification, on polished samples in a conventional X-ray automatic powder diffractometer (PW-3020 goniometer, Philips) with a Cu Kα tube, operated at 40 mA and 40 kV. SEM was conducted on a FEI XL-30 microscope equipped with an energy dispersive spectrometer (EDS) and a wavelength dispersive spectrometer (WDS) (Oxford Instruments). A detailed study of the microstructure was conducted by conventional TEM. For the TEM investigations specimens were prepared by cutting thin slices from the bulk using a diamond wafering blade, followed by mechanical polishing, mechanical dimpling, and ion milling (Gatan PIPS) at 3.0–5.0 kV. The chemical composition and microstructure of the phases and grain boundaries were analyzed by analytical TEM, scanning transmission electron microscopy (STEM) and high-resolution TEM (HRTEM). Conventional and analytical TEM were performed on a 200 kV microscope (Model 2000 FX, JEOL) equipped with EDS (Model Link AN10000, Oxford Instruments). STEM was performed using a VG HB501 UX dedicated STEM (Vacuum Generators) with a beam diameter of <1 nm equipped with a Noran thin window Si(Li) EDS detector and a parallel electron energy loss spectrometer (PEELS) (Gatan 766). HRTEM was conducted using a 300 kV microscope (Model 3010UHR, JEOL) with a point resolution of less than 0.16 nm.

The Si and Ca excess were determined by EDS analysis in STEM. The data was acquired for 100 s while the electron beam was scanned over a rectangular area of
4 × 3 nm². One measurement was performed in the area containing the interface, and two in the nearby interface-free materials.

3. Results

3.1. General microstructure of composites

The typical morphologies found in the glass-doped and undoped Cu–alumina composites are shown in Fig. 1(a) and (b), respectively. A few important morphological differences should be noted: the glass-doped sample contains both occluded pores and occluded metal particles, while in the undoped samples only pores were found to be occluded in the alumina grains. The alumina grain size in the glass-doped samples was measured from SEM micrographs using Digital Micrograph (Gatan). The values are based on the average of the minimum and maximum grain diameters. The average alumina grain size in the glass-doped Cu–alumina composite was found to be more than ~2 times larger than in the undoped samples (4.2 ± 1.0 and 1.7 ± 0.3 μm, respectively). An aspect ratio of ~2.2 was measured for the glass-doped samples and ~2 for the undoped samples.

The increase in alumina grain growth rate, as well as anisotropic growth, are known to occur during sintering of alumina containing Ca and Si impurities in the absence of MgO additions [2,18]. The Ni–alumina composites showed a similar general behavior, although a few isolated occluded Ni particles were found in the undoped samples. This is probably due to localized contamination, introduced during the processing procedure (Table 1) [19]. The occlusion of metal particles and their size distribution relative to particles located at grain boundaries and triple junctions has been reported in other works [20–22]. However, the relatively large amount of occluded particles observed in the present study is exceptional, and was reported in a previous publication [19].

The addition of glass-forming additives also resulted in the formation of glass pockets at triple grain junctions (Fig. 2(a)). EDS measurements of the glass pockets performed in TEM showed they were rich in Si for both composites (Table 2). However, the Ca content was found to be higher in the Ni–alumina glass-doped samples. In both glass-doped composites the glass composition was found to be in the anorthite phase field [23]. EDS measurements performed in SEM to evaluate the total amount of additives introduced

![Fig. 1. Bright field TEM micrographs showing the general morphology of the Cu–alumina composites: (a) glass-doped sample; (b) undoped sample.](image)

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ (mol%)</th>
<th>CaO (mol%)</th>
<th>Metal (mol%)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Cu–alumina</td>
<td>0.04 ± 0.007</td>
<td>0.006 ± 0.003</td>
<td>–</td>
<td>WDS</td>
</tr>
<tr>
<td>Undoped Cu–alumina</td>
<td>–</td>
<td>–</td>
<td>3.7 ± 0.5</td>
<td>EDS</td>
</tr>
<tr>
<td>Doped Cu–alumina</td>
<td>1.1 ± 0.2</td>
<td>1.24 ± 0.7</td>
<td>4.8 ± 1.6</td>
<td>EDS</td>
</tr>
<tr>
<td>Undoped Ni–alumina</td>
<td>0.06 ± 0.02</td>
<td>0.04 ± 0.01</td>
<td>–</td>
<td>WDS</td>
</tr>
<tr>
<td>Undoped Ni–alumina</td>
<td>–</td>
<td>–</td>
<td>3.6 ± 0.2</td>
<td>EDS</td>
</tr>
<tr>
<td>Doped Ni–alumina</td>
<td>0.9 ± 0.2</td>
<td>0.6 ± 0.1</td>
<td>4.8 ± 0.35</td>
<td>EDS</td>
</tr>
<tr>
<td>Detection limit</td>
<td>0.004</td>
<td>0.002</td>
<td>–</td>
<td>WDS</td>
</tr>
</tbody>
</table>
during the processing indicated the Cu–alumina glass-doped samples had an overall higher Ca content (relative to the Ni–alumina glass-doped samples, Table 1), which resulted in the formation of a secondary CaO–6Al₂O₃ (CA₆) phase [15]. The formation of CA₆ depleted Ca from the glass pockets, resulting in lower Ca content in the glass pockets.

It should be noted that the EDS measurements performed on the glass pockets were conducted using a TEM with a LaB₆ source. Measurements conducted using a FEG-TEM showed a decrease of the Ca concentration as a function of electron beam exposure time, leading to an underestimation of the Ca concentration.

Fig. 2(a) presents a bright field TEM micrograph of the glass-doped Cu–alumina composite, showing the morphological configuration in which the metal–ceramic intergranular films were generally found. The intergranular film extends along an interface from a glass pocket (at the bottom side of the micrograph), and then continues to another interface forming a discontinuous film with small glass pockets located at the faceted steps. An EDS line-scan performed across the glass pocket shows Ca segregation to the glass–alumina interface, as well as Al and Ca segregation to the Cu–glass interface (Fig. 2(b)). No Si depletion or excess was detected at the alumina–glass interface.

### 3.2. Interface structure and chemistry

Thin (~1 nm) amorphous films were detected at all of the metal–alumina interfaces in the glass-doped samples, which were characterized in this study (more than 17 interfaces were studied). Examples of films found at the metal–ceramic interfaces for each of the doped composites is given in Fig. 3. For the micrographs shown in Fig. 3(a) and (b), the alumina terminating plane is the (0001) basal plane. Intergranular films were also found at interfaces terminated with (1012) and (1213) alumina planes, but these were found less frequently (Fig. 3(c) and (d)). Table 3 presents the results from intergranular film thickness measurements for the two different metal–alumina interfaces and alumina grain boundaries. Each film was measured at 10 different locations along the interface. The measurements were performed using Digital Micrograph (Gatan), and the length scales were calibrated using the alumina lattice spacing. Measurement of the film thickness was limited to cases in which the interfaces were observed to be parallel to the optical axis of the microscope (edge-on condition). This was the experimental factor that limited the study to 17 different interfaces. The edge-on condition was determined by observing the Fresnel fringes at both sides of the interface as a function of objective lens defocus [13]. The measurements were taken at objective lens defocus val-

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**Table 2**

<table>
<thead>
<tr>
<th>Composite</th>
<th>Al (at.%)</th>
<th>Ca (at.%)</th>
<th>Si (at.%)</th>
<th>Metal (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–Al₂O₃</td>
<td>31.8 ± 6.7</td>
<td>26.6 ± 7.8</td>
<td>40.1 ± 11.6</td>
<td>1.6 ± 1.3</td>
</tr>
<tr>
<td>Cu–Al₂O₃</td>
<td>27.5 ± 4.8</td>
<td>13.4 ± 4.1</td>
<td>56.9 ± 8.8</td>
<td>2.2 ± 0.4</td>
</tr>
</tbody>
</table>

The results are averages from 15 measurements.
ues between 10 and 15 nm, to slightly enhance the interfacial contrast. The tendency of the alumina interfaces to form faceted planes was beneficial in the case of metal–alumina interfaces, since the edge-on condition was predominately defined by the alumina terminating plane.

Examination of the metal–alumina interfaces by HRTEM indicated that the presence of the films persisted after occlusion of the metal–particles by the alumina grains, and extended along all the facets, as shown in Fig. 4, where a Cu particle is occluded in an alumina grain. Intergranular films at occluded particle

<table>
<thead>
<tr>
<th>Composite</th>
<th>Interface</th>
<th>Terminating plane</th>
<th>Thickness (nm)</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Al₂O₃ (Doped)</td>
<td>Al₂O₃–Al₂O₃</td>
<td>–</td>
<td>1.45 ± 0.15</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>Cu–Al₂O₃</td>
<td>(0001)</td>
<td>1.0 ± 0.1</td>
<td>(5)</td>
</tr>
<tr>
<td></td>
<td>Cu–Al₂O₃</td>
<td>(1213)</td>
<td>0.8 ± 0.1</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>Cu–Al₂O₃</td>
<td>(1012)</td>
<td>0.8 ± 0.1</td>
<td>(1)</td>
</tr>
<tr>
<td>Ni–Al₂O₃ (Doped)</td>
<td>Al₂O₃–Al₂O₃</td>
<td>–</td>
<td>1.0 ± 0.1</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>Ni–Al₂O₃</td>
<td>(0001)</td>
<td>0.87 ± 0.1</td>
<td>(7)</td>
</tr>
<tr>
<td></td>
<td>Ni–Al₂O₃</td>
<td>(0112)</td>
<td>0.96 ± 0.1</td>
<td>(3)</td>
</tr>
</tbody>
</table>

Fig. 3. HRTEM micrographs showing intergranular films at (a) a Cu–alumina interface and (b) a Ni–alumina interface. The terminating alumina plane in both (a) and (b) is (0001). (c) and (d) present examples of films at interfaces with (0112) and (1213) terminating alumina planes, respectively.
interfaces were observed for (0001), (1 I 0 2) and (1 2 1 3) alumina terminating planes.

Fig. 5 presents an example of an intergranular film at a faceted alumina grain boundary in the Cu–Al\textsubscript{2}O\textsubscript{3} glass-doped sample. EDS line-scans and spot measurements performed at such alumina grain boundaries (using VG-STEM) indicated the presence of Ca and Si in the grain boundary films. Similar measurements of films at metal–alumina interfaces in the glass-doped samples confirmed that they also contained Ca and Si. The Ca to Si excess ratios (atomic) measured at alumina grain boundaries and metal–alumina interfaces, is presented in Table 4. The excess is presented as a Ca/Si ratio, since in most cases the sample thickness was not measured for both interface-forming crystals, and differences in the thickness between the two phases may lead to errors in the absolute values. Some of the grain boundary excess measurements were quantified following Brydson et al. [2], which yielded a combined (Si + Ca) excess of 4.0 ± 0.5 at./nm\textsuperscript{2}. These values agree with Brydson et al., where excess values between 5.9 and 6.5 ± 30% at./nm\textsuperscript{2} were reported for alumina grain boundary films with a thickness of 1.2–2 nm.

Some of the intergranular films at Ni–alumina interfaces appeared to be partially ordered (Fig. 3(d)), although the contribution of the microscope operating conditions (objective lens defocus and lens aberrations) to the appearance of partial ordering remains to be investigated. The appearance of partial ordering usually correlated to conditions in which the Ni grain was close to a low-index zone axis. Ordering at interfaces between crystalline and amorphous (liquid) phases has been experimentally demonstrated [24], and has recently been investigated in depth by molecular dynamic studies [25,26]. In particular, simulations performed by Garofalini and co-workers [27,28] showed ordering of SiO\textsubscript{2} at glass–alumina interfaces. The ordering was increased by additions of Ca, which segregated to the interface and stabilized cage-like structures of SiO\textsubscript{2} tetrahedras. However, more HRTEM observations are required to confirm that the structure seen at the interface is a result of ordering of the intergranular film rather than an imaging effect.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Interface</th>
<th>Ca:Si excess ratio</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Al\textsubscript{2}O\textsubscript{3} (Doped)</td>
<td>Al\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3}</td>
<td>1:1.9 ± 0.5</td>
<td>(4)</td>
</tr>
<tr>
<td></td>
<td>Cu–Al\textsubscript{2}O\textsubscript{3}</td>
<td>1:2.1 ± 0.3</td>
<td>(2)</td>
</tr>
<tr>
<td>Ni–Al\textsubscript{2}O\textsubscript{3} (Doped)</td>
<td>Al\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3}</td>
<td>1:1.5 ± 0.2</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>Ni–Al\textsubscript{2}O\textsubscript{3}</td>
<td>1:0.2 ± 0.1</td>
<td>(3)</td>
</tr>
</tbody>
</table>

Fig. 4. (a) HRTEM micrograph of an intergranular film at a Cu–alumina interface, where the Cu particle was occluded in the alumina grain (Cu–alumina glass-doped composite). (b) A higher magnification micrograph of one of the corners of the Cu particle shown in (a).

Fig. 5. HRTEM micrograph of intergranular films at a faceted alumina grain boundary in the glass-doped Cu–alumina composite.
HRTEM analysis of the Cu–Al$_2$O$_3$ interfaces in the undoped sample did not reveal any intergranular films, but a strong contrast is seen at the interfaces (see Fig. 6). This is probably due to impurity segregation, which was detected both from S/TEM-EDS measurements conducted at the interfaces, as well as from WDS analysis of the bulk samples (see Table 1). In one undoped Ni–alumina sample, isolated Ni–alumina interfaces were found to have an intergranular film. No films were observed at the alumina grain boundaries in the undoped samples. It is important to emphasize here that although it is evident that the “clean” samples were not free from impurities, intergranular films did not develop in the Cu–alumina composite, indicating that a threshold amount of impurities is needed to form the films, which was not reached in this case.

Fig. 7 presents a HRTEM micrograph taken from an alumina \( \Sigma 3 \) grain boundary [29] in the glass-doped sample. This grain boundary is a low-energy grain boundary and therefore was not infiltrated by the glass [1,30]. While no intergranular film was detected at this boundary, studies of low energy alumina grain boundaries have shown the presence of impurity excess [9,11].

One case was observed in the glass-doped Ni–alumina composite where a Ni–Al$_2$O$_3$ interface was found with only a partial intergranular film (Fig. 8). EDS analysis performed on the same interface in an area free of the film showed the Ca content was below the detection limit. This EDS measurement was performed in TEM mode using a relatively large electron beam diameter (~30 nm). Under the same TEM conditions Ca and Si were clearly detected from Ni–alumina interfaces with an intergranular film.

4. Discussion

4.1. Structural aspects of intergranular films

4.1.1. Film stability

The experimental results in this study clearly indicate the stability of equilibrium intergranular films at metal–ceramic interfaces. By adding predetermined amounts of glass-forming additives to metal–alumina composites it was shown that the formation of the intergranular film was a direct result of the additives, and their formation...
was associated with a minimum doping level. HRTEM analysis of both (Ni and Cu) types of metal–alumina interfaces revealed the presence of intergranular films with a constant film thickness at all metal–alumina interfaces investigated (Fig. 3), with the exception of only one case where a partial film was found (Fig. 8). Films were found at the metal–alumina interfaces for particles located at alumina grain boundaries, and (occluded) particles located within alumina grains (Fig. 4).

It should be emphasized that the sintering process was performed at a high temperature, involving significant mass transport and grain growth (from a 0.3 μm powder to 5–10 μm grain size), so the presence of intergranular films at the end of the sintering process is an indication of their stability. The fact that these films persist even after occlusion of the metal particles by the growing alumina grains supports this conclusion. In addition, the two types of metal–alumina composites were prepared using different sintering conditions (temperature, total pressure and P(O2)), and both were prepared in a completely different manner than the samples investigated by Scheu et al. [13].

4.1.2. The effect of segregation levels on film formation

An interesting feature is the effect of the different doping levels on film formation. Scheu et al. [13] reported that only Cu–alumina interfaces were observed to have intergranular films, while the alumina grain boundaries were free of films. From the present investigation and the results from Scheu et al., four different cases may be identified, representing different levels of impurities: (1) no film formation, as in the undoped Cu–alumina composites in this study (0.04 ± 0.007 at.% SiO2, 0.006 ± 0.003 at.% CaO); (2) a slightly higher level of impurities resulting in non-uniform film formation at the metal–alumina interfaces as seen in the undoped Ni–alumina sample (0.06 ± 0.02 at.% SiO2, 0.04 ± 0.01 at.% CaO); (3) film formation at all of the metal–alumina interfaces as seen in the Cu-infiltrated alumina samples investigated by Scheu et al. (0.08 at.% SiO2, 0.04 at.% CaO); and (4) films found at both alumina grain boundaries and metal–ceramic interfaces as observed in the glass-doped samples from the present investigation. Since the processing parameters used for the various experiments differed, their role in the formation of intergranular films cannot be determined at this stage.

4.1.3. Interfacial energy and film formation

The Ni–alumina interface possessing a partial film was defined by a low-index orientation relationship between the alumina and Ni grains. From reports on films at ceramic grain boundaries, it is known that films are not formed at low-energy grain boundaries [1,30]. The same behavior was observed in the present study, where general high-energy alumina grain boundaries in the glass-doped samples were observed to possess intergranular films (Fig. 5), while a Σ3 alumina grain boundary (Fig. 7) was found without a film.

In Si3N4 composites reinforced with SiC particles, it was reported that for some low energy interface orientations no films were formed, whereas for high energy interfaces an intergranular film was present [31]. Kaplan et al. [9,10] reported the presence of Ca segregation to Al–alumina interfaces and to a basal twin boundary in a composite prepared by liquid infiltration of Al into a porous alumina preform. However, these samples did not contain a high enough concentration of glass forming additives to form glass pockets, and this may be the reason for the absence of intergranular films. Al–alumina interfaces are known to have a lower energy than Ni–alumina interfaces [32,33], where in the latter Al segregation reduces the Ni–alumina interface energy. The partially dry Ni–alumina interface in the present study (Fig. 8) may have had some Ca and Si excess at levels below the detection limit.

The results from the present investigation compared to the Cu-infiltrated alumina samples studied by Scheu et al. imply that intergranular film formation at metal–alumina interfaces is preferred over film formation at alumina grain boundaries, possibly due to a larger reduction in interface free energy. It is interesting to note that thermal etching conducted on the Cu–alumina glass-doped samples at a temperature of 1300 °C for 2 h (under Ar 5% H2) resulted in exudation of glass from the grain boundaries to grain boundary surface grooves, at a temperature similar to that used to infiltrate Cu into the samples investigated by Scheu et al. [13]. Kleebe et al. [34] and Luo et al. [6] showed in different systems that the intergranular film stability in some cases depends on temperature, and changes in thermodynamic parameters can cause the film to withdraw from an interface. It is possible that under the processing conditions used in Scheu’s study the films at the alumina grain boundaries were not stable, and only the films at the Cu–alumina interfaces were retained. In studies of model alumina grain boundaries [35,36], changes in the wetting behavior with temperature were reported, which lead to exudation of glass from the boundary to the surface, and then retraction of the glass upon cooling. For different sapphire free surfaces the exuded glass was found to spread to a different extent. This behavior is supported by thermodynamic calculations performed by Brada et al. [37].

Could grain boundary films withdraw at a temperature of 1300 °C and yet be stable at Cu–alumina interfaces? The answer is probably yes, given that at these temperatures exudation of glass to grain boundary grooves was observed in the current study, and the film at the Cu–alumina interface should be able to form via enhanced diffusion in the presence of liquid Cu [38]. This type of enhanced diffusion was observed under the same
working conditions at sapphire–Cu interfaces in dewetting experiments (in the absence of glass) at a temperature of 1000 °C due to dissolution of the sapphire substrate [39].

4.1.4. The role of the alumina terminating plane

HRTEM analysis of the films revealed only small differences in the film thickness between the two types of metal. The average thickness of the films at Ni–alumina interfaces and Cu–alumina interfaces was 0.9 ± 0.1 and 1.0 ± 0.1 nm, respectively (for the (0001) α-Al2O3 terminating plane). In the Ni–alumina glass-doped composite, films at rhombohedral terminating planes were found to be slightly thicker than at the alumina basal planes. However, in the Cu–alumina glass-doped samples the results were reversed; the rhombohedral and prismatic-planes had thinner films than at the basal plane. In Scheu et al.’s [13] study, the films found at the Cu–alumina interfaces showed a similar behavior to the Cu–alumina interfaces in the present study, although the thickness measured for the rhombohedral planes was significantly lower than in the present work (0.4–0.6 and 0.8 nm, respectively). This issue is discussed in the following.

4.2. Chemical aspects of intergranular films

4.2.1. Excess at interfaces and boundaries

Chemical analysis of the interfacial films indicated they consist of Ca and Si, resulting from the introduced dopants. EDS analysis of the alumina grain boundaries in the Cu–alumina and Ni–alumina glass-doped composites showed some variation in the Ca:Si excess concentration ratio: 1:1.9 and 1:1.5, respectively, while the films in both samples are Si rich. This variation might be due to inhomogeneous distribution of Ca in the sample. The Cu–alumina interfaces in the glass-doped samples showed a similar Ca:Si excess ratio (1:2.1) to the alumina grain boundaries. This is comparable to the Ca:Si concentration ratio of anorthite, and a similar result was reported by Powell-Dogan et al. [40]. On the other hand, the Ni–alumina interfaces were found to be significantly Ca rich with a Ca:Si ratio of 1:0.2. However, unlike the Cu–alumina samples there is a significant difference in the Ca:Si ratio between the alumina grain boundaries and the Ni–alumina interfaces within the same sample. This result is important since it indicates that the metal has an influence on the film chemistry. The difference in interface behavior between the Ni and Cu may possibly be a result of the low P(O2) which was maintained during the experiment with the Ni–alumina composite. For both Ni and Cu there is a dependence of the interfacial energy with alumina on P(O2), even below pressures needed to form oxides or aluminates, due to oxygen adsorption to the metal–alumina interface [32,38,41]. The fact that the P(O2) at which the two composites were prepared was in different regimes (the Cu–alumina in the oxygen adsorption regime while the Ni–alumina was in the reduction regime) may have influenced the segregation behavior at the metal–film interface, thereby modifying the film composition. This issue is of interest, given the results of Brydson et al. [2] on alumina grain boundary films with a nominal composition of CA6, which are closer to the values in the present work for Ni–alumina interfaces.

4.2.2. Role of bulk composition

It is important to note, that although bulk EDS analysis of the samples showed a wide distribution in the Ca composition within each sample, as well as between the samples, the alumina grain boundary Si:Ca ratio in both composites was relatively similar. This is emphasized, since both composites originated from the same initially doped alumina preform, which was cut into three parts and then infiltrated with the two different metal nitrates. The sol–gel process used to introduce the SiO2 resulted in a uniform distribution in the samples. However, Ca infiltration resulted in a wider concentration distribution. The Cu–alumina composite was Ca rich, resulting in the formation of CA6, while in the glass-doped Ni–alumina composite, which was Si rich, no CA6 was observed.

Tanaka et al. [8] showed that changing the bulk concentration of Ca in the ppm level resulted in alteration of the equilibrium film thickness at Si3N4 grain boundaries. Gu et al. [42] investigated the same samples and found that increasing the Ca bulk concentration up to a threshold of 220 ppm increased the Ca concentration in the film. However, above this value, the Ca concentration in the film remained constant although the film thickness continued to increase. A dependence of the film thickness on the film chemistry was also observed for grain boundary films in ruthenate resistors [4]. In the present study, a difference in alumina grain boundary film thickness was measured between the two composites. However, since only one film was measured for each case it is not possible to conclude if this represents a general behavior. The film thickness measured for the Cu–alumina interfaces in all cases were smaller than the grain boundary film thickness, and smaller than the values reported by Brydson et al. [2] for alumina grain boundaries.

4.2.3. Structure and chemistry of intergranular films

The line-scans performed between a Cu particle and an alumina grain across a glass pocket showed that Ca segregated to the alumina surface, while Al and some Ca segregated to the Cu particle surface (Fig. 2(b)). This type of measurement should be repeated on the Ni–alumina-doped sample to determine a possible difference in segregation behavior. In addition, high resolution chemical analysis of the elemental distribution in the film is
lacking and will have to be addressed in a future study. The same behavior of Ca segregation to the Cu and alumina surfaces was reported by Scheu et al. [13]. Molecular dynamics simulations performed by Bolonski et al. and Litton et al. [27,28] predicted the segregation of Ca to the alumina–film interface. When considering the composition difference between the films and glass pockets, which is one of the basic characteristic features of intergranular films, interfacial segregation should be taken into account. The difference in the film thickness for the different terminating planes could be a result of anisotropy of the alumina surface energy leading to anisotropy in segregation to the different terminating planes. This is considered the prime reason for elongated grain growth in the presence of Ca and Si impurities [43].

From the excess measurements of Ca and Si at the alumina grain boundaries in the present study, and the results from Brydson et al. [2], it is clear that the film composition is primarily based on Al₂O₃. A simple calculation based on the possible density of the film and its thickness shows that at the very least 50% of the film is made up of Al₂O₃. This point should be emphasized, since calculations of the Hamaker coefficient for the force balance leading to intergranular films in alumina were based on the assumption that the film is primarily composed of SiO₂ [1,44]. Since the films are primarily based on Al₂O₃, and given the experimentally proven presence of Ca, the properties of the film and the parameters needed for estimation of the Hamaker coefficient are different from those considered in the past. These aspects are discussed in detail in a companion paper [16].

The present results indicate that the film thickness cannot merely be explained based on the alumina surface anisotropy, but a more intricate behavior exists, including the influence of the metal on the film through modification of the chemical composition. In this sense it is very important to correlate the thickness measurements to the composition of the film.

4.3. Wetting versus nonwetting films

It is important to differentiate between two morphologically different types of intergranular films. The first is characterized by a thickness of a few atomic layers, and governed by long-range forces as described by Clarke's model [1,12]. In this case the dihedral angle is finite (a non-wetting film) and the addition of glass to the system will not result in deflocculation of the particles or grains. The second type of film has microscopic dimensions (micron range) and is a result of complete wetting of the matrix by the second phase. In this case the film thickness depends on the amount of second phase. The latter is controlled by classical thermodynamic considerations [45], and the liquid penetrating the grain boundaries (or interfaces) will essentially have the same composition as the bulk liquid.

It is feasible that the films characterized in the present study would be of the second type (wetting conditions), where external forces (such as capillary forces) reduce the intergranular film thickness to values in the nanometer range. Under such conditions, repulsive forces at the interfaces would be dominant in establishing a finite and constant film thickness.

In the present work initial inspection of the metal alumina triple junctions showed relatively small but finite dihedral angles. On the other hand, at alumina triple junctions the observed dihedral angles are always larger and tend to vary as a result of faceting of the alumina grains. If the entrance angle to the intergranular film is investigated at high enough magnification, it is possible to observe a small but finite dihedral angle (in Fig. 2 an angle of ～10° was measured). Furthermore, intergranular films with a constant thickness were found at the interfaces of occluded particles, adjacent to solidification voids containing a small amount of residual glass. If this system was under wetting conditions and the van der Waals forces were insignificant, then the films at the occluded particle interfaces would thicken. These findings, together with the measured differences in composition of the films versus the glass pockets at triple-junction, indicate the intergranular films characterized in this study are non-wetting equilibrium thickness films, where the finite thickness is dictated by long-range forces.

5. Summary and conclusions

The main objective of the present research was to establish the stability of equilibrium intergranular films at metal–ceramic interfaces. This was performed by detailed microstructural investigations of model metal–Al₂O₃ nanocomposites.

All the characteristic features of intergranular films commonly observed at ceramic grain boundaries are found for films located at metal–alumina interfaces. This includes a constant film thickness along specific interfaces, very small thickness variations for different metal–ceramic interfaces, a significant difference in composition of the glass pockets at triple junctions compared to the intergranular films, and film stability over a relatively wide range of thermodynamic conditions.

Variations in the chemical content of the films was measured for the two different metal–alumina interfaces, and for the alumina grain boundaries, indicating that the metal plays a role in defining the film chemistry, and thus thickness.

The presence of intergranular films at metal–ceramic interfaces can have important implications for metal–ceramic joining and metal–ceramic composites.
cant changes in the metal particle morphology were seen in the film containing composites, indicating an important role of intergranular films in the microstructural evolution of these materials.

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