

Nickel-Alumina Interfacial Fracture Toughness Using the Thick Foil Technique

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submitted to *Engineering Fracture Mechanics*, Jan. 2001

Abstract.

The interfacial fracture toughness of the nickel-alumina bond and the influence of interfacial chemistry are studied experimentally. Nickel and alumina form a relatively strong bond, thus many of the well-known methods for experimental determination of toughness fail due to the crack deflecting into the ceramic rather than cracking along the interface. Thus a thick foil technique that forces the crack to run along the interface without kinking into the ceramic was developed. This new technique eliminates any chemical masking agents on the interface, greatly reducing surface contamination and increasing bond strength. By varying the oxygen partial pressure during hot press bonding we show that higher oxygen partial pressure, as long as it remains below the threshold for formation of nickel aluminate spinel, increases the toughness by forming a NiO layer. We also show that even when spinel is formed a strong interface can still be obtained as long as the spinel layer is thin, below approximately 3 μm .

Key words:

fracture, interface, metal-ceramic, bonding, reactions

1. Introduction

Motivated by the potential for use of metal-ceramic composites as structural materials, and noting that the interface between the two components plays an important role in determining the material's performance, numerous studies on metal-ceramic bonding have been performed. However, despite recent, extensive efforts by researchers from different disciplines, metal-ceramic interfacial toughness is still not fully understood. Although many chemical and mechanical aspects of the interface are important, in this study we focus on the toughness of the metal-ceramic bond, and on the influence of interfacial chemistry on toughness. The interfacial toughness is influenced

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by a variety of factors, such as material purity, bonding conditions, (including temperature, pressure, hold time and atmosphere), and thermodynamics at the interface.

A range of different test methods has been developed to investigate the fracture resistance of metal-ceramic interfaces. Examples include the double cantilever beam method Suo and Hutchinson[1], and the four-point-bend specimen method, Charalambides et al.[2,3]. However, these methods are useful only for measuring the toughness of interfaces with low fracture resistance relative to the two components of the composite. Other test methods, such as the peel test and Double Cleavage Drilled Compression (DCDC) specimen, Turner et al.[4], are useful for measuring toughness of interfaces with high fracture resistance. However, they have a number of limitations to their application. For example, in peel tests, most of the work needed to peel a metal film from a substrate is dissipated by plastic flow in the film. This makes it very difficult to determine the work of fracture of the interface. Only a limited range of phase angles (ratio of crack tip shear to tension) can be applied using the DCDC specimen. Thus a new test method and sample geometry must be developed to obtain the desired information of toughness over a wide range of phase angles.

In the present study, nickel-alumina interfaces are selected as a model system for metal ceramic interfacial bonding, and the interfacial fracture toughness of nickel (Ni) and alumina ($\alpha\text{-Al}_2\text{O}_3$) is investigated. A sandwich sample with a relatively thick nickel foil is used to obtain the desired interfacial failure mode at the strongly bonded interface. The diffusion-bonded specimens are then loaded at four different angles to study the interfacial fracture toughness and its dependence on phase angle. A three dimensional finite element simulation is conducted to interpret the failure load test results from each specimen, with the measured failure loads used as input to the models. Residual stresses generated due to thermal mismatch between the two components during the cooling-down stage in the interfacial bonding process are also considered.

Although the influence of oxygen on interfacial strength has been widely studied, Ohuchi[5], Calow et al.[6], Trumble[7], Wan and Dupeux[8], most of these works concentrate on the interfacial chemical reactions. The resulting mechanical properties, such as interfacial strength, are rarely addressed. In the current work, the influence of oxygen on the strength of the nickel-alumina interface is investigated. Interfaces with and without the formation of a spinel interphase are

obtained and studied. In particular, the influence of oxygen partial pressure in the bonding atmosphere on the interfacial strength is studied for the case of interfaces containing no spinel.

2. Experimental Procedures

The interfacial fracture toughness testing geometry employed for this work was the sandwich specimen shown in Figure 1. It consists of a nickel foil bonded between two alumina plates. The nickel foil is polycrystal, 99.9% pure nickel² 2mm thick (reduced to 1mm after the diffusion bonding), while the two alumina pieces are polycrystal, 99.9% pure α -Al₂O₃³. As shown in Figure 2, the sample can be loaded at different angles relative to the interface to produce different mixes of interfacial shear to tension stresses. The two major challenges involved in designing tests for measuring the toughness of strong metal-ceramic interfaces are creating a precrack and controlling the path of the fracture.

In many material systems a precrack can be introduced by placing a masking layer on the interface before bonding. This layer inhibits the formation of a chemical bond. For example, in the Cu-SiO₂ system, a carbon coating over part of the Cu prevents bonding, resulting in a well-defined precrack, Thurston and Zehnder[9]. In other material systems boron nitride (BNi) can be used as a coating. However, in the Ni-Al₂O₃ system, it was found that although BNi suppressed bonding, resulting in a precrack, it could also diffuse along the interface, resulting in a weakened interface, Thurston and Zehnder[10]. To circumvent these problems a novel technique for introducing a mechanical precrack was developed. As shown in Figure 1, one of the alumina blocks is ground at an angle of 5° over the portion of the sample that will form the precrack. Next, a thin slice of alumina is glued to the now sloped section of the alumina block. This assembly is then ground flat and diamond polished to a roughness of 1µm. During hot press bonding, the glue between the wedge and block burns away, leaving this interface unbonded. In this manner, a slightly angled, yet sharp precrack is formed without chemically contaminating the interface we wish to test.

To measure interfacial fracture toughness, the crack must grow along the interface. In many attempts to measure the toughness of strong metal-ceramic bonds, the failure occurs not on the interface, but in the ceramic, as sketched in Figure 3. In initial test attempts, nickel layers of

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0.125mm and 0.25mm thickness were used, and two types of cracking were observed depending on the loading angle. When the loading angle was negative, or positive but with a small angle, say less than 15° , the crack tended to kink into the brittle alumina phase on the same side as the pre-crack, as shown in Figure 3a. If the loading angle is large and positive, the crack tended to jump across the nickel layer, into the alumina plate on the other side, see Figure 3b. Our solution to this problem is two fold. We load the specimen with at an angle that would tend to drive the crack into the metal. To circumvent the problem of the crack jumping across the metal foil and into the upper ceramic block, the metal foil thickness is increased. This has the effect of moving the high stresses due to the crack tip stress singularity away from the upper ceramic block. The upper ceramic block, then never sees stresses high enough to induce fracture from a pre-existing flaw. A foil thickness of 1mm was found to be sufficient for this. Thicker foils could be used, or a nickel block could replace the top alumina block. However, as the nickel foil increases in thickness, more plastic flow is allowed to occur in the system, meaning that the measured toughness will have more to do with the plastic flow of the metal than with the intrinsic toughness of the interface.

The specimens are prepared by first diamond polishing the alumina surfaces to a roughness of $1\mu\text{m}$, followed by degreasing with acetone, ultrasonically cleaning, and further cleaning by heat-treating at 1300°C for two hours, in the bonding atmosphere, before hot-pressing. The nickel and alumina are diffusion bonded by hot-pressing the sample for two hours at a temperature of 1300°C and pressure of 8.9MPa . During hot pressing, diffusion bonding occurs between nickel and alumina, but not at the alumina-alumina wedge interface (It was observed in all experiments that the cracks initiate from the pre-crack tip).

After hot pressing, the sandwich specimens, with pre-crack length of 12mm, are tested using the fixture sketched in Figure 2. This steel loading fixture allows θ , the angle between the applied load and the normal to the metal-ceramic interface, to be varied over the range $-90^{\circ} < \theta < 90^{\circ}$ in 15° increments. The samples are loaded to failure by an INSTRON universal testing machine at a constant cross-head speed of $0.2\text{mm}/\text{min}$.

3. Finite Element Analysis and Results

Finite element simulations were performed both to calibrate the sample, i.e. enable us to interpret the failure load data versus load angle in terms of critical values of the J-integral, J_c , at failure, and to investigate the influence of residual stresses and three dimensional effects on the resulting toughness values. The simulations were performed in 3D using the commercial FEM code, ABAQUS.

Figure 4 shows the finite element mesh for the sandwiched specimen. Half of the sample is modeled by using symmetry boundary conditions at the midplane. Twenty node solid (continuum), full integration, second-order interpolation, brick elements are used to simulate this non-homogeneous and non-linear three-dimensional fracture problem. A $1/r$ singular field at the crack tip is introduced by using twenty-node brick elements with collapsed faces and quarter point nodes. Furthermore, contact surfaces are defined on the crack faces to prevent the interpenetration of the crack surfaces. A linear-elastic calibration was first performed to verify the accuracy of the mesh designed for this study. In this calibration, a 3-D finite element analysis with homogeneous, linear-elastic material was performed using the same mesh designed for the non-homogeneous, elastic-plastic FEM simulation. The calibration results agree with those obtained using 2D analyses, Thurston and Zehnder[9].

Due to the mismatch in thermal expansion between nickel and alumina, as the sample cools large residual tensile stresses develop in the nickel foil. In order to interpret the measured interfacial strength correctly in terms of fracture toughness, the influence of the thermal residual stresses must be considered. Using the material model of Thurston and Zehnder[10] and the known cooling rate, the residual stresses were calculated analytically with and without considering high temperature creep above 777°K . The resulting evolution of tensile stress in the nickel foil shows that although the effect of creep is to reduce the initial stresses, most of the residual stress is built up after cooling below 777°K . The results indicate that in the thermal stress computation, creep of nickel at high temperature can be neglected, and thus the FEM thermal stress analysis can be conducted with the assumption that the specimen is at a stress-free state at 777°K and is cooled down from there. In the FEM simulation, uncoupled heat transfer and thermal stress analyses are first performed to calculate the residual stresses in the specimen. The results of this residual stress

analysis are then used as the pre-stress for the stress analysis of the sample under mechanical loading.

In the interfacial fracture of two linear elastic materials, the crack tip stress state is characterized by a complex stress intensity factor and a corresponding phase angle, Rice[11]. Fracture toughness is evaluated as the critical value of this stress intensity factor as a function of phase angle. This approach must be modified for interfaces in which one or both of the materials deforms plastically. Shih *et al.*[12] proposed that under SSY conditions, the crack tip fields could be represented by the J-integral and a near-tip plastic phase angle that characterizes the ratio of shear to tensile stress at the crack tip. This approach is taken in our analysis where fracture toughness is specified in terms of the critical J-integral value, J_c , computed as the value of J at the failure loads of the specimens, and the mode mixity or phase angle. In a three dimensional FEM simulation, the stresses vary along the crack front through the thickness, and thus J_c is obtained by integrating the corresponding two dimensional J line integrals across the thickness.

The method employed by Thurston and Zehnder[10] for calculating the phase angle is used in our study. The phase angle, or mode mixity, is associated with a length scale, \hat{L} , which should be within the K -dominant region, the region in which the stresses are given by the elastic $r^{-1/2}$ field. The near-tip elastic phase angle, $\hat{\Psi}$, can be evaluated directly from the ratio of shear to normal stress at a distance \hat{L} ahead of the crack, and is defined by

$$\hat{\Psi} = \tan^{-1} \frac{\sigma_{xy}(\hat{L}, 0)}{\sigma_{yy}(\hat{L}, 0)}.$$

A full-field finite element solution is used to locate the K -field, in which region, both σ_{yy} and σ_{xy} on the line $\theta = 0$ are proportional to $r^{-1/2}$, such that the curve of $\log(\sigma)$ versus $\log(r)$ has a slope of $-1/2$. The length \hat{L} is thus chosen within this K -dominant region. In our calculation, \hat{L} is chosen by fitting the $\log(\sigma_{yy})$ and $\log(\sigma_{xy})$ versus $\log(r)$ curves as discussed above, and is $200\mu\text{m}$. We use the approximation for the near-tip plastic phase angle, ξ , given by Shih *et al.*[12] for mixed mode fields under SSY conditions,

$$\xi = \hat{\Psi} + \varepsilon \ln \left(\frac{K^2}{\sigma_0^2 \hat{L}} \right), \quad (1)$$

where ε is the bimaterial constant Rice[11] ($\varepsilon = 0.017$ for Ni-Al₂O₃), σ_0 is the tensile yield stress, and K is the magnitude of the stress intensity factor, \mathbf{K} . This approximation is valid only for $|\xi| < \pi/6$, which is satisfied in our experiment. In our three-dimensional analysis, the mode mixity varies along the crack front, and thus the average mode mixity, or phase angle, is calculated across the specimen thickness.

4. Test Results

4.1 Toughness as a function of phase angle for fixed bonding atmosphere

We first present the test results for a group of samples bonded under one oxygen partial pressure and in conditions that do not form nickel alumina spinel at the interface. The influence of oxygen partial pressure in the bonding environment on fracture toughness will be presented in 4.2.

According to the phase diagram of the Al-Ni-O system at the 1300°C bonding temperature, a threshold pressure exists such that when hot-pressing is performed in an atmosphere with an oxygen partial pressure higher than the threshold of log of oxygen partial pressure -8.45, nickel alumina spinel forms at the interfaces, and the corresponding interfacial bond is formed through the spinel interphase. However, when the log of oxygen partial pressure is below the threshold, spinel is no longer an equilibrium phase at the interface. In all of our experiments, the bonding was performed well below the threshold. For the results in this section, X-ray diffraction analysis of the samples showed no evidence of nickel-aluminate spinel.

When samples were tested at a load angle of 15° cracks consistently deflected into the ceramic from the interface. Thus load angles of 30°, 45°, 60°, and 75° were used to drive the crack along the interface. The failure loads versus load angle are plotted in Figure 5. At least three tests were performed at each load angle. It can be concluded from Figure 5 that as the load angle increases, the failure load is higher. The results agree qualitatively with those obtained by Thurston and Zehnder[10]. However, in the present study, the fracture loads are much higher since the interface is free of boron nitride and other contaminants.

The results of the critical J-integral versus plastic phase angle are shown in Figure 6. Note that for a given loading angle, the phase angle depends somewhat on the load. Thus, although only four load angles were tested, there are several phase angles represented in Figure 6, as all samples for a given load angle did not fracture at exactly the same load. The results show that in this range of ξ the toughness is not a strong function of phase angle. Analysis of the J-integral considering the residual stresses demonstrates that the interpreted interfacial toughness will be greatly underestimated if the residual stresses due to thermal mismatch are not included in the FEM simulation. This increase is also consistent with what we observed in a study using cohesive zone analysis, Kolhe et al.[13].

As demonstrated, the sandwich sample geometry employed by our study contains a relatively thick nickel foil in order to force interfacial crack propagation along the strongly bonded interface. For this geometry the stress state and thus the J-integral, vary along the crack front from the surface of the specimen to the center of it. It shows that the J-integral at the surface is lower than that at the mid-plane by about 30%.

4.2. Influence of Oxygen on Interfacial Toughness

A number of studies on metal-ceramic interfaces have shown that both chemical and mechanical bonding, Lu et al.[14] determine the strength of the interfaces. However, chemical bonding takes a dominant role in metal-ceramic interfacial bonding and is necessary for strong adhesion. During diffusion bonding to form a metal-ceramic interface, a variety of products can form due to interfacial reactions. The formation of these products depends on the oxygen partial pressure and temperature used in the processing. As suggested by the phase diagram for the Al-Ni-O system at the 1300^o C bonding temperature, the products include intermetallic compounds, new oxides or solid solutions. The mechanical properties of the interface depend on the product and can thus be controlled by interfacial reactions.

Several models have been proposed to explore the mechanisms of joining metal to ceramic, and especially nickel to alumina. In some cases, it is supposed that the formation of an intermediate phase of the nickel aluminate spinel, NiAl₂O₄, plays an important role on interface strength, whereas, the bonding between nickel and alumina can also be achieved without the formation of

spinel but rather by bonding between Ni and O at the interface, Calow[6,15], Wasynczuk[16], Trumble[7], Wan[8].

In the present work, the influence on interfacial strength of oxygen both in the bonding atmosphere and dissolved in the nickel foil before diffusion bonding is investigated. Two types of interfaces form under different oxygen concentration conditions. One involves a direct bond between the two components, nickel and alumina, the other involves bonding through the formation of a spinel interphase. In section 4.1, the sample interfaces were formed with a nickel foil whose concentration of dissolved oxygen was below a critical level for the formation of spinel, and in an atmosphere where the oxygen partial pressure was also below its threshold for the formation of spinel at the bonding temperature. In this case, no nickel aluminate spinel (NiAl_2O_4) interphase formed at the interface. X-ray diffraction on the debonded interfaces detects no evidence of nickel oxide or nickel aluminate spinel within its resolution. Strong bonding between nickel and alumina is obtained under this condition. When the oxygen partial pressure is above the threshold, or/and the oxygen dissolved into nickel foil is above a critical level, nickel aluminate spinel (NiAl_2O_4) forms at the interface. Contrary to the results of Trumble and Rühle[17], we find that a strong interface can also be obtained in this case.

4.2.1 Influence of Oxygen Partial Pressure in the Bonding Atmosphere on Interface Toughness When No Nickel Aluminate Spinel Forms

It is observed that the oxygen activity in the atmosphere during diffusion bonding has a strong influence on the chemistry of interfacial bonding, Ohuchi[5], Trumble[7]. However, no quantitative work of this influence on nickel-alumina interface is found.

Within the range below the threshold level, 3.55×10^{-9} , the formation of the nickel aluminate spinel via the reduction of $\alpha\text{-Al}_2\text{O}_3$ by nickel is infeasible, since the change of Gibbs free energy for the reaction is very high. A strong bond at the nickel-alumina interface can normally be obtained. To investigate the influence of oxygen partial pressure on interface strength within this range, samples are fabricated at different oxygen partial pressures below the threshold. Their interfacial fracture toughnesses are then analyzed by fracture toughness testing combined with 3-D FEM simulation as discussed before.

The sample geometry, preparation, and testing procedure are the same as demonstrated in section 2, except that during hot-pressing, the atmosphere is changed in order to obtain different oxygen partial pressure levels. This level is controlled by varying the carbon monoxide (CO) to carbon dioxide (CO₂) ratio; the corresponding oxygen partial pressure can be calculated accordingly, Peters[18]. The same materials are employed for this study, in particular, the nickel foil is 99.9% pure nickel with very low dissolved oxygen concentration. The nickel-alumina interface bonded under three different log oxygen partial pressure levels, -10.2, -10.54, and -10.78 respectively is investigated. A constant load angle of 45° is applied.

The test and numerical simulation results are as shown in Figure 7 and Table 1, where the fracture load and toughness versus three different oxygen partial pressures is displayed. The results show that as the log of oxygen partial pressure increases (its absolute value decreases), or the oxygen partial pressure increases in the bonding atmosphere, the interfacial toughness increases. X-ray diffraction analysis of all three of the interfaces after debonding shows, within its resolution, no evidence of the formation of any other compounds such as nickel-aluminate-spinel or nickel oxides. This is consistent with the prediction based on the phase diagram. In summary, within a range below the threshold for spinel formation, higher oxygen partial pressure during bonding correlates with a stronger nickel-alumina interface, although the increase is modest.

To understand the mechanism behind the strong influence of oxygen partial pressure on interfacial bond strength, the nature of the bond between the metal and ceramic must be understood. This knowledge can also serve as a guide for obtaining desirable metal-ceramic interfaces. It is known that a chemical bond forms between metals and ceramics for metals with high affinity for oxygen, Ohuchi[5], Vossen[19]. The observation of the bonding between Cu and Al₂O₃ showed that the Cu atoms bind preferentially to the surface oxygen (O) atoms to form metal-oxygen bonds, Kasowski[20]. A chemical bond between nickel and oxygen atoms is also possible in our circumstances due to the high affinity of nickel for oxygen.

Two requirements must be satisfied to form a chemical bond, Pask[21]. First, a chemical bond must exist in which atomic contact exists either with van der Waals attractive force or an electronic structure across the interface. Second, there must be a stable chemical thermodynamic equilibrium at the interface. For metal-ceramic interfaces an oxide phase can form by interfacial reactions

involving the oxidation of the metal and the reduction of a cation in the ceramic (releasing oxygen). In the case that this occurs, the interface is saturated with a molecular or multimolecular layer of a metal oxide, which is compatible with both the metal and ceramic phases. An example is shown schematically in Figure 8a. In the case where the interface is not saturated with the metal oxide, as shown in Figure 8b, the electronic structure across the interface is lost because of a lack of balance of bond energies with the formation of van der Waals bonding. A weak bond is generally formed under this condition.

As observed in our investigation as well as by others, Wan[8], when the oxygen partial pressure in the bonding atmosphere is below the threshold, solid state bonding between nickel and alumina can be achieved without the formation of nickel aluminate spinel. The observation of a nickel-alumina interface formed under the same condition, i.e., with oxygen partial pressure below the threshold, by high-resolution TEM showed a 2nm thick layer of nickel oxide (NiO) at the interface achieved under the condition that no spinel is expected from thermodynamic equilibrium, Drillet[22]. This is consistent with the interface model described in Figure 8a, and suggests that a higher oxygen partial pressure in the bonding atmosphere (but still below the threshold for the formation of nickel aluminate spinel) helps the formation of the metal oxide, NiO, layer across the Al_2O_3 interface, which in turn results in a stronger chemical bond through the formation of the electronic structure at the interface.

4.2.2 Interfacial Toughness in the Presence of Nickel Aluminate Spinel at the Interface

During diffusion bonding of metal-ceramic interfaces, chemical reactions between the two components occur under certain circumstances. For example, when metal-ceramic interfaces are formed under oxidizing conditions, intermediate oxide phases are often formed, Ohuchi[5]. The reaction process can create interface roughness and local stress concentrations, thus affecting the mechanical bonding at the interface, Handwerker[23]. In addition, the chemical reaction can change the interface microchemistry which in turn has a critical influence on the interfacial chemical bond.

The formation of intermediate phases (interphases) is one of the several chemical reactions occur at metal ceramic interfaces. The typical scale of this reaction is on the order of one micrometer, Trumble[17]. Trumble[17] studied the interfacial reaction at nickel alumina interfaces,

and concluded that the formation of nickel aluminate spinel, NiAl_2O_4 , at the interface occurs when the oxygen activity of oxygen-containing nickel is above a threshold. Some studies claim that spinel formation at the interface leads to an increase in the interfacial strength, Sutton[24], Calow[6], Bailey[25], whereas others conclude that it weakens the interface a great deal, Calow[15], Vardiman[26]. However, no quantitative study of this effect on nickel-alumina interfacial fracture toughness has been performed.

In this section, three situations under which spinel forms at the interface are investigated. The resulting interfacial toughness is calculated from the FEM simulation based on the interface failure load. These results are then compared with those obtained previously from interfaces without spinel formation. Interfacial microscopic analysis is also performed to provide a better understanding of the interfacial bonding difference.

The same sandwich geometry used in the previous investigation is employed here. Materials chosen for this study are 99.9% pure polycrystalline nickel and α -alumina again. After the same sample preparation and hot-pressing procedure, the wedged sandwich samples are fractured with a load angle of 45° .

Three groups of samples are fabricated in this case. For the first two groups, nickel foils with an initially dissolved oxygen concentration higher than the threshold for the formation of nickel aluminate spinel at the interface are employed. This threshold is called the dissolved oxygen threshold in this work, and its thermodynamic calculation will be given later. (The threshold of the oxygen level in the bonding atmosphere for the formation of spinel, discussed earlier in chapter two, is called the bonding atmosphere oxygen threshold). The first group is obtained by hot-pressing in an atmosphere with the log of oxygen partial pressure of -10.54, which is two orders of magnitude below the bonding atmosphere oxygen threshold, -8.54. The second group is fabricated with a carbon monoxide (CO)/carbon dioxide (CO_2) ratio of 0.25, which corresponds to a log of oxygen partial pressure of -8.38, which is above the bonding atmosphere oxygen threshold. In the third group, the initially oxygen free nickel foil is used, however, the oxygen partial pressure in the bonding atmosphere is above the threshold, at a log of oxygen partial pressure of -8.38, the same as that used for group two specimens.

In all these groups, the nickel aluminate spinel interphase is observed at the interface. However, the source of oxygen for the formation of the spinel is different. Two diffusion paths for oxygen are involved. The oxygen dissolved in nickel reaches the interface by normal diffusion, whereas, the oxygen in the bonding atmosphere reaches the interface by lateral diffusion. For group one, the oxygen for the formation of nickel aluminate spinel is obtained from that dissolved in the nickel foil. In group three, the oxygen comes from the bonding atmosphere. For group two, the oxygen is from both of these two sources, and normal as well as lateral diffusion of oxygen occur in this case. This interphase layer can be easily observed due to its bright blue-green color. X-ray diffraction analysis of these surfaces verifies the formation of nickel aluminate spinel (NiAl_2O_4). Electron Microprobe analysis on the polished cross section of the interface also confirms this phase and shows that the spinel interphase is approximately 2 μm thick for the group one samples.

The thermodynamics of reaction at metal-ceramic interfaces are discussed by Klomp[27]. Trumble and Rühle[17] formulated the reaction that produces nickel aluminate spinel at nickel alumina interfaces when there is oxygen initially dissolved in the nickel. The standard free energy change for a temperature range between 900 and 1400°C was also calculated. In the calculation, nickel aluminate is represented as $\text{NiO} \cdot (1+x) \text{Al}_2\text{O}_3$ due to the considerable solubility of NiAl_2O_4 for $\alpha\text{-Al}_2\text{O}_3$, where the value of x varies from zero for NiAl_2O_4 to x_{max} which defines the Al_2O_3 saturated composition. The overall reaction of the spinel formation is:



where $(\text{O})_{\text{Ni(s)}}$ denotes oxygen in solution in solid Ni.

The standard free energy of this reaction is obtained as:

$$\Delta G_1^\circ = -62,800 + 7.0T \text{ (} \pm 10,000 \text{) (J/g-mole)} \quad (3)$$

For our case, with the bonding temperature of 1300°C, the calculated standard Gibbs free energy for the formation of spinel is, according to equation (3):

$$\Delta G_1^\circ = - 51,787 \pm 10,000 \text{ (J/mole)} \quad (4)$$

The decrease in free energy for this reaction indicates that the formation of nickel aluminate spinel at the interface is favored.

Assuming $\text{NiO} \cdot (1+x_{\text{max}}) \text{Al}_2\text{O}_3$ (s), Ni and $\alpha\text{-Al}_2\text{O}_3$ all have unit activities, Trumble[17] shows that the activity of oxygen dissolved in the nickel at equilibrium can be expressed as a function of temperature as:

$$[\text{at.}\% (\text{O})_{\text{Ni(s)}}] = \exp\left(\frac{-7557 \pm 1200}{T} + 0.84\right) \quad (5)$$

Below the threshold oxygen level, the oxygen containing nickel is in equilibrium with $\alpha\text{-Al}_2\text{O}_3$, whereas, above the threshold level, the spinel is stable. Given the nickel layer and spinel layer thickness, the initial oxygen concentration can also be estimated [17] based on the fact that when the concentration of oxygen in nickel is higher than the threshold, nickel aluminate spinel forms, which consumes the excess oxygen until the oxygen level decreases to the threshold.

The same interphase layer was also observed from nickel alumina diffusion bonding by many other researchers, Trumble[17], Sutton[24], Calow[6,15], Bailey[25], Vardiman[26]. However, discrepancies exist among researchers concerning the influence of this interphase on interfacial bond strength.

The interfacial strength results in terms of both fracture loads and the fracture toughness in terms of the critical value of J-integral from these investigations are listed in Tables 2 and 3, together with those with no spinel formed at the interface obtained previously for comparison. For very strong bonds, interfacial crack propagation is rarely obtained even under the load angle of 45°. Cracks that grow into alumina due to this kind of strong interface are indicated in the tables by the ">" signs. The current experiments show that the spinel interphase layer increases interfacial fracture resistance. A strong interfacial bond is always obtained in current study no matter if the oxygen necessary for the spinel formation is from that dissolved in nickel foil or from the gaseous source in the bonding atmosphere, although the interface strength varies for different bonding conditions. For samples in group one and three, i.e., when there is only one source for oxygen, the interfacial bond strength is very strong with the formation of the spinel interphase of about 2 μm thick. However, when the oxygen levels dissolved in nickel foil and in bonding atmosphere are

both above their corresponding thresholds, as in the case of samples in group two, a somewhat weaker bond is observed compared to those in groups one and three. The interfacial spinel layer was about 3 to 3.5 μm (measured in the SEM) for samples in group two. Furthermore, the crack was observed to propagate within the spinel interphase layer.

The observation from our investigation described above can also be explained according to Pask[21], that the formation of the nickel aluminate spinel under the proposed conditions satisfies the critical requirement for a strong interfacial bond, that is, the presence of a stable chemical thermodynamic equilibrium at the interface. The spinel layer is compatible with both nickel and alumina, thus chemical bonding can be achieved between these two components through their bonds with the interphase layer, nickel aluminate spinel.

The test results suggest that when the interphase layer is very thin, its mechanical property will not affect the interface strength. In other words, when a thin interphase layer forms at the interface, the interface strength is determined by the strength of the chemical bond formed through the interphase layer. However, when the interphase layer is thicker than some critical thickness, the overall property of the interface is decided by the physical properties of the interphase layer. In our case, the interphase spinel formed in group two is thicker than the other two cases, due to its extensive source of oxygen. The nickel aluminate spinel is a brittle material with low fracture toughness. Thus a weaker interface is observed in this case whose strength is degraded by the low fracture toughness phase spinel. The observation that the crack propagates within the spinel interphase layer is consistent with the demonstration.

5. Summary

The interfacial fracture toughness of metal-ceramic composite materials is investigated using a wedged sandwich specimen consisting of polycrystalline α -alumina and pure nickel. The interfacial bond is obtained from diffusion bonding under a pressure of 8.9 MPa at 1300°C for two hours. Two types of bonds are investigated. In one case, formation of a nickel aluminate spinel at the interface is not permitted. In the second, sufficient oxygen is available that the spinel interphase layer can develop. In the samples bonded without the spinel interphase, the bonded specimens were tested under different load angles, and the failure loads were used as input for a three-dimensional finite element simulation. Results of this simulation were used to infer the

fracture toughness of this nickel-alumina interface in terms of the critical value of the averaged J-integral across the crack front, J_c . The toughness is found to be between 170 to 250 J/m² for phase angles from 7 to 34°. It is also observed that the fracture toughness slightly decreases as the phase angle increases.

In the case when no spinel forms, the influence of oxygen partial pressure on interfacial toughness was studied by varying the oxygen level in the atmosphere through the change of CO/CO₂ ratio. It was found that as oxygen partial pressure in the bonding atmosphere increased, the interfacial toughness increased slightly, indicating that the oxygen helps the formation of a stronger bond between the two components at the interface. The interfacial atomic structure model proposed by other researchers was adopted to explain this effect. We conclude that higher oxygen partial pressure in the bonding atmosphere makes it possible to form a molecular or multi-molecular layer of nickel oxide at the interface. This oxide layer can further bond with both nickel and alumina sides chemically, and thus results in a strong interfacial chemical bonding.

When the oxygen concentration in either the bonding atmosphere or the nickel foil is higher than a certain level (two corresponding thresholds exist), spinel forms at the interface. Our observation shows that the formation of a spinel interphase can result in a strong bond between nickel and alumina. However, the toughness depends on the oxygen level during the diffusion bonding. When the oxygen level is controlled so that the spinel interphase layer is thin, a very strong bond, which is even stronger than the bonds obtained when there is no spinel forms at the interface, can be obtained at the interface. Otherwise, if the spinel layer is thicker than about 3 μm thickness, the interface strength is determined by properties of spinel, and hence a somewhat weaker interface is obtained. The source of oxygen for the spinel formation does not appear to influence the bonding strength.

Our results show interfacial fracture toughnesses of the nickel-alumina system that are much higher than those obtained by Thurston[10] for interfaces formed under the same bonding conditions. This difference is primarily due to the fact that the contamination of the interface was avoided by using the wedged sandwich geometry rather than boron nitride to create the interfacial pre-crack, and thus a stronger interfacial bond is achieved. In addition, the three-dimensional stress

simulation takes into account edge effects, which contribute to an increase of the calculated J-integral for a given applied load.

Acknowledgments

This work was supported by the Cornell Center for Materials Research (CCMR), a Materials Research Science and Engineering Center of the National Science Foundation (DMR-0079992). Particular acknowledgment is made of the use of the Materials, Research Computing, Electron and Optical Microscopy and X-Ray Diffraction facilities of the CCMR. The authors thank HKS Corporation for permission to use ABAQUS under academic license.

References

1. Suo, Z. and Hutchinson, J. W., Interface crack between two elastic layers, *Int. J. Frac.*, 1990;43:1-18.
2. Charalambides, P.G., Lund, J., Evans, A.G. and McMeeking, R. M., A test specimen for determining the fracture resistance of bimaterial interfaces, *J. Appl. Mech.*, 1989;56:77-82.
3. Charalambides, P.G., A mixed mode fracture specimen: analysis and experiments, in *Metal Ceramic Interfaces*, M. Rühle (ed.), Pergamon Press, 1990.
4. Turner, M. R., Dagleish, B. J., He, M. Y. and Evans, A. G., A fracture resistance measurement method for bimaterial interfaces having large debond energy, *Acta Metall. Mater.* 1995;43:3459-3465.
5. Ohuchi, F. S., Metal-ceramic interfacial reactions: a surface science approach, in *Metal Ceramic Interfaces*, M. Rühle (ed.), Pergamon press, 1990
6. Calow, C. A., Bayer, P. B. and Porter, I. T., The solid state bonding of nickel chromium and nichrome sheets to α -Al₂O₃, *J. Mater. Sci.*, 1971;6:150-155.
7. Trumble, K.P., The role of oxygen in spinel interphase formation during Ni/Al₂O₃ diffusion bonding, *Mater. Res. Soc. Symp. Proc.*, 1989;138:551-555.
8. Wan, C. and Dupeux, M., Solid-state bonding of single-crystals of Ni_(1 1 1)/Al₂O_{3(0 0 0 1)}, *Journal of Materials Science* 1993;28:5079-5087.
9. Thurston, M.E., and Zehnder, A.T., Experimental determination of silica/copper interfacial toughness, *Acta Metall. Mater.* 1993;41:2985-2992.
10. Thurston, M.E. and Zehnder, A.T, Nickel-alumina interfacial fracture toughness: experiments and analysis of residual stress effects, *Int. J. Frac.* 1996;76:221-241.

11. Rice, J.R., Elastic fracture mechanics concepts for interfacial cracks, *J. Appl. Mech.* 1988;55:98-103.
12. Shih, C.F., Asaro, R.J. and O'Dowd, N.P., Elastic-plastic analysis of cracks on bimaterial interfaces: Part III-large scale yielding, *J. App. Mech.* 1991;58:450-463.
13. Kolhe, R., Hui, C.-Y., Ustundag, E. and Sass S.L., Residual thermal stresses and calculation of the critical metal particle size for interfacial crack extension in metal-ceramic matrix composites, *Acta Metall. Mater.*, 1996;44:279-287.
14. Lu, Y.C., Sass, S.L., Bai, Q, Kohlstedt. D.L. Gerberich, W.W., The influence of interfacial reactions on the fracture toughness of Ti-Al₂O₃ interfaces, *Acta Metall. Mater.* 1995;43:31-41.
15. Calow, C.A. and Porter, I.T., The solid state bonding of nickel to alumina, *J. Mater. Sci.* 1971;6:156-163.
16. Wasynczuk, J.A., and Rühle, M., Microstructural characterization of Ni/Al₂O₃ diffusion bonds, *Proceedings of Ceramic Microstructures' 86, Role of interfaces*, J.A. Pask and A. Evans (eds.), Plenum Press 1987, 341-348.
17. K. P. Trumble and M. Rühle, The thermodynamics of spinel interphase formation at diffusion-bonded Ni/Al₂O₃ interfaces, *Acta Metall. Mater.* 1991;39:1915-1924.
18. H. Peters and H. H. Möbius, Electrochemical investigation of the formulae $\text{CO} + \frac{1}{2} \text{O}_2 = 2\text{CO}$, *Z. Phys. Chem.* 1958;209:298-309.
19. Vossen, J.L., Measurements of film-substrate bond strength by laser spallation, in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings*, ASTM, STP 640, K.L. Mittal (ed.), 1978, p.122-133.
20. Kasowski, R.V., Ohuchi, F.S. and French, R.H., Theoretical and experimental studies on Cu metallization of Al₂O₃, *Physica, B* 1988;150:44-46.
21. Pask, J.A., From technology to the science of glass/metal and ceramic/metal sealing, *Ceramic Bulletin* 1987;66:1587-1592.
22. Drillet, P., *Doctorate thesis*, University of Rennes, France, 1991.
23. Handwerker, C. A., Vaudin, M. D., Kattner, U. R. and Lee, D.J., Interface reactions and phase stability in the Al-SiC system, in *Metal Ceramic Interfaces*, M. Rühle (ed.), Pergamon Press, 1990.
24. Sutton, W.H. and Feingold, *The Role of Grain Boundaries and Surfaces in Ceramics*, Plenum Press, 1966.

25. Bailey F.P., and Borbidge, W.E., Solid state metal-ceramic reaction bonding, Mater. Sci. Res. 1981;14:525-533.
26. Vardiman, R.G., Preferred orientation of NiAl_2O_4 spinel grown on sapphire, Mater. Res. Bull. 1972;7:699-710.
27. Klomp, J.T. and Rühle, M., Ceramic-metal reactions and their effect on the interface microstructure, Proceedings of Ceramic Microstructure '86, Role of Interfaces, J.A. Pask and A. Evans (eds.), Plenum Press, 1987, 307-317.

Figure Captions

Figure 1: Sandwich specimen with wedge to create pre-crack between nickel and alumina

Figure 2: Mixed-mode loading fixture for wedged sandwich specimen. Positive loading angle as drawn.

Figure 3: Failure modes under different loading angles for thin foils. (a) low positive or negative angle. (b) high positive angle.

Figure 4: Finite element mesh for analysis of wedged sample.

Figure 5: Failure load versus load angle for samples bonded at an oxygen partial pressure of $\log P_{\text{O}_2} = -10.54$.

Figure 6: Fracture toughness in terms of critical J-integral, J_c , versus phase angle.

Figure 7: Fracture toughness in terms of critical J-integral, J_c , versus oxygen partial pressure. The load angle is 45° .

Figure 8: Bonding between metal and ceramic at the interface when no spinel forms, Pask[21]. (a) Multimolecular layer of oxide. (b) van der Waals bonding (no electronic structure across the interface).

Table 1: Fracture loads and corresponding fracture toughnesses, in terms of the critical J-integral values, J_c , for specimens bonded under different oxygen partial pressures.

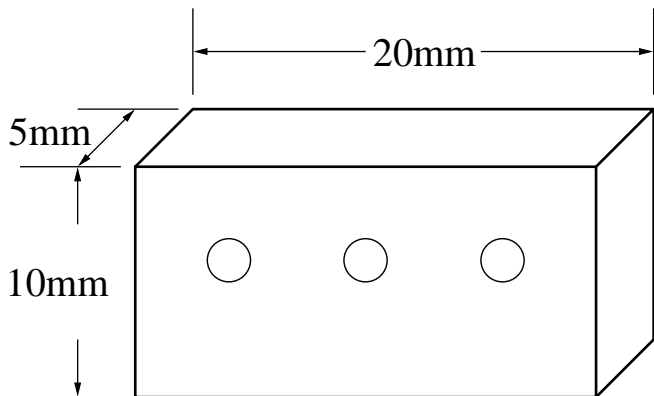
Log P_{O_2}	Log $P_{O_2}=-10.78$	Log $P_{O_2}=-10.54$	Log $P_{O_2}=-10.2$
Fracture load (N)	750± 49	869± 47	1099± 126
J_c (J/m²)	183± 6	198± 7	244± 30

Table 2: Fracture load of samples from four different bonding conditions. The combinations of P_{O_2} below and above threshold, with and without oxygen dissolved in the nickel before diffusion bonding. The load angle for all samples is 45° .

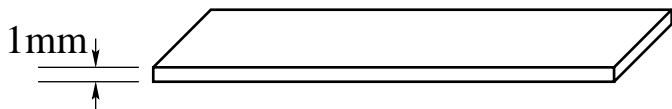
Nickel foil	Fracture Load (N)	
	Log P_{O_2} = -10.54 P_{O_2} below threshold	Log P_{O_2} = -8.38 P_{O_2} above threshold
with oxygen dissolved	> 1,000	670
with no oxygen dissolved	870 ± 50	> 1,100

Table 3: Fracture toughness in terms of critical J-integral, J_c , for samples from four different bonding conditions: The combinations of P_{O_2} below and above threshold, with and without oxygen dissolved before diffusion bonding. The load angle for all samples is 45°

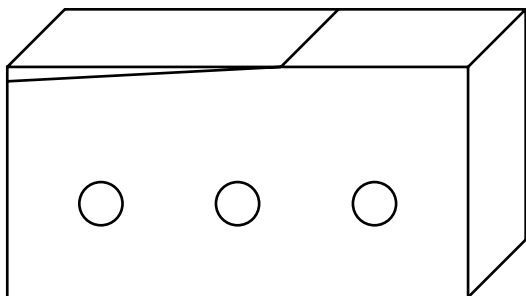
Nickel foil	FractureToughness, J_c (J/m²)	
	Log P_{O_2} =-10.54 P_{O_2} below threshold	Log P_{O_2} =-8.38 P_{O_2} above threshold
with oxygen dissolved	> 230	170
with no oxygen dissolved	198 ± 6	> 240



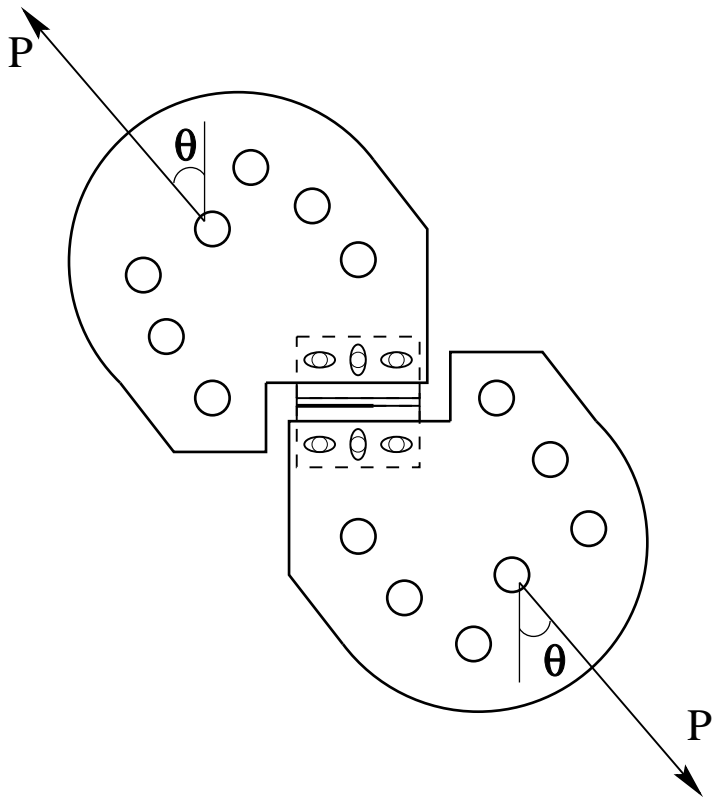
← Alumina

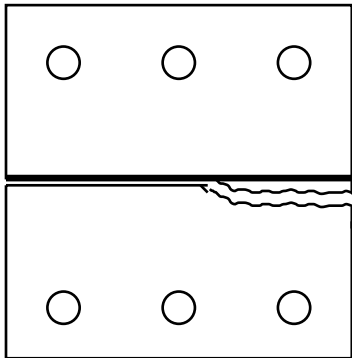


← Nickel

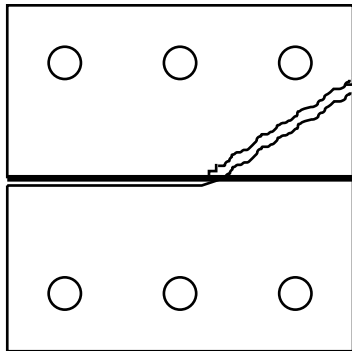


← Wedged
Alumina





(a)



(b)

