Surfaces, Interfaces and Science of Ceramic Joining

Edited by
K. Scott Weil
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Surfaces, Interfaces, and the Science of Ceramic Joining
Technical Resources

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Preface

This volume contains the proceedings of "Surfaces, Interfaces, and the Science of Ceramic Joining," a symposium held in Indianapolis, IN, April 18–21, 2004 as part of the 106th Annual Meeting of The American Ceramic Society. With over 50 presentations and posters, the symposium was the successful outgrowth of prior symposia on surface science, interfacial analysis, and ceramic joining. In keeping with our objective to offer a forum for those interested in discussing the fundamental aspects of ceramic surface and interfacial phenomenon and their relationship to the nature of bonding/joining in ceramic materials, a wide range of subject matter was covered during the three days of presentations—from ceramic surface characterization and molecular dynamic modeling to interfacial phenomenon, such as boundary layer transitions between metal/ceramic interfaces in cermet composites and observations on intergranular phase transformations, as well as topics of particular significance to ceramic joining, including wetting, adhesion, and interfacial mechanics.

The breadth of the symposium is well represented in this proceedings volume, which includes papers on: the development of photocatalytic titania coatings, the mechanics of functionally graded ceramic-to-metal joints, new techniques for measuring coating adhesion and ceramic joint strength, characterization of surface wetting as a function of substrate and wetting liquid composition, and the development of chiral surfaces as templates for catalytic thin film growth. We would like to thank all of the participants in the symposium and especially those who contributed to this volume. Many thanks are also due to the staff at The American Ceramic Society for their assistance in handling numerous details before, during, and after the meeting and for helping to produce this proceedings.

K. Scott Weil
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Surface and Interfacial Phenomena
THE ROLE OF INTERFACIAL PHENOMENA IN WETTING-BONDING RELATIONSHIP IN Al/CERAMIC COUPLES

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ABSTRACT

The wetting-interface strength relationship in high-temperature ceramic/metal couples must be interpreted in light of nano- and micro-scale structure of the interface. New experimental results on the effect of liquid-phase joining parameters on the wetting-structure-strength response of Al/Al2O3 and Al/TiO2 couples are discussed. The influence of time, temperature, alloying, ceramic additives, and metal films on Al2O3 is examined, and it is observed that non-equilibrium phenomena (segregation, sedimentation, dissolution, and defects) markedly influence the interface behavior. It is argued that data on the classical liquid-state joining science parameters (contact angle and work of adhesion) must be coupled with the structural information to develop a scientific understanding of the joining process.

INTRODUCTION

The wetting-bonding relationships in ceramic/metal couples become increasingly complex at elevated temperatures due to the extreme sensitivity of the nano- and micro-scale structure of the interface to the joining process variables, and a host of ubiquitous imperfections that reside at the interface. Interpretations of wetting-bonding relationship based solely on the classical surface thermodynamic parameters, without consideration of the microstructural, compositional and morphological features of the interface, have led some investigators to conclude that recipes designed to lower the contact angle, \( \theta \), or increase the work of adhesion, \( W_{ad} \), might not lead to an increase in the joint strength.

The purpose of this paper is to discuss the effect of liquid-phase joining process parameters on the interface response with a view to understanding the wetting-bonding-interface structure relationship in two technologically important couples: Al/Al2O3 and Al/TiO2. In particular, the role of high-temperature wettability and reactivity in the evolution of the interface structure, and their effect on joint strength will be discussed. The influence of contact time, temperature, alloying additions to Al, ceramic additives in Al2O3, and thin Ti and Sn films on Al2O3 will be examined. The role of universally-present residual oxygen and non-equilibrium phenomena (e.g., phase segregation, sedimentation, dissolution, and defects) in the evolution of the interface and joint strength will be highlighted. The paper will conclude with the proposition that the classical liquid-state joining science parameters might be inadequate to assess the effectiveness of a joining technology in systems where the interface undergoes substantial metallurgical transformation during joining. For such systems, empirical measures of adhesion strength should yield criteria to design an optimum ceramic/metal joint.

EXPERIMENTAL

Sessile-Drop Test: The contact angles were measured using the sessile-drop method described in Ref. 1. The test is carried out in a dynamic vacuum of \(~0.2\ \text{mPa}\) for different contact times and at different temperatures. Three sample heating procedures were employed: 1) fast contact heating
(FCH) (~40 K/min) was achieved by introducing the couple into the furnace previously heated to the test temperature; 2) slow contact heating (SCH) (~10 K/min) was achieved when the couple was first placed in the furnace and then heated to the test temperature; and 3) capillary purification (CP) in which the substrate and the metal were heated separately under vacuum, the metal in a graphite syringe. At the test temperature, a droplet of the metal is mechanically squeezed out of the graphite syringe and brought in contact with the preheated ceramic. Separate heating of the metal and the substrate in CP eliminates chemical interactions that would occur during contact heating to the test temperature, while the extrusion of the liquid out of the syringe forms droplets free of oxide film, thus establishing true substrate/metal physical contact. To reduce the thermal stress during heating, the ceramic/metal couple can be heated slowly, and at the conclusion of the test, cooled slowly (~ 10 K/min). With metal-coated substrates, the coating dissolution is minimized by faster heating (40 K/min) and cooling (~20 K/min).

The key test variables in the sessile-drop tests were temperature, time, type of substrate coating (Ti or Sn), the substrate (polycrystalline $\alpha$-Al$_2$O$_3$ and sapphire single crystals $\alpha$-Al$_2$O$_3$), and the droplet metal composition (e.g., 99.9999% pure Al, Al-Si, Al-Ti and Al-Sn alloys). The polycrystalline $\alpha$-Al$_2$O$_3$ substrates were sintered at 1923 K from the powder containing less than 0.1% impurities (0.009% CaO, 0.053% SiO$_2$, 0.0029% MgO, 0.023% Fe$_2$O$_3$, and 0.0036% Na$_2$O). The TiO$_2$ substrates were hot pressed from powder containing less than 0.1% impurities. All the substrates were polished with diamond paste up to an average roughness of $R_a$=100-120 nm. Thin coatings (800 nm to <2 μm) were deposited onto one face of selected substrates using physical vapor deposition.

Droplet Push-Off Test: A simple yet elegant approach to relate $\theta$ to bond strength is the droplet push-off shear test first employed in early studies on Al$_2$O$_3$/Me couples (Me = Al, Ni, Ag, or Cu). The push-off test measures the shear stress (applied parallel to the substrate) required to debond solidified sessile-drops from the substrate. A methodological limitation of the droplet push-off shear test is the difficulty in applying a shear stress to thin droplets with $\theta$>90°. An improved push-off test allows shearing of both non-wetting ($\theta$>90°) and wetting ($\theta$<90°) couples because the solidified droplet/ceramic couple is bisected perpendicular to the interface at the mid-plane of the contact circle, and one-half of the bisected droplet is used for bond strength measurement (the other half is either thermally cycled and tested for interface strength, or used for microstructural examination of the joint). For the shear test, a load is applied to the flat end of the bisected couple at a constant rate (1 mm/min), and the load versus displacement data are recorded until failure under shear occurs. By enabling the measurement of $\theta$ and $\tau$ (shear bond strength) on each individual test specimen, the improved push-off shear test allows characterization of the wetting, bonding, structure, and chemistry of the interface in the same test coupon. Recently the test was applied to Al/Al$_2$O$_3$, Al/Si$_3$N$_4$, Al/NiAl, Ni/Al$_2$O$_3$, and Cu/Al$_2$O$_3$ couples.

RESULTS AND DISCUSSION

Effect of temperature and testing procedure

Much work has been done on measuring the wettability in metal/Al$_2$O$_3$ couples. The general conclusion is that alumina is not wetted by Al at the latter's melting point, and the non-wetting-to-wetting transition temperature, $T^*$, exhibits wide dispersion (1083–1373 K). $T^*$ depends upon the test technique, furnace atmosphere, substrate roughness, crystal orientation, and chemical purity of the substrate and the metal.
Figure 1(a) shows the $\theta$-time data in SCH Al/Al$_2$O$_3$ at 953–1323 K, and in CP Al/Al$_2$O$_3$ at 973 K. At 953 K and 1023 K, $\theta$ for SCH samples decreases somewhat sluggishly with time, stabilizing at 130° and 128°, respectively, indicating poor wetting. The poor wetting is due to the residual oxygen present in the furnace even under relatively “clean” test conditions, which forms an oxide film on Al droplet that hinders spreading. The $\theta$ in CP Al/Al$_2$O$_3$ at 973 K shows a marked and rapid (almost immediate upon contact) decrease, and a stable value of ~93° is attained. Such a low $\theta$ is not achieved in Al/Al$_2$O$_3$ at the low-test temperature of 973 K when contact heating is employed. This indicates that CP causes oxide to rupture, thus yielding a clean, oxide-free solid/liquid interface, and good wetting. Extremely short times are needed to achieve an equilibrium $\theta$ in the CP couple even at 973 K; in SCH, this would normally occur only at higher temperatures. At $T>T^*$, $\theta$ exhibits a stronger time-dependence, and becomes acute, indicating good wetting (e.g., $\theta$ stabilizes at ~80° and ~75° at 1223 K and 1323 K, respectively). The non-wetting-to-wetting transition ($\theta=90^\circ$) occurs at ~1150 K, which agrees with the literature range for $T^*$ (1083–1373 K, depending upon the test conditions).

![Fig. 1. Effect of temperature of wettability test on (a) wetting and (b) shear behavior of Al/Al$_2$O$_3$ couples: data for SCH from Ref. 6, except data for CP marked by (*) - from Ref. 7.](image)

When oxide is removed from the droplet surface prior to test via CP (or when low oxygen partial pressure exists in the furnace), acute values of $\theta$ ($\leq 90^\circ$) are obtained even at low temperatures ($T<T^*$). On the other hand, at $T>T^*$, the destruction of the oxide film under vacuum aids in lowering of $\theta$. The oxide removal occurs due to 1) the formation of the volatile suboxide, Al$_4$O by the reaction: $4\text{Al}(l) + \text{Al}_2\text{O}_3(s) \rightarrow 3\text{Al}_2\text{O}(g)$, and 2) partial dissolution of $\text{Al}_2\text{O}_3$ skin in molten Al drop. Simultaneous measurements of $\theta$ and oxide thickness in quenched sessile drops (tested under varying oxygen partial pressures, $P_{O_2}$) have been used to extrapolate the “true” contact angle at zero oxide thickness. Figure 1(b) shows the room-temperature shear stress ($\tau$) versus displacement ($l$) data in SCH Al/Al$_2$O$_3$ couples produced at different wettability test temperatures, and in CP Al/Al$_2$O$_3$ at 973 K. The maximum shear stress ($\tau_{\text{max}}$) on each curve is a measure of the interfacial shear strength; $\tau_{\text{max}}$ increases with increasing temperature. The $\tau_{\text{max}}$ of CP Al/Al$_2$O$_3$ is greater than that of SCH Al/Al$_2$O$_3$ at $T<1123$ K, and is due to the beneficial effect of mechanical removal of oxide skin from the droplet surface by CP.

The effect of testing procedure on the wetting and shear behaviors of SCH and SCP Al/Al$_2$O$_3$ couples is presented in Fig. 2. For the same temperature of wettability test, the SCH samples show better wetting under higher vacuum (Fig. 2(a)) and the shear behavior (Fig. 2(b)) is consistent with the wettability results. For the same vacuum level and time of interaction, an increase in temperature results in improvement of both wetting and bonding of SCH couples.

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