Surfaces, Interfaces and Science of Ceramic Joining

Edited by
K. Scott Weil
Ivar E. Reimanis
Charles A. Lewinsohn

Surfaces, Interfaces, and the Science of Ceramic Joining
Technical Resources

Journal of the American Ceramic Society

With the highest impact factor of any ceramics-specific journal, the Journal of the American Ceramic Society is the world's leading source of published research in ceramics and related materials sciences.

Contents include ceramic processing science; electric and dielectric properties; mechanical, thermal and chemical properties; microstructure and phase equilibria; and much more.

Journal of the American Ceramic Society is abstracted/indexed in Chemical Abstracts, Ceramic Abstracts, Cambridge Scientific, ISI's Web of Science, Science Citation Index, Chemistry Citation Index, Materials Science Citation Index, Reaction Citation Index, Current Contents/Physical, Chemical and Earth Sciences, Current Contents/Engineering, Computing and Technology, plus more.

View abstracts of all content from 1997 through the current issue at no charge at www.ceramicjournal.org. Subscribers receive full-text access to online content.

Published monthly in print and online. Annual subscription runs from January through December. ISSN 0002-7820

American Ceramic Society Bulletin

The American Ceramic Society Bulletin, is a must-read publication devoted to current and emerging developments in materials, manufacturing processes, instrumentation, equipment, and systems impacting the global ceramics and glass industries.

The Bulletin is written primarily for key specifiers of products and services: researchers, engineers, other technical personnel and corporate managers involved in the research, development and manufacture of ceramic and glass products. Membership in The American Ceramic Society includes a subscription to the Bulletin, including online access.

Published monthly in print and online, the December issue includes the annual ceramicSOURCE company directory and buyer's guide. ISSN 0002-7812

International Journal of Applied Ceramic Technology

Launched in January 2004, International Journal of Applied Ceramic Technology is a must read for engineers, scientists, and companies using or exploring the use of engineered ceramics in product and commercial applications.

Led by an editorial board of experts from industry, government and universities, International Journal of Applied Ceramic Technology is a peer-reviewed publication that provides the latest information on fuel cells, nanotechnology, ceramic armor, thermal and environmental barrier coatings, functional materials, ceramic matrix composites, biomaterials, and other cutting-edge topics.

Go to www.ceramics.org/act to see the current issue's table of contents listing state-of-the-art coverage of important topics by internationally recognized leaders.

Published quarterly. Annual subscription runs from January to December. ISSN 0196-6219

Ceramic Engineering and Science Proceedings (CESP)

Practical and effective solutions for manufacturing and processing issues are offered by industry experts. CESP includes five issues per year: Glass Problems, Whitewares & Materials, Advanced Ceramics and Composites, Porcelain Enamel. Annual subscription runs from January to December. ISSN 0196-6219

ACerS-NIST Phase Equilibria Diagrams CD-ROM Database Version 3.0

The ACerS-NIST Phase Equilibria Diagrams CD-ROM Database Version 3.0 contains more than 19,000 diagrams previously published in 20 phase volumes produced as part of the ACerS-NIST Phase Equilibria Diagrams Program: Volumes I through XIII; Annuals 91, 92 and 93; High Tc Superconductors I & II; Zirconium & Zirconia Systems; and Electronic Ceramics I. The CD-ROM includes full commentaries and interactive capabilities.
Copyright 2005. The American Ceramic Society. All rights reserved.

Statements of fact and opinion are the responsibility of the authors alone and do not imply an opinion on the part of the officers, staff, or members of The American Ceramic Society. The American Ceramic Society assumes no responsibility for the statements and opinions advanced by the contributors to its publications or by the speakers at its programs. Registered names and trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without prior written permission from the publisher.

Authorization to photocopy for internal or personal use beyond the limits of Sections 107 and 108 of the U.S. Copyright Law is granted by the American Ceramic Society, ISSN 1042-1122 provided that the appropriate fee is paid directly to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923 USA, www.copyright.com. Prior to photocopying items for educational classroom use, please contact Copyright Clearance Center, Inc.

This consent does not extend to copying items for general distribution or for advertising or promotional purposes or to republishing items in whole or in part in any work in any format.

Please direct republication or special copying permission requests to the Staff Director, Technical Publications, The American Ceramic Society, PO Box 6136, Westerville, Ohio 43086-6136, USA.

For information on ordering titles published by The American Ceramic Society, or to request a publications catalog, please call 614-794-5890, or visit our website at www.ceramics.org

### Contents

Preface ................................................................. vii

### Surface and Interfacial Phenomena

The Role of Interfacial Phenomena in Wetting-Bonding Relationship in Al/Ceramic Couples ................................. 3
  N. Sobczak and R. Asthana

Interface Structures and Diffusion Paths in SiC/Metal Couples ............ 19
  M. Naka, T. Fukai, and J.C. Schuster

Photocatalytic Titania Coatings by a Low Temperature Sol-Gel Process .... 29
  W.A. Daoud and J.H. Xin

Effect of Surface Treatment on Chiral and Achiral SrTiO₃ Surface Morphology and Metal Thin Film Growth .................... 37
  A.J. Francis and P.A. Salvador

Surface Characterization of Low-Temperature Processed Titania Coatings Produced on Cotton Fabrics .............................. 47
  W.A. Daoud and J.H. Xin

Thermodynamics of Refractories for Black Liquor Gasification ............ 53
  A. Rezaie, W.L. Headrick, and W.G. Fahrenholtz

### Mechanics

An Investigation of Wettability, and Microstructure in Alumina Joints Brazed with Ag-CuO-TiO₂ ..................................... 65
  J.T. Darsell, J.S. Hardy, J.Y. Kim, and K.S. Weil

An Engineering Test Useful in Developing Glass Seals for Planar Solid Oxide Fuel Cells ............................................ 73
  K.S. Weil, J.E. Deibler, J.S. Hardy, D.S. Kim, G.-G. Xia, and C.A. Coyle

Fracture in Nb/Al₂O₃ Particulate Composites ................................ 81
  J. Matterson, I.E. Reimanis, and J. Berger

Practical Adhesion and Cohesion Assessments of Al₂O₃ (0.1μm) Oxide Layer on Top of AlN Substrates by Microscratch Technique .......... 91
  L. Chouanine, M. Takano, O. Kamiya, and M. Nishida

Wetting and Mechanical Characteristics of the Reactive Air Braze for Yttria-Stabilized Zirconia (YSZ) Joining ....................... 101
  J.Y. Kim, K.S. Weil, and J.S. Hardy

Surfaces, Interfaces, and the Science of Ceramic Joining • v
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
Ivar E. Reimanis
Charles A. Lewinsohn
Surface and Interfacial Phenomena
THE ROLE OF INTERFACIAL PHENOMENA IN WETTING-BONDING RELATIONSHIP IN Al/CERAMIC COUPLES

Natalia Sobczak
Foundry Research Institute
73 Zakopianska St 326 Fryklund Hall
30-418 Krakow, POLAND

Rajiv Asthana
University of Wisconsin-Stout
326 Fryklund Hall
Menomonie, WI 54751, U.S.A.

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 mPa for different contact times and at different temperatures. Three sample heating procedures were employed: 1) fast contact heating

To the extent authorized under the laws of the United States of America, all copyright interests in this publication are the property of The American Ceramic Society. Any duplication, reproduction, or republication of this publication or any part thereof, without the express written consent of The American Ceramic Society or fee paid to the Copyright Clearance Center, is prohibited.
(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 α-Al₂O₃ PC and sapphire single crystals α-Al₂O₃ SC), and the droplet metal composition (e.g., 99.9999% pure Al, Al–Si, Al–Ti and Al–Sn alloys). The polycrystalline α-Al₂O₃ substrates were sintered at 1923 K from the powder containing less than 0.1% impurities (0.009% CaO, 0.053% SiO₂, 0.0029% MgO, 0.023% Fe₂O₃, and 0.0036% Na₂O). The TiO₂ 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 Rd=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 θ to bond strength is the droplet push-off shear test first employed in early studies on Al₂O₃/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 θ<90°. An improved push-off test allows shearing of both non-wetting (θ>90°) and wetting (θ<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 θ and τ (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/Al₂O₃, Al/Si₃N₄, Al/AlN, Ni/Al₂O₃, and Cu/Al₂O₃ couples.

RESULTS AND DISCUSSION
Effect of temperature and testing procedure

Much work has been done on measuring the wettability in metal/Al₂O₃ 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). 5.13-19 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/$\text{Al}_2\text{O}_3$ at 953–1323 K, and in CP Al/$\text{Al}_2\text{O}_3$ 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/$\text{Al}_2\text{O}_3$ 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/$\text{Al}_2\text{O}_3$ 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 ($\theta=90°$) occurs at ~1150 K, which agrees with the literature range for $\theta$ (1083–1373 K, depending upon the test conditions).

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$90°) are obtained even at low temperatures ($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, $\text{Al}_2\text{O}$ 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 ($r$) versus displacement ($l$) data in SCH Al/$\text{Al}_2\text{O}_3$ couples produced at different wettability test temperatures, and in CP Al/$\text{Al}_2\text{O}_3$ at 973 K. The maximum shear stress ($r_{max}$) on each curve is a measure of the interfacial shear strength; $r_{max}$ increases with increasing temperature. The $r_{max}$ of CP Al/$\text{Al}_2\text{O}_3$ is greater than that of SCH Al/$\text{Al}_2\text{O}_3$ at $T<\leq1123$ 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/$\text{Al}_2\text{O}_3$ 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.

![Fig. 1. Effect of temperature of wettability test on (a) wetting and (b) shear behavior of Al/$\text{Al}_2\text{O}_3$ couples: data for SCH from Ref. 6, except data for CP marked by (*) - from Ref. 7.](image-url)
However, for different vacuum levels, the time of interaction becomes an important factor, particularly for bonding properties, and this effect is more pronounced for higher temperature of wettability test. Among the SCH samples, the 15 min 1023 K sample produced in a vacuum of 0.4 mPa has the lowest shear strength while its contact angle is slightly lower than that of the 60 min 953 K sample produced in a vacuum of 0.3 mPa, indicating that despite higher temperature more oxide had formed in the former due to higher $\text{PO}_2$ (oxide removal did not occur as $T<T_w$). The CP procedure dramatically lowers the $\theta$, with $\theta_{\text{eq}} \approx 93^\circ$ at 973 K and $\theta_{\text{eq}}$ is attained in a very short time unlike the SCH samples. The results of $\theta-r$ relationship proves the hypothesis by Laurent et al.\textsuperscript{18} that the oxide film covering aluminum drop prevents a true contact with ceramic substrate and it is responsible for a lack of low-temperature wettability.

Fig. 2. Effect of testing procedure (SCH, CP) on wetting (a) and shear (b) behavior of Al/Al$_2$O$_3$**.$^\text{PC}$.

The structural features of the interface in Al/Al$_2$O$_3$ sessile-drop couples will now be discussed. Figure 3 shows the scanning electron microscope (SEM) views at three regions of the substrate-side Al/Al$_2$O$_3$**.$^\text{PC}$ interface: far from TL (Fig. 3(a)), under the drop in the proximity of TL (Fig. 3(b)), and under the droplet near the center (Fig. 3(c)). These figures show that fine Al$_2$O$_3$ crystallites are formed at the S/L interface in Al/Al$_2$O$_3$**.$^\text{PC}$ and Al/Al$_2$O$_3$**.$^\text{SC}$ (Fig. 3(d)) couples at 1223 K after 30 min contact. Similar observations have been reported by others.\textsuperscript{15,17}

The fine Al$_2$O$_3$ crystallites on bare substrate far from TL and located in the area surrounding Al droplet in the Al/Al$_2$O$_3$**.$^\text{PC}$ (Fig. 3(a)) are formed, most probably, due to interaction between evaporated Al and the Al$_2$O$_3$**.$^\text{PC}$ substrate. Larger ($<1$ to about 2 µm) crystallites of Al$_2$O$_3$ form under the droplet near TL (Fig. 3(b)) on polycrystalline substrate; these crystallites are distributed randomly on Al$_2$O$_3$ grains of the substrate rather than preferentially located at pre-existing Al$_2$O$_3$ grain boundaries (GB). This suggests that they probably did not form at the GB (although it is possible that crystallites that had nucleated at GB's could have undergone some rearrangement due to liquid flow accompanying solidification contraction during cooling, provided they were not strongly bonded to the substrate). The coarsest (~2-5 µm) Al$_2$O$_3$ crystallites are located at the S/L interface near the center of the drop, and these also do not show any evidence of preferential nucleation at pre-existing Al$_2$O$_3$ GB's (Fig. 3(c)). The Al$_2$O$_3$ crystallites also are noted at S/L interface on single-crystal (Al$_2$O$_3$**.$^\text{SC}$) substrates as shown in Fig. 3(d). These crystallites have sharp faceted surfaces, and possibly grow epitaxially (i.e., growth of one layer is in a particular crystallographic orientation relationship to the underlying layer). The epitaxial growth could possibly be due to the slow cooling rates employed at the conclusion of sessile-drop tests in our study. It has been suggested\textsuperscript{16} that Al$_2$O$_3$ crystallites are formed near the drop center by O
diffusion along S/L interface through a nanometer size layer. However, as the approximate crystallite size (Fig. 3(d)) is larger than a few nm, it appears that O must diffuse to the growth front (e.g., top face of the crystallite marked with an arrow in Fig. 3(d)) through the crystallite and/or along its surface. As the crystallites appear to be ordered and grow epitaxially, they will likely have a very small defect population (e.g., vacancies) that could assist O diffusion to the growth front. It is possible that mechanisms other than O diffusion along S/L interface could also be playing a role. One possibility is the dissolution of Al₂O₃ of the substrate in Al(l), and reprecipitation of fresh Al₂O₃ from O-saturated Al(l). The dissolution reaction generates Al–O clusters (or an O-rich Al layer) at the interface that decrease σ₈ due to adsorption. These clusters could serve as precursor (or seed) to an O-rich interphase, which will lead to the epitaxial growth of fine Al₂O₃ crystallites at the S/L interface especially favorable during slow cooling.

Fig. 3. The droplet/substrate interface structure (1223 K.) as revealed by scanning electron microscope; (a) through (c) are for Al/Al₂O₃ and (d) is for Al/Al₂O₃; (a) far from TL outside the droplet, (b) under the droplet near TL, (c) at the center under the droplet, (d) under the droplet.

If a dissolution-precipitation process is operative, then the energy released by oxide dissolution could locally raise the temperature at the S/L contact region and the O solubility in the melt. Some studies²⁰ have actually measured the temperature rise due to chemical dissolution by placing highly sensitive thermocouples exactly "inside" the drop/substrate interface. As the energy released from the dissolution reaction is dissipated, the interface temperature decreases, resulting in the discontinuous precipitation of microcrystalline Al₂O₃. Note that the solubility limit of oxygen in liquid Al could not be precisely determined and it might be much higher than the value given in the literature. Moreover, contrary to literature data, in our study we used Al of spectral purity and we expect even higher amount of alumina to dissolve.
Molten Al continues to dissolve the bare substrate between the discontinuously precipitated crystallites, resulting in a repetitive, self-sustaining process of ceramic dissolution, increased oxygen solubility in Al(l), and heterogeneous nucleation and epitaxial growth of oxide crystallites on the alumina substrate. Such a growth mechanism is consistent with the model of liquid-phase epitaxial growth due to Y. Bolkhovityanov\(^{21}\) (Fig. 4). It has been suggested\(^{16}\) that epitaxial growth of Al\(_2\)O\(_3\) occurs because the first few atomic layers of liquid Al in contact with a monocrystalline substrate are ordered and structurally similar to the substrate (these layers, however, contain excess point defects, which enable O diffusion along the S/L interface toward the droplet center). Thus, it may be conjectured that microcrystalline Al\(_2\)O\(_3\) observed at the S/L interface forms by 1) O diffusion along S/L interface, and/or 2) substrate dissolution, O enrichment (or Al–O adsorption), and reprecipitation of alumina.

Another possibility for crystallite growth is the reduced O solubility during droplet cooling and precipitation of Al\(_2\)O\(_3\).\(^{17}\) In general, whatever the dominant process for microcrystalline Al\(_2\)O\(_3\) formation, experimental results (Figs. 3(a) to 3(c)) show that more Al\(_2\)O\(_3\) crystallites precipitate in the center of the droplet than near the TL; this could possibly be due to a longer S/L contact in the center than near the TL (at TL, ridging occurs at high temperatures\(^ {22}\)). Besides diffusion of O along S/L, convective transport of O to the S/L interface at the droplet center is also possible. At large Peclet numbers, fluid convection will contribute to O transport \((Pe = V R / D)\), where \(V\) is the fluid velocity, \(R\) is the droplet base radius (a few mm), and \(D\) is the diffusion coefficient of O in Al; \(D \approx 2.2 \times 10^{-10} \text{ m}^2/\text{s at 1373 K}^{16}\). For \(R = 2 \text{ mm}\), \(Pe = 9.09 V\), where \(V\) is in \(\mu\text{m/s}\). For \(V\) greater than a few tens of \(\mu\text{m/s}\), fluid convection may play a role.

### Alloying

Table 1 shows the effect of alloying Al with Ti, Si and Sn at different temperatures on the contact angle, \(\theta\), and shear strength, \(\tau_{\text{max}}\). Alloying Al with 6 wt\% Ti slightly increase the \(\theta\) in Al/Al\(_2\)O\(_3\). Higher temperatures decrease the \(\theta\), but wetting is achieved only at \(T > 1273 \text{ K}\).
Similarly, AlSn7 alloys show larger $\theta$ compared to pure Al. The poor wetting of Al–Sn/Al$_2$O$_3$ and Al–Ti/Al$_2$O$_3$ is consistent with the literature, and is due to a non-profitable change in the interface structure and chemistry.

No stable reaction products form in AlTi6/Al$_2$O$_3$ under the present test conditions as per the Al–Ti–O phase diagram: this was verified in our SEM/EDS studies that ruled out Ti-rich interfacial phases. In addition, interfacial discontinuities due to shrinkage porosity and cracks (Fig. 5) formed during cooling due to mismatch of coefficients of thermal expansion (CTE) also adversely affect the interface strength. Furthermore, after the dissolution of AlTi6 alloy in HF solution, Al$_2$O$_3$ substrate exhibited "smooth" surface profile (Fig. 6), indirectly confirming an absence of any interfacial phases and decreased substrate dissolution.

An important distinction must be made between how $\theta$ and $\tau_{\text{max}}$ respond to interfacial processes. Whereas the value of $\theta$ is determined mainly by the interactions at or near TL, the shear strength, $\tau_{\text{max}}$, is determined by the interactions at the S/L interface.

For AlSi11/Al$_2$O$_3$ couples (Table I), $\theta$ decreases with increasing temperature, approaching $125^\circ$, $123^\circ$, and $84^\circ$ at 1073 K, 1123 K, and 1273 K, respectively. At 1273 K ($T>T^\ast$), there is a strong positive effect of oxide removal on $\theta$. Similarly, the $\theta(\text{CP})$ of AlSi11/Al$_2$O$_3$ at 973 K approaches $88^\circ$ in 18 min; thereafter, $\theta$ increases and stabilizes at $\sim98^\circ$. It has been established that $\alpha$-Al$_2$O$_3$ loses O from its basal
Fig. 7. Microstructure of AlSi11/Al2O3 interface (1273 K, 30 min) showing nucleation of Si crystals at the interface.

Table II. Effect of alloying on $\theta$–$\tau_{\text{max}}$ relationship (SCH, 1273 K, 30 min)

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\theta$ (°)</th>
<th>$\tau_{\text{max}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>77</td>
<td>46.8</td>
</tr>
<tr>
<td>AlCu2</td>
<td>133</td>
<td>18.16</td>
</tr>
<tr>
<td>AlCu5.65</td>
<td>90</td>
<td>$\geq 71.43^*$</td>
</tr>
<tr>
<td>AlCu32</td>
<td>99</td>
<td>22.81</td>
</tr>
<tr>
<td>AlSi5</td>
<td>91</td>
<td>75.55</td>
</tr>
<tr>
<td>AlSi11</td>
<td>84</td>
<td>66.19</td>
</tr>
<tr>
<td>AlSi20</td>
<td>99</td>
<td>32.44</td>
</tr>
<tr>
<td>AlTi0.8</td>
<td>93</td>
<td>30.97</td>
</tr>
<tr>
<td>AlTi2</td>
<td>100</td>
<td>33.13</td>
</tr>
<tr>
<td>AlTi6</td>
<td>103</td>
<td>17.81</td>
</tr>
<tr>
<td>AlFe1</td>
<td>101</td>
<td>53.47</td>
</tr>
<tr>
<td>AlFe5</td>
<td>113</td>
<td>29.65</td>
</tr>
<tr>
<td>AlFe10</td>
<td>111</td>
<td>0.37</td>
</tr>
<tr>
<td>AlFe30</td>
<td>80</td>
<td>6.79</td>
</tr>
</tbody>
</table>

*one sample was broken in ceramic

During cooling, Si precipitates at the S/L interface (Fig. 7), where silicon (and the reaction-formed Al2O3 crystallites) strengthens the ceramic/metal joint relative to unalloyed Al/Al2O3. High Si contents are, however, detrimental to the shear strength as also high Fe contents in the case of Al–Fe/Al2O3 (Table II).

Fig. 8 shows that mechanical removal of oxide film from AlTi6 drop improves the wetting but not bonding. The strongest effect of mechanical drop surface purification was noted with AlSi11 alloy, i.e., in oxide-free droplets formed near the melting point of Al (973 K), the contact angle and shear strength are comparable to those of the droplet formed at 300 K higher temperature when in situ cleaning of the drop from oxide layer takes place.

In the case of Al–Sn/Al2O3 (Fig. 9) interfacial shrinkage porosity forms along with a Sn-rich layer on the substrate-side of the AlSn7 drop. The Sn-rich layer indicates that sedimentation of the heavier Sn in Al occurs due to density mismatch ($\rho_{\text{Sn}} \approx 6710 \text{ kg/m}^3$, $\rho_{\text{Al}} \approx 2710 \text{ kg/m}^3$) (0001) planes during heating in a vacuum to very high temperatures (1500 K), causing surface reconstruction (roughening). However, in the presence of Al and Si vapors, Al2O3 surface reconstruction occurs even at 1200 K or lower temperatures, thus increasing the solid's surface energy ($\sigma_s$), lowering the $\theta$, and enhancing the metal/Al2O3 adhesion. Profilometry of the substrate (Fig. 6) and microstructural examination (Fig. 7) suggest that Si alloying increases the dissolution of Al2O3 in the droplet, leading to appreciable roughening.

Fig. 8. Effect of testing procedure (SCH, CP) on shear behavior in AlTi6/Al2O3 and AlSi11/Al2O3.