

Low-temperature Metal/Zerodur Heterogeneous Bonding through Gas-phase Processed
Adhesion Promoting Interfacial Layers

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Abstract

The bonding of ceramic to metal has been challenging due to the dissimilar nature of the materials, particularly different surface properties and the coefficients of thermal expansion (CTE). To address the issues, gas phase-processed thin metal films were inserted at the metal/ceramic interface to modify the ceramic surface and, therefore, promote heterogeneous bonding. In addition, an alloy bonder that is mechanically and chemically activated at as low as 220 °C with reactive metal elements was utilized to bond the metal and ceramic. Stainless steel (SS)/Zerodur is selected as the metal/ceramic bonding system where the Zerodur is chosen due to the known low CTE. The low-temperature process and the low CTE of Zerodur are critical to minimizing undesirable stress evolution at the bonded interface. Sputtered Ti, Sn, and Cu (300 nm) were deposited on the Zerodur surface, and then dually activated molten alloy bonders were spread on both surfaces of coated Zerodur and SS at 220 °C in air. The shear stress of the bonding was tested with a custom-designed fixture in a universal testing machine and was recorded through a strain indicator. The mechanical strength and the bonded surface property were compared as a function of interfacial metal thin film and analyzed through thermodynamic interfacial stability/instability calculations. The maximum shear strength of the bonding of 4.36 MPa was obtained with Cu interfacial layers, while Sn was 3.53 MPa and Ti was 3.42 MPa. These bonding strengths are significantly higher than those (~0.04 MPa) of contacts without interfacial reactive thin metals.

1. Introduction

There has been an increased use of heterogeneously bonded ceramic/metal structures in various practical and advanced applications such as displays¹, sensors², dentistry^{3, 4}, and aerospace manufacturing⁵, where high bonding strength needs to be achieved at the bonded interface⁶. Particularly, in aerospace applications, the bonding between the metal and ceramic is widely considered for fuel systems, power units, and fuel cells due to ceramics' light weightiness while maintaining the bonded parts' required mechanical strength⁷.

In general, the bonding of ceramic and metal is difficult given the dissimilar properties of the two differently categorized materials such as surface properties and thermal behaviors (e.g., thermal expansion). Due to the different surface properties such as roughness and wetting, direct contacts and bonding from a liquid or molten binder and epoxy have been challenged or led to a critically weak bonding strength at the metal/ceramic contact. Furthermore, typical high-temperature processes ($> 500\text{ }^{\circ}\text{C}$) such as soldering, brazing, and welding required to bond these dissimilar materials result in residual stresses in the bonded structure^{8, 9}. Metal to ceramic bonding has also been used in constructing electronic packages¹⁰ where Cu has been picked due to its strength and fabrication costs being low. However, to complete the packaging process it needs to be fired at around $500\text{-}700\text{ }^{\circ}\text{C}$, of which the relatively high temperature is limited since the melting or glass transient temperature of glass-ceramic, such as Zerodur, is close to the processing temperature range¹⁰. Therefore, it is required to establish a strategy to achieve high bonding strength between metal and ceramic at low temperatures (e.g., $\leq 250\text{ }^{\circ}\text{C}$).

The goal of this study is to enhance the mechanical strength of the heterogeneous metal/ceramic bonding and address the low temperature requirement. To this end, we will combine the

advantages of (i) chemically and mechanically activated alloy bonders and (ii) adhesion promoting interfacial metal films that are deposited through gas-phase processing. The working hypotheses for the approach include (i) the mechanical agitating and (ii) gas-phase processing will coat uniform metal films on the ceramic surface, compared to liquid-phase processing, which alters the surface property of ceramics. These hypotheses are rationally formulated on the rationale that (i) the mechanical agitation removes surface oxides and contaminants on the metal surface and (ii) in gas-phase coating processes, surface wetting is not critically required.

In this report, a ceramic to metal bond was created heterogeneously using a low-temperature process alloy bonder incorporating active ingredients of Ti, Sn, and Ag. A lithium-aluminosilicate glass-ceramic (Zerodur) is known to have a very low coefficient of thermal expansion ($<10^{-7}$ /K) and consequently it is widely considered for high-precision applications and extremely cold environments (e.g., deep space). Therefore, Zerodur is selected as a model ceramic material to test our hypothesis objectively and evaluate the mechanical strength of the heterogeneous bonding. An interfacial metal film was sputtered over the ceramic in order to create a metal-to-metal bonding with enhanced strengths, compared to that without an interfacial film. In order to test our rationalized hypotheses objectively and evaluate and compare the bonding strength of the heterogeneous contact between samples with and without an interfacial film, uniaxial tensile tests were conducted in a universal testing machine with a custom-designed fixture and LabView codes. To establish bonding strategies for heterogeneous metal and ceramic contacts, thermodynamic interfacial stability/instability was estimated on possible interfacial reactions.

2. Experimental details

Adhesion-promoting thin metal films were inserted as an interfacial layer in between the heterogeneous metal (stainless steel, denoted as SS) and Zerodur glass- specimens. Thin films of reactive metals Sn, Cu, and Ti were selected and sputter-deposited onto a Zerodur glass substrate to a thickness of approximately 300 nm at a DC power of 40 W and a pure Ar sputter gas condition with a working pressure of 2×10^{-3} Torr. Prior to the depositions, the sputter chamber was pumped down to a base pressure of $\sim 4 \times 10^{-7}$ Torr or below and metal targets were pre-sputtered for 5 min to remove any contaminants on the target surface and to ensure uniform sputter gas flow in the chamber. All the sputter depositions were conducted at room temperature. Once the thin film was prepared on Zerodur substrates, an alloy bonder (SB-220, S-Bond Technologies), consisting of Ti, Sn, and Ag, and free of toxic elements (e.g., Pb and Cd), that is chemically and mechanically activated for bonding was applied to both the metal and ceramic. Before bonding, the surface of the metal was mechanically polished with a series of sandpapers, and ceramic was used as procured with the highly polished surface state. The alloy bond (including metal elements of Ti, Sn, and Ag) is chemically activated through heat (at 220 °C) and mechanically activated through agitation of the molten alloy bond on the surface of thin metal-coated Zerodur and SS. Then, the molten alloy-spread samples were placed together. On top of the two materials, a weight (3 kg) was placed to press the metal and ceramic together. The samples were left to cool slowly. The bonding and cooling processes were performed in an ambient air condition. Once cooled, the tensile strength of the bonded specimens was evaluated on a universal testing machine (UTM) with custom-designed attachments, where the design allowed for the UTM to measure the shear stress by creating a pulling tension between the SS metal and Zerodur glass. A 22,241 N load cell was used with a strain indicator monitoring the load applied for the strength test. The data from the samples were collected and processed using a LabView. In order to confirm the repeatability, multiple samples

were prepared and more than 20 tensile tests were conducted. The bonding and measurement procedures are schematically presented in Figure 1.

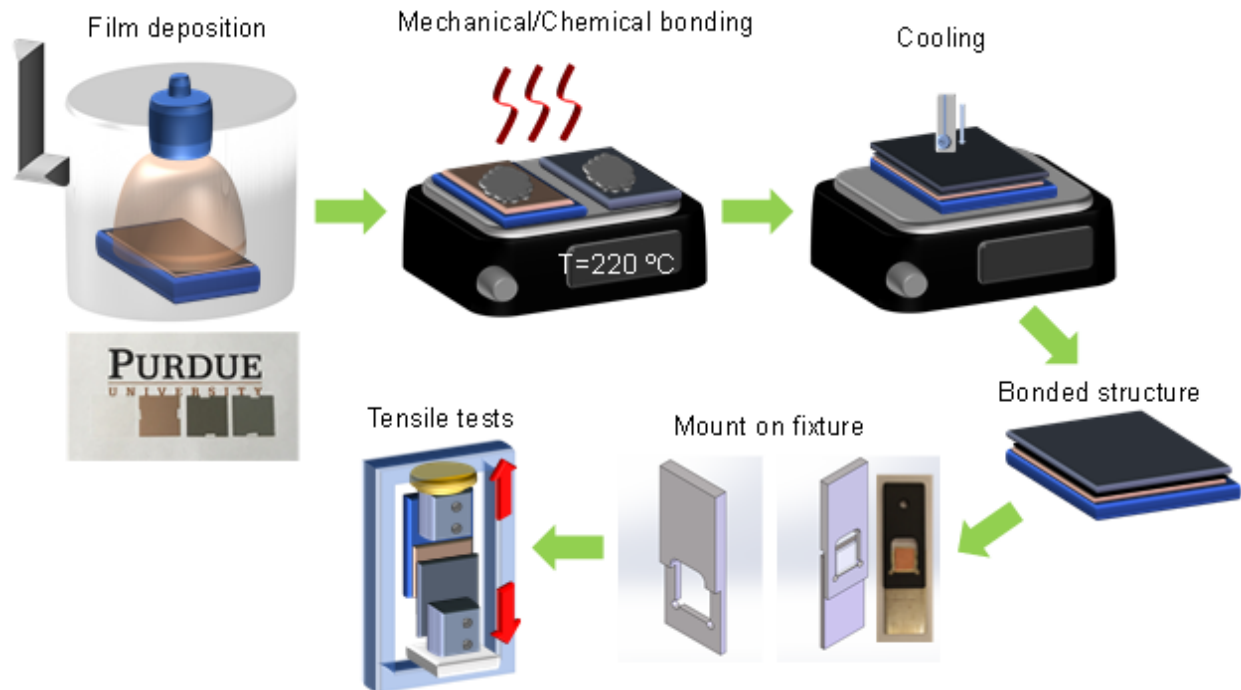


Figure 1. Process scheme describing sputtering thin film deposition (inset photographs of bare and metal-coated samples of Cu, Ti, and Sn-coated glasses from the left); mechanical/chemical bonding of Zerodur and stainless steel at a low temperature of $200\text{ }^{\circ}\text{C}$; cooling the bonded sample in ambient air; mounting the bonded sample on a custom-designed fixture; and tensile tests with a UTM.

3. Results and Discussion

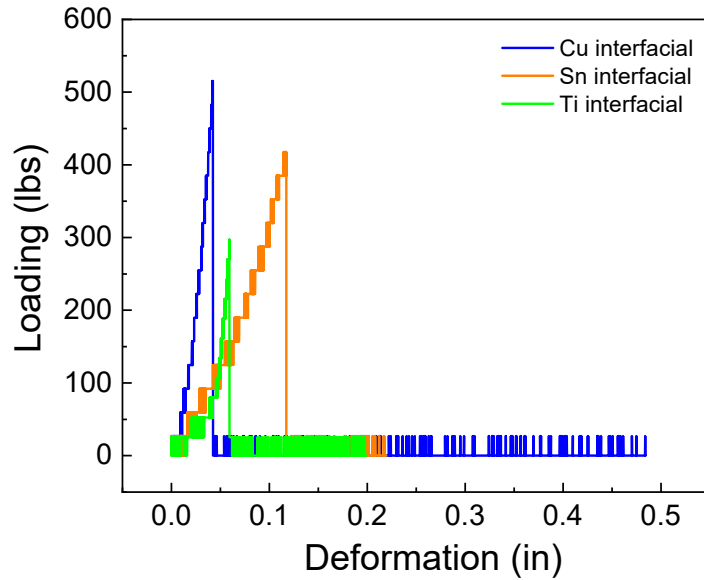


Figure 2. Typical shear strength results of the SS/Zerodur bonded with alloy bonders and adhesion promoting interfacial metal films of Cu, Sn, and Ti for which the loading applied was monitored with a 22,241 N load cell through a strain indicator. The shear strength was calculated by the measured loading at the fracture and the bonded area of 6.45 cm².

The mechanical properties of the hetero-bonded SS/Zerodur specimens, where a thin metal film (300 nm) was inserted at the interface, were evaluated through a UTM. Figure 2 compares the maximum shear loading that can be endured by the bonded specimens over the area of 6.45 cm² contact, from which the maximum shear strength is determined. The Cu film-inserted bond was able to withstand $2,313.08 \pm 271$ N, by which the maximum shear stress was found to be 4.37 ± 0.51 MPa. The obtained strength of Cu film-inserted bonding is more than two orders of magnitude enhanced, compared to that of SS/Zerodur (~ 0.04 MPa) without interfacial metal films. The Sn and Ti both had smaller maximum shear stress of 3.53 ± 0.31 MPa and 3.42 ± 0.24 MPa. The obtained bonding strength is higher than those made by anodic bonding with Al (300 nm-thick) interfacial layer at 300 °C ~ 2 - 2.7 MPa¹¹. The shear strength obtained from this study is lower by a factor of 1/4-1/3, compared to the “tensile” strength of ~ 17 - 20 MPa from epoxy-bonded Ti/Zerodur or CoCr alloy/dental ceramic (SiO₂-based) bonding made through selective laser

melting^{12, 13} (typically generated temperatures of ~ 1000 °C or higher^{14, 15}). The lower shear strength obtained in this study than the tensile strength is reasonable since the shear strength is typically smaller by similar factors than that of the tensile strength.

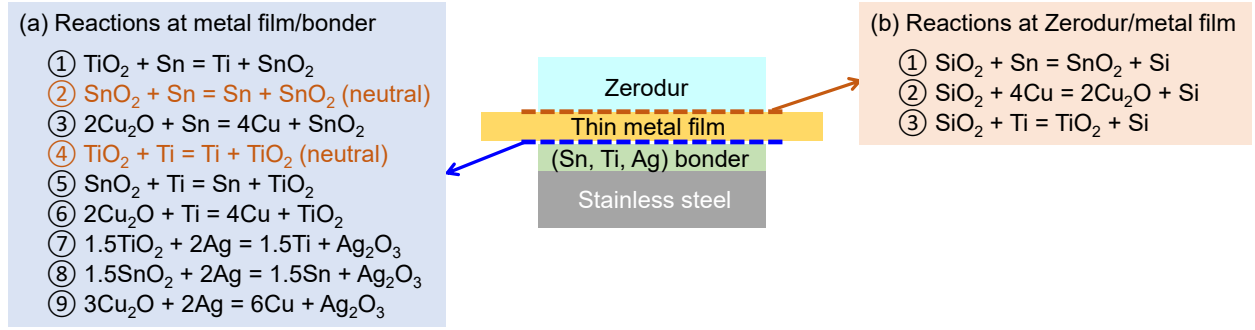


Figure 3. Chemical reactions available at the interfaces of (a) adhesion promoting oxidized-metal film/alloy bonder contact and (b) Zerodur/metal film contact

In order to investigate the factors that determine the strength of the heterogeneous bonding of SS/Zerodur as a function of metal film inserted at the contact, all available interfacial reactions are listed in Figure 3. Particularly, at the adhesion promoting thin metal/alloy bonder interface in Figure 3(a), the reactions were considered with an additional oxide layer on top of the metal/Zerodur structure, of which the oxide on the metal films is formed due to the oxidation of the metals during the heating of the metallized Zerodur surface and the melting of alloy bonder on SS at a temperature of 220 °C. All the constituent elements (Sn, Ti, Ag) in the alloy bonder were considered in the reactions with the top oxide layer of the employed thin metals of Sn, Ti, and Cu. Therefore, a total of nine reactions are considered with two neutral oxide/metal reactions at the SnO_2/Sn and TiO_2/Ti interfaces. At the other contact interface of Zerodur/metal film in Figure 3(b), three available reactions at the Zerodur major component of SiO_2 and three adhesion-promoting interfacial metal films are counted in the investigations.

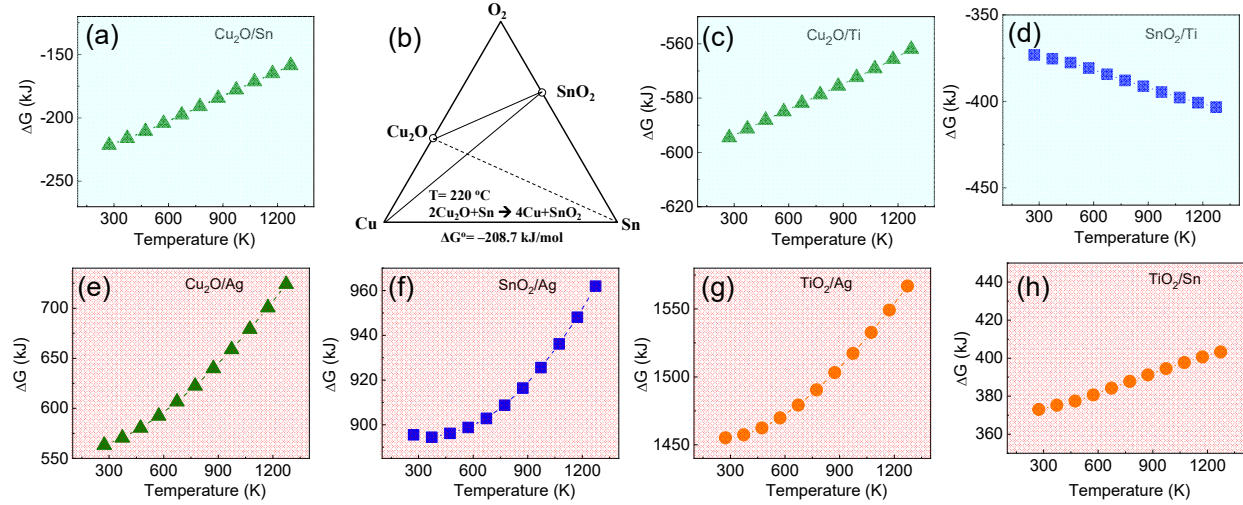


Figure 4. Gibbs free energy of reaction (ΔG) at the oxidized metal film/alloy bonder interface of: (a) $\text{Cu}_2\text{O}/\text{Sn}$; (b) A conventional molar equilibrium Cu-Sn-O_2 ternary phase diagram; (c) $\text{Cu}_2\text{O}/\text{Ti}$; (d) SnO_2/Ti ; (e) $\text{Cu}_2\text{O}/\text{Ag}$; (f) SnO_2/Ag ; (g) TiO_2/Ag ; and (h) TiO_2/Sn , where the oxidized Cu (i.e., Cu_2O) and Sn (i.e., SnO_2) are found to have negative ΔG with certain metal elements in the alloy bonder, while the oxidized Ti (i.e., TiO_2) results in no negative ΔG with all the metal elements in the alloy bonder.

Interfacial reactions, particularly forming a compound between the reactants, may lead to higher bonding strength between the two reactants¹⁶⁻¹⁸. Among the seven potential reactions at the oxidized metal/alloy bonder, the reactions that take place and hence contribute to the bonding strength need to be identified. We suggest a thermodynamic approach to the discrimination of all seven potential reactions based on standard Gibbs free energy of reaction (ΔG), where the negative ΔG indicates that the forward direction reactions are favored. The proceeded forward reactions mean that chemically activated, more strongly adhered chemo-physical interfaces are formed than simply physisorbed surfaces. Out of the seven possible interfacial reactions, Cu_2O (oxidized Cu surface) is found to be reacted with the two elements of Sn and Ti in the alloy bonder (Fig. 4a and c), and SnO_2 is also determined to be chemo-physically bound with Ti in the bonder (Fig. 4d) at a wide range of temperatures. This chemo-physical bonding behavior can be represented on a molar equilibrium ternary phase diagram. For example, in the case of oxidized Cu (Cu_2O) in contact with

Sn in the alloy bonder shown in Figure 4b, the direction (forward or reverse) of the reaction $2\text{Cu}_2\text{O} + \text{Sn} = 4\text{Cu} + \text{SnO}_2$ is predicted by subtracting the free energy of molar formation of Cu_2O from SnO_2 : $\Delta G = \Delta G_{\text{F},\text{SnO}_2} - \Delta G_{\text{F},\text{Cu}_2\text{O}}$. At 220 °C, ΔG° is determined to be negative (−208.7 kJ/mol) which indicates that the forward direction is dominant and, in the absence of kinetic constraints, chemical reducing Cu_2O provides oxygen to Sn to produce SnO_2 . In the Cu-Sn- O_2 ternary phase system, due to negative free energy, a stable tie-line (solid) connects Cu and SnO_2 while an unstable dotted line ties Sn and Cu_2O . It should be noted that TiO_2 (oxidized Ti surface in the ambient air annealing condition) does not form any chemically reacted interface with the elements in the alloy bonder, and Ag in the alloy bonder is not chemically activated with the oxidized metal surfaces as shown in Figure 4e-h.

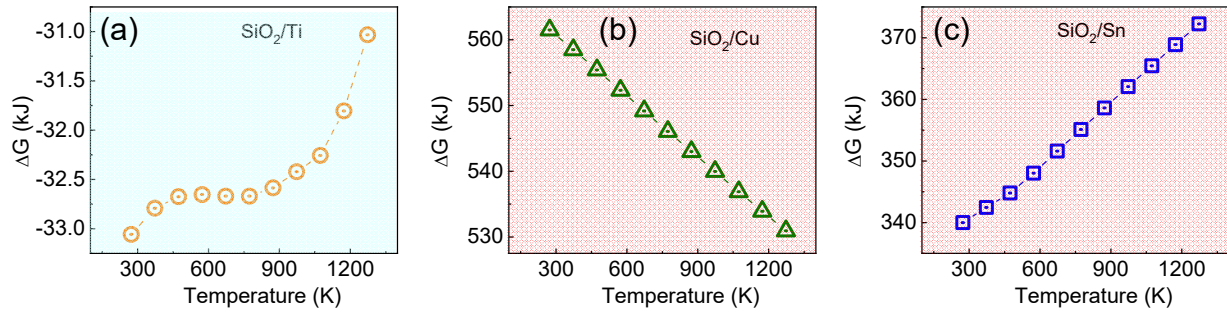


Figure 5. Gibbs free energy of reaction (ΔG) at the Zerodur (dominant SiO_2)/adhesion metal film interface of: (a) SiO_2/Ti ; (b) SiO_2/Cu ; and (c) SiO_2/Sn , where Ti films are found to have negative ΔG with SiO_2 , indicating that the mechanical properties of the heterogeneously bonded structure are dominated by the adhesion with the alloy bonder (i.e., metal film/alloy bonder in this study) rather than that between Zerodur and metal film.

In addition to the interfacial reaction characteristics at the oxidized metal film/alloy bonder interface, the interfacial bonding properties at the alloy bonder/Zerodur contact need to be considered. The ΔG calculations at the metal film/Zerodur contact were conducted, similar to those of the oxidized metal film/alloy bonder. For the ΔG calculation, SiO_2 , the major

component (75 wt%) of Zerodur is considered in contact with each of the three adhesion promoting metal films, and the results are shown in Figure 5. The detailed thermodynamic data used for the estimation of Gibbs free energy of reaction are provided in the Supporting Information. Among the three potential reactions, Ti adhesion promoting layers are found to have negative ΔG and form chemo-physical bonding at the contact (Fig. 5a). The ΔG of the other two metal films with SiO_2 (or Zerodur) is positive, indicating no chemical reactions are favored to form chemo-physical bonding at the metal film/Zerodur interface. It should be noted that the highest shear strength of the heterogeneous bonding of SS/Zerodur inserted with thin metal films was obtained with Cu, the second with Sn, and the least with Ti. Therefore, from the ΔG investigations considering the two interfaces (oxidized metal film/alloy bonder and metal film/Zerodur), the chemo-physical adhesion between the coated metal films and alloy bonder may be crucial to achieving the higher bonding strength between the selected metal (i.e., SS) and Zerodur, compared to that of metal film/Zerodur, as observed in the bonding strength tests and the thermodynamic predictive estimations.

4. Conclusion

This study reports on a low temperature strategy to achieve high strength bonding of heterogeneous SS/Zerodur (metal/ceramic) contacts. To mitigate the two main bottlenecks of dissimilar surface properties and stress evolution for the heterogeneous metal/ceramic bonding, vapor phase-processed interfacial metal films and a two-fold activation alloy bonder (activation temperature of 220 °C) were leveraged, respectively. The bonding strength in shear of the metal-coated Zerodur and SS contacts was evaluated with a custom-built sample fixture in a UTM unit. The mechanical properties of thin metal-coated Zerodur/SS bonding were related to the

thermodynamic-based interfacial stability/instability behaviors. Among the three interfacial metal films (Sn, Cu, and Ti), the highest bonding strength in shear was obtained with Cu as high as 4.36 MPa which is more than two orders of magnitude enhancement, compared to that without the interfacial film. The obtained strength is higher than that from anodic bonding and comparable to epoxy bonding or selective laser melting. The observed strength trend among the specimens well concurs with the thermodynamic estimations by which the Cu_2O (the oxidized Cu surface) is found to strongly form reaction phases with the alloy bond elements (Sn and Ti), compared to other oxidized surfaces. The demonstrated bonding strategy and the thermodynamic-based estimation can be generally applied to other metal/ceramic bonding where high bonding strength needs to be secured.

SUPPLEMENTARY MATERIAL

See supplementary material for the thermodynamic data used for the interfacial reaction calculations.

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Conflict of interest

The authors have no conflicts to disclose.

Data and materials availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

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