Improvement of Si3N4 Wettability by Sputtered Al and Post-Brazing Interfacial Microstructure

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Abstract

The wetting behavior of sputtered Al on Si3N4 and the brazing of Si3N4 ceramics with Al and Al-Ni alloy thin-film fillers were investigated. The results indicate that direct impact of high-energy sputtered Al particles can achieve 'wetting' of Al on Si3N4, thereby enabling brazing of Si3N4 ceramics upon melting of the Al and Al-Ni alloy thin films. The obtained joints exhibited dense and complete brazing seams, forming good metallurgical bonding with the ceramic without a reaction transition layer. The shear strength of the pure Al brazed joint was 106 MPa, that of the Al-1.0 at.% Ni hypoeutectic brazed joint increased to 148 MPa, while the strength of the Al-3.0 at.% Ni joint slightly decreased to 132 MPa due to the formation of eutectic structure in the brazing seam. In contrast to the aforementioned joints where shear fracture occurred within the brazing seam, when sputtered Al particles were blocked by a Ni layer and could not directly impact the Si3N4 surface, the Al-1.0 at.% Ni thin-film filler failed to wet Si3N4 after melting, resulting in shear fracture at the brazing seam/ceramic interface and a reduced strength of 81 MPa.

Full Text

Wettability Improvement and Brazing of Si3N4 by Sputtered Al

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Abstract: In current practice, brazing of Si N requires reactive transition layers to address the non-wetting problem of conventional metal fillers. While aluminum can wet Si N without interfacial reaction, brazing is extremely difficult due to the required wetting temperature exceeding 1000 °C. This work reveals the wetting effect of sputtered Al films on Si N and its underlying physical mechanism, enabling direct brazing of Si N ceramic with Al or Al-Ni film fillers near their melting temperatures. The results demonstrate that brazing joints produced by direct sputtering of Al onto Si N surfaces exhibit dense, fully-filled seams that form sound metallurgical bonds with the ceramic without reactive transition layers. The shear strength of pure Al/Si N joints reached 106 MPa, which increased to 148 MPa for Al-1.0%Ni hypoeutectic filler joints due to the formation of a hypoeutectic structure in the seam. Further increasing Ni content to 3.0% produced a eutectic seam structure that slightly reduced joint strength to 132 MPa. All these joints fractured within the seam. In contrast, joints made with Al-1.0%Ni film filler where Ni was first sputtered as an interlayer fractured at the seam-ceramic interface with a significantly lower strength of only 81 MPa. This comparison reveals the "wetting" effect achieved through bombardment of energetic sputtered Al particles, which persists after filler melting and enables direct brazing of Si N ceramic without reactive transition layers.

Keywords: Si N ceramic, wetting, sputtered film, brazing

As a fundamental physical phenomenon, the wetting of ceramics by liquid metals finds extensive applications in materials processing fields such as metal matrix composites and ceramic brazing. As the primary method for joining ceramic-to-ceramic and ceramic-to-metal components, brazing requires molten filler metals to wet the ceramic substrate. However, most metals exhibit poor wettability on ceramics including Si N . Current industrial practice mainly employs ceramic surface metallization methods involving sintering or coating with active elements such as Ti, V, and Nb [1~3], or active brazing approaches where reactive metals are directly added to the filler [4~6]. Both methods achieve brazing by forming a wettable reaction transition layer on the ceramic surface. Nevertheless, the presence of such reaction layers inevitably reduces joint strength and degrades service properties including thermal fatigue resistance and thermal conductivity.

Aluminum, like Ni, Cu, and Ag which are common brazing filler constituents, possesses an fcc crystal structure that facilitates deformation to relieve residual stresses and improve fatigue performance in ceramic joints. The relatively low melting temperature of Al and its alloys also fills the gap for brazing temperatures in the 600–700 °C range that other metal-based fillers cannot provide. More importantly, unlike conventional Ni-, Cu-, or Ag-based fillers that cannot wet ceramics, molten Al and Al alloys can wet certain ceramics when the temperature is sufficiently elevated, including Al O (>850 °C [7]), AlN (>850 °C [8]), TiO (>1210 °C [9]), and Si N (>1000 °C [10]). Leveraging this characteristic, Naka et al. [11] used Al-Si alloys as filler metals to achieve wetting and brazing of Si N ceramic at 1100 °C with a prolonged holding time of 1 h,

obtaining high shear strengths of 130 MPa. However, this brazing temperature —approximately 500 °C above the melting point of Al-Si alloys (around 600 °C) —and the extended holding time not only complicate the brazing process but may also produce detrimental effects on joint performance. Consequently, this approach has not been adopted industrially. The key to reducing brazing temperature lies in achieving wetting of Si N by Al and its alloys near their melting points.

Recently, our research group successfully achieved direct brazing of Al O [12] and AlN [13] ceramics at relatively low temperatures (600–700 °C) using sputtered Al and Al-Cu alloy films as filler metals, obtaining joint shear strengths of approximately 160 MPa. This work investigates the improvement of Si N wettability by sputtered Al and the brazing of Si N with Al and Al-Ni alloy films.

High-purity Si N ceramic substrates were selected for experiments. The substrates were polished with 1 m diamond paste, ultrasonically cleaned in acetone, and then loaded onto the substrate holder in the vacuum chamber of an ANELVA SPC-350 multi-target magnetron sputtering system. After the chamber base pressure reached better than 4×10 Pa, the substrates were baked at 400 °C for 30 min to remove adsorbed gases and contaminants. When the substrate temperature decreased below 200 °C, 99.999% pure Ar gas was introduced to maintain a pressure of 0.6 Pa. Al (99.99% purity) and Ni (99.99% purity) targets with 76 mm diameter were controlled by DC and RF cathodes, respectively. For depositing Al and Al-Ni film fillers, approximately 7 m thick Al films were first deposited on Si N surfaces, followed by thin Ni layers of 50 nm and 150 nm thickness on the Al film surface. These ultrathin Ni layers prevented oxidation of the Al film and, after melting, served as alloying elements in the Al-based filler. Based on the thickness ratio of Al and Ni films, the Ni contents in the two Al-Ni alloy film fillers after melting were calculated to be 1.0% and 3.0% (atomic fraction), corresponding to hypoeutectic and eutectic compositions, respectively.

Brazing of Si N ceramics was performed in vacuum: two ceramic substrates coated with Al-Ni films were placed face-to-face in intimate contact inside a vacuum furnace, with small weights placed on top to apply pressure and fix the samples. After achieving a vacuum of 0.1 Pa, the samples were brazed at 680 °C for 10 min, followed by furnace cooling. Shear strengths of the brazed joints were measured using an SJX-200 electronic tensile testing machine. The shear plane dimensions were 3 mm × 2 mm, and the reported strengths represent averages of over ten measurements per joint type. The microstructure, elemental distribution, and fracture surfaces of the joints were examined using an S-3400N scanning electron microscope (SEM) equipped with an Apolloxp energy-dispersive spectrometer (EDS) and a VHX-1000 high-depth-of-field optical microscope (OM).

2.1 Brazing

Table 1 presents the film structures of Al and Al-Ni filler metals and the shear strengths of the corresponding Si N brazed joints. The pure Al/Si N joint exhibited a shear strength of 106 MPa. Adding 1.0% Ni to form a hypoeutectic structure in the seam increased the joint strength to 148 MPa. Further increasing Ni content to the eutectic composition of 3.0% slightly decreased joint strength to 132 MPa.

SEM images of the brazed joints in Figure 1 [Figure 1: see original paper] reveal excellent seam filling with nearly 100% brazing coverage, dense and fully-filled seams, and sound metallurgical bonding at the Si N interface without reaction transition layers. The seam in Figure 1a consists of pure Al. With 1.0% Ni addition, light-colored Al Ni intermetallic compounds appear in the seam, indicating an Al + Al Ni hypoeutectic structure (Figure 1b). Figure 1c shows that with increased Ni content to 3.0%, the seam primarily forms an Al + Al Ni eutectic structure.

Optical microscopy examination of shear fracture surfaces in Figure 2 [Figure 2: see original paper] demonstrates that all joints fractured within the seam, indicating that the seam-ceramic interface strength exceeded that of the seam itself. The fracture surface of the pure Al/Si N joint exhibits pronounced plowing morphology (Figure 2a), characteristic of high-plasticity Al undergoing shear-induced scratching. For the Al-Ni hypoeutectic alloy seam with 1.0% Ni, the area of plowing morphology formed by the lower-strength Al phase decreased significantly (Figure 2b), as the solid solution + eutectic two-phase structure enhanced joint strength. In Figure 2c, the fracture surface of the Al-3.0%Ni eutectic seam shows minimal plowing morphology, with joint strength slightly reduced due to the eutectic structure.

2.2 Wetting

Based on the successful brazing results using Al and Al-Ni alloy film fillers, it can be concluded that the molten filler metals wet the Si N ceramic at the brazing temperature of 680 °C. However, previous studies [10] have reported that molten Al can only wet Si N at temperatures above 1000 °C. To investigate this discrepancy, comparative experiments were conducted.

Sample No.2 from Table 1, containing 1.0% Ni, was selected to create a new sample (No.2b) by altering the deposition sequence. Sample No.2b had the structure Si N /Ni(50 nm)/Al(7 m), where a 50 nm Ni layer was first deposited on Si N followed by a 7 m Al layer. Both samples yield Al alloys containing 1.0% Ni after melting, with the sole difference being that in sample No.2, sputtered Al particles directly bombard the Si N surface, whereas in sample No.2b, the pre-deposited Ni layer prevents direct Al particle impact. Brazing and wettability comparisons were then performed on these two samples with identical Ni content but different deposition sequences.

After brazing sample No.2b using the same process, the resulting joint exhibited a shear strength of only 81 MPa, significantly lower than that of sample No.2 (148 MPa) with identical composition. Fracture surface observation revealed that unlike sample No.2 where fracture occurred within the seam metal, sample No.2b joints fractured at the seam-ceramic interface (Figure 3 [Figure 3: see original paper]). This indicates that although the oxide film between filler and ceramic was eliminated during film deposition, enabling brazing, the absence of direct Al particle bombardment prevented wetting after melting, and the resulting weak interfacial bonding substantially reduced shear strength.

Further wetting comparison was performed by heating both samples to 680 °C in vacuum, holding for 10 min after filler melting, and furnace cooling. Figure 4 [Figure 4: see original paper] shows three-dimensional OM images of the solidified alloys on Si N surfaces. For sample No.2 with direct Al deposition, although the melt showed some coalescence tendency, it remained completely covering the Si N surface (Figure 4a). In contrast, on the Ni-blocked sample No.2b surface, the Al melt exhibited significant coalescence with exposed ceramic substrate visible (Figure 4b). This comparison confirms that the Al-Ni melt wetted Si N in sample No.2 but failed to wet in sample No.2b.

These comparative experiments on wettability and brazing joints for films with and without direct Al deposition on Si N demonstrate that wetting of Si N by molten Al is not achieved during the molten state but rather during the sputter deposition of the Al filler film onto the Si N surface.

3.1 Wetting of Si N by Molten Al

Extensive research has been conducted on the wettability of Si N by molten Al [11,14~20]. Mouradoff et al. [14] reported that molten Al does not directly wet Si N , exhibiting contact angles of 150°–160° that remain virtually unchanged with increasing temperature and time up to 1050 °C. Only above 1050 °C does the contact angle gradually decrease below 90° due to interfacial reactions, enabling wetting.

In Young' s equation describing the relationship between interfacial tensions and contact angle ( ) among solid, liquid, and gas phases, the solid/gas (_sv) and liquid/gas (_lv) interfacial tensions may vary slightly with temperature and time but not significantly. The primary cause of reduction is the decrease in solid/liquid interfacial tension (_sl), which stems from changes in the solid/liquid interface structure. The mechanism of temperature-dependent wettability improvement in Al/Si N systems can be referenced from molecular dynamics studies by Zhang et al. [21] on Al/Al O wettability. They found that at lower temperatures, Al atoms adsorb on Al O surfaces through "gapped" physical adsorption, whereas above 850 °C, the adsorption state transitions to "gapless" chemical adsorption with Al-O bonds, reducing interfacial tension and achieving wetting. This indicates that only when Al atoms gain sufficient kinetic energy through temperature elevation can they overcome the energy barrier to

form Al-O chemical bonds with surface O atoms. A similar mechanism exists in Al/Si N systems, where increased temperature provides Al atoms with enough energy to form low-interfacial-tension Al-N chemical bonds with Si N surface N atoms, constituting a necessary condition for wetting.

Alternatively, Al atoms can acquire high energy through other means. During magnetron sputtering deposition of Al films on Si N in this work, the kinetic energy of sputtered Al particles (atoms, ions, or clusters) can reach approximately 100 eV—significantly higher than the thermal kinetic energy of Al atoms in 1000 °C molten metal and an order of magnitude greater than the ~10 ^{1} eV energy of evaporated Al atoms at this temperature [22]. Such high-energy Al particle bombardment provides sufficient energy to overcome the barrier for Al-N chemical bond formation. The resulting high-strength Al-N covalent bonds persist after subsequent heating and melting of the Al film, maintaining a low interfacial tension state between molten Al and Si N , thereby enabling wetting and brazing near the Al melting point. The results for sample No.2b in our comparative experiments also demonstrate that when sputtered Al particles cannot directly impact the Si N surface, the molten filler fails to wet Si N , forming only physical adsorption.

It should be specifically noted that direct characterization of this bond energy transition from high-interfacial-tension physical adsorption to low-interfacial-tension chemical adsorption at elevated energy (or temperature) is extremely difficult with existing techniques, as the transition occurs only within several atomic layers at the interface between Al and N atoms, producing minimal detectable signals. This work reveals the existence of this bond energy transition through comparative analysis of wetting states, joint strengths, and fracture surface observations by altering the film deposition sequence.

3.2 Removal of Oxide Film and Brazing

Similar to solid Al surfaces, molten Al surfaces are covered by a dense, robust Al O oxide film. This solid oxide film has a melting point as high as 2050 °C and exhibits exceptional chemical stability; even at 1000 °C, its decomposition requires oxygen partial pressure below 10 ^{3} Pa [23]. This difficult-to-decompose oxide contributes to scattered data in wettability studies of Al on ceramics. Some studies [24,25] have suggested that the oxide film on molten Al surfaces hinders wetting of Si N , and that effective removal of this oxide film between Al and Si N could reduce the wetting temperature to below 900 °C.

The presence of oxide films also represents a major challenge in Al brazing technology (including brazing of Al alloys and using Al-based fillers). In conventional vacuum brazing, removal of oxide films from Al surfaces and prevention of re-oxidation require not only vacuum levels above 10 ^{3} Pa but also reduction by Mg vapor.

This study effectively overcomes the two detrimental effects of Al O films on brazing. At the filler-ceramic interface, the vapor deposition approach elimi-

nates the Al oxide film, allowing molten Al to directly contact the ceramic for brazing. The experimental results for sample No.2b further indicate that even when sputtered Al particles cannot directly bombard the Si N surface due to Ni layer obstruction, the absence of an oxide barrier still enables brazing with interfacial strength reaching 81 MPa. Regarding the oxide film on the Al filler surface, the Ni coating on the Al film surface effectively eliminates its adverse effects. Moreover, experiments show that even without Ni coating (sample No.1), the relative placement and contact of Al films on two ceramic surfaces during brazing cause the intervening oxide film to fracture and disperse into the melt as the Al films melt. This process proceeds smoothly even at a relatively low vacuum of 0.1 Pa, substantially reducing vacuum requirements for brazing.

Based on these experimental results and discussions, using sputtered Al and Al-Ni alloy films as filler metals not only changes the filler addition method but also solves two critical brazing issues: wetting of Si N by Al and oxide film removal, enabling brazing of Si N ceramic near the Al melting point. Building on the revelation and resolution of these two key issues, we can anticipate that: (1) using vapor-deposited Al films as filler can enable direct brazing of highly stable nitride ceramics such as AlN, TiN, and ZrN without interfacial reaction transition layers; (2) since Al particles in various physical vapor deposition methods possess energy far exceeding that of molten atoms, film filler deposition can employ not only sputtering and higher-energy ion plating but also relatively lower-energy thermal evaporation to achieve Al film "wetting" and direct brazing of ceramics.

4 Conclusions

(1) Using sputtered films as filler metals enabled brazing of Al and Al-Ni alloys on Si N ceramic near their melting points. The resulting joints exhibited dense, fully-filled seams forming sound metallurgical bonds with the ceramic without reaction transition layers. Pure Al brazed joints achieved a shear strength of 106 MPa, which increased to 148 MPa for Al-1.0%Ni hypoeutectic filler joints. Further increasing Ni content to 3.0% slightly reduced strength to 132 MPa due to the eutectic seam structure. All joints fractured within the seam.

(2) The "wetting" required for brazing Si N with Al film filler is achieved through direct bombardment of Si N by high-energy sputtered particles. When sputtered Al particles are blocked by a Ni layer and cannot directly impact the Si N surface, the Al-1.0%Ni film fails to wet Si N after melting, resulting in fracture at the seam-ceramic interface and reduced shear strength of only 81 MPa.

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