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Short communication

Evaluation of Pd-based brazes to join silicon nitride to copper-clad-molybdenum

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Abstract

Si_3N_4 (SN-281)/Cu-clad-Mo joints, brazed using a soft (YS: 341 MPa) and ductile (43% elongation) Pd–Co braze were sound and exhibited an interaction zone comprised of $Pd_{66}Mo_{14}Cu_{10}Co_6Si_3$ and $Pd_{74}Mo_{11}Co_8Cu_6Si$. Similar joints made using a less ductile and stronger Pd–Ni braze led to cracking from large CTE mismatch-induced strain energy (~64 mJ to 348 mJ).

Keywords: Silicon nitride; Cu-clad-Mo; Pd–Co braze; Pd–Ni braze; Scanning electron microscopy; Energy dispersive spectroscopy; Knoop microhardness

1. Introduction

Light-weight, creep-resistant silicon nitride ceramics possess excellent high-temperature strength and find use in engine components, bearings, cutting tools, melting crucibles, arc welding nozzles and specialized kiln furniture. They are also proposed to be used in next-generation turbo-shaft turbine engines to achieve higher operating temperatures and efficiencies. In many such applications, Si_3N_4 needs to be joined to itself or to metals. Molybdenum is sometimes used as an interlayer between Si_3N_4 and metals to mitigate residual stresses at a joint. Mo is also resistant to high-temperature corrosion and its coefficient of thermal expansion (CTE) is 5.3×10^{-6}/K close to the CTE of Si_3N_4 (3.3×10^{-6}/K). However, the thermal conductivity of Si_3N_4 is low (30 W/m K). In contrast, Mo has a higher conductivity (138 W/m K), and, with a clad layer of Cu, Mo can be imparted even higher conductivity. The conductivity and CTE of Cu-clad-Mo depend upon the clad layer thickness and vary in the ranges 138–235 W/m K and $\sim 5.6 \times 10^{-6}$/K to 11.6×10^{-6}/K, respectively, for 0–30% clad layer thickness per side of Mo substrate [1]. Thus, high conductivity for efficient thermal dissipation can be achieved in Si_3N_4/Cu-clad-Mo joints at relatively large clad layer thicknesses at the cost of increasing the CTE mismatch with Si_3N_4. The ductile Cu cladding may, however, facilitate residual stress accommodation and preserve the joint integrity. Thus, Si_3N_4/Cu-clad-Mo joints may be designed to maximize the benefits of high thermal conductivity while exploiting the ductility of Cu cladding to minimize the deleterious effects of CTE-mismatch induced residual stresses during joining and service. Recently, Cu-clad-Mo was successfully joined to C–C composites [2,3] and ZrB_2-based ultra-high temperature ceramic composites [4] for thermal management applications.

Si_3N_4 has been joined to Mo by diffusion bonding [5] and brazing [6,7]. Drew and coworkers [5–7] have studied the microstructure of Si_3N_4/Mo interfaces made either via diffusion bonding (1373–2073 K) or brazing (1473–1573 K). They noted relatively thick reaction layers composed chiefly of Mo_3Si and Mo_5Si_3 at the interface. With Ni–Cr–Si brazing alloys, complex intermetallic reaction products formed at the interface [6]. Ito et al. [8] noted reaction layers of V_3Si in vacuum hot-pressed Si_3N_4/Mo joints made using vanadium interlayers. Flores et al. [9] diffusion bonded Si_3N_4 to Mo using Cu interlayers in the order: Si_3N_4/Cu/Mo/Cu/Si_3N_4 at 1223–1423 K. They found that Si_3N_4 bonded to Mo only above 1423 K (in contrast, Si_3N_4/Cu/Ti/Cu/Si_3N_4 joints formed even at 1323 K because of extensive reactions due to the presence of Ti).

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To realize full benefits of the excellent oxidation resistance of Mo in Si_3N_4/Cu-clad-Mo joints, it is beneficial to utilize filler metals that also have good oxidation resistance. Palladium-base brazes offer excellent oxidation resistance and high use temperatures. In this study, two commercial Pd-base brazes, Palco (65Pd–35Co) and Palni (60Pd–40Ni) were used to join Si_3N_4 to Cu-clad-Mo. The Pilling–Bedworth ratios of Pd, Ni and Co are 1.60, 1.52 and 1.99, respectively [10] which indicates that these metals tend to form protective oxide films in oxidizing atmospheres.

2. Experimental procedure

The two brazes, Palco ($T_L \sim 1492$ K) and Palni ($T_L \sim 1511$ K) were obtained in foil form (thickness ~50 μm) from Morgan Advanced Ceramics, CA. The yield strength of Palco and Palni are 341 MPa and 772 MPa, respectively, and the brazes have good ductility (43% for Palco, 23% for Palni) which can aid in accommodating residual stresses. The Cu-clad-Mo plates were obtained from H.C. Stark, Inc., Newton, MA; the material was manufactured by rolling a Mo core sandwiched between two Cu layers. The Cu/Mo/Cu layer thickness ratio was 0.33 mm/1.9 mm/0.33 mm (13–74–13%). Silicon nitride (SN-281) was obtained from Kyocera America, WA. It contains about 9–10 wt.% Lu_2O_3 as a sintering additive.

The ceramic substrates, metal panels, and braze foils were sliced into 2.54 cm × 1.25 cm × 0.25 cm pieces, and ultrasonically cleaned in acetone for 15 min. Two braze foils were sandwiched between Cu-clad-Mo and Si_3N_4, and a pressure of 1.2–4.7 kPa was applied to the assembly during brazing. The assembly was heated in a furnace to ~15 K to 20 K above the braze liquidus under vacuum (~10^{-6} Torr), soaked for 5 min, and slowly cooled to room temperature. The brazed joints were examined using SEM and EDS on a JEOL840 A unit. Microhardness scans were made across the joint region with a Knoop micro-indenter on a Struers Duramin A-300 machine under a load of 200 g and loading time of 10 s.

3. Results and discussion

Fig. 1(a)–(e) shows the microstructure of a Si_3N_4/Cu-clad-Mo joint made using Palco. The joint exhibits good bonding and evidence of strong chemical interaction, and is devoid of micro-porosity. There is evidence of considerable interdiffusion over a distance of ~50 μm across the Si_3N_4/Palco interface (Fig. 1c) and relatively large amounts of Pd, Si, Mo, Co and Cu are detected in the interaction zone (Fig. 2(a)). The reaction layer has a rather inhomogeneous morphology and is comprised of multiple phases such as the dark-gray Pd-rich blocky particles (marked 'A' in Fig. 1(d)) with a nominal composition (in at.%) of 66Pd–14Mo–10Cu–6Co–3Si and the lighter Pd-rich phase (marked 'B' in Fig. 1(d)) with a nominal composition of 74Pd–11Mo–8Co–6Cu–Si. Clearly, the joint microstructures have been strongly influenced by the diffusion of Pd, Mo, Si and other alloying elements, which led to sound metallurgical bonding. A similar evidence of extensive chemical interaction is noted at the Palco/Cu-clad-Mo interface (Figs. 1(e) and 2(b)).

With Palni braze, the Si_3N_4/Cu-clad-Mo joint (Fig. 3) shows a prominent reaction layer but also pronounced cracking at the interface between the reaction zone and Si_3N_4 substrate

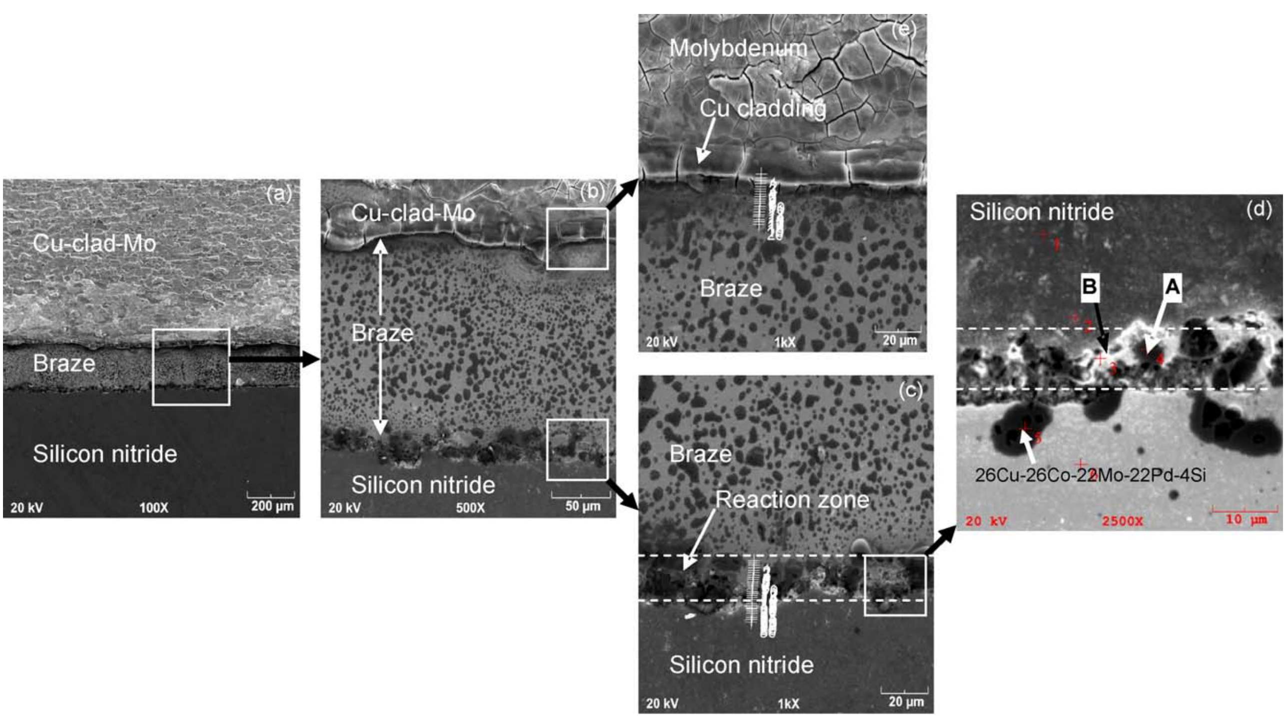

Fig. 1. Microstructure of a Si_3N_4 (SN-281)/Palco/Cu-clad-Mo joint showing (a) and (b) overall views of the joint, (c) Si_3N_4/braze interface, (d) interaction zone, and (e) Palco/Cu-clad-Mo interface. In (d) the phases marked 'A' and 'B' have the compositions of 66Pd–14Mo–10Cu–6Co–3Si and 74Pd–11Mo–8Co–6Cu–Si, respectively.

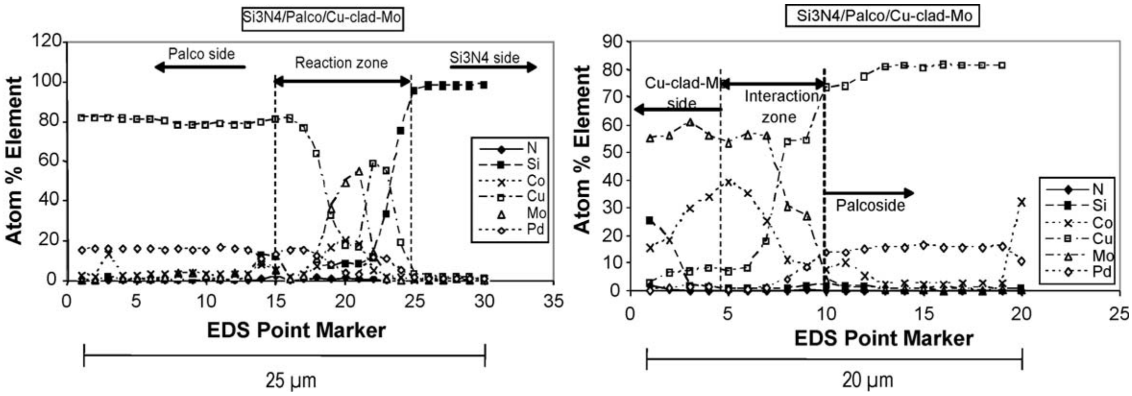

Fig. 2. Relative atomic percentages of alloying elements at point markers at (a) Si_3N_4/Palco interface shown in Fig. 1(c), and (b) Cu-clad-Mo/Palco interface shown in Fig. 1(e).

(Fig. 3(b)). The interaction zone consists mainly of Cu, Pd, Ni and some Mo; interestingly, Si content of the interaction zone is low. Interfacial cracking in Palni-based joint is due chiefly to residual stresses from CTE mismatch; the higher yield strength (772 MPa) and lower ductility (23%) coupled with a slightly larger temperature excursion (ΔT) led to ineffective residual stress relief in joints made using Palni. In contrast, the appreciably lower yield strength (341 MPa) coupled with larger

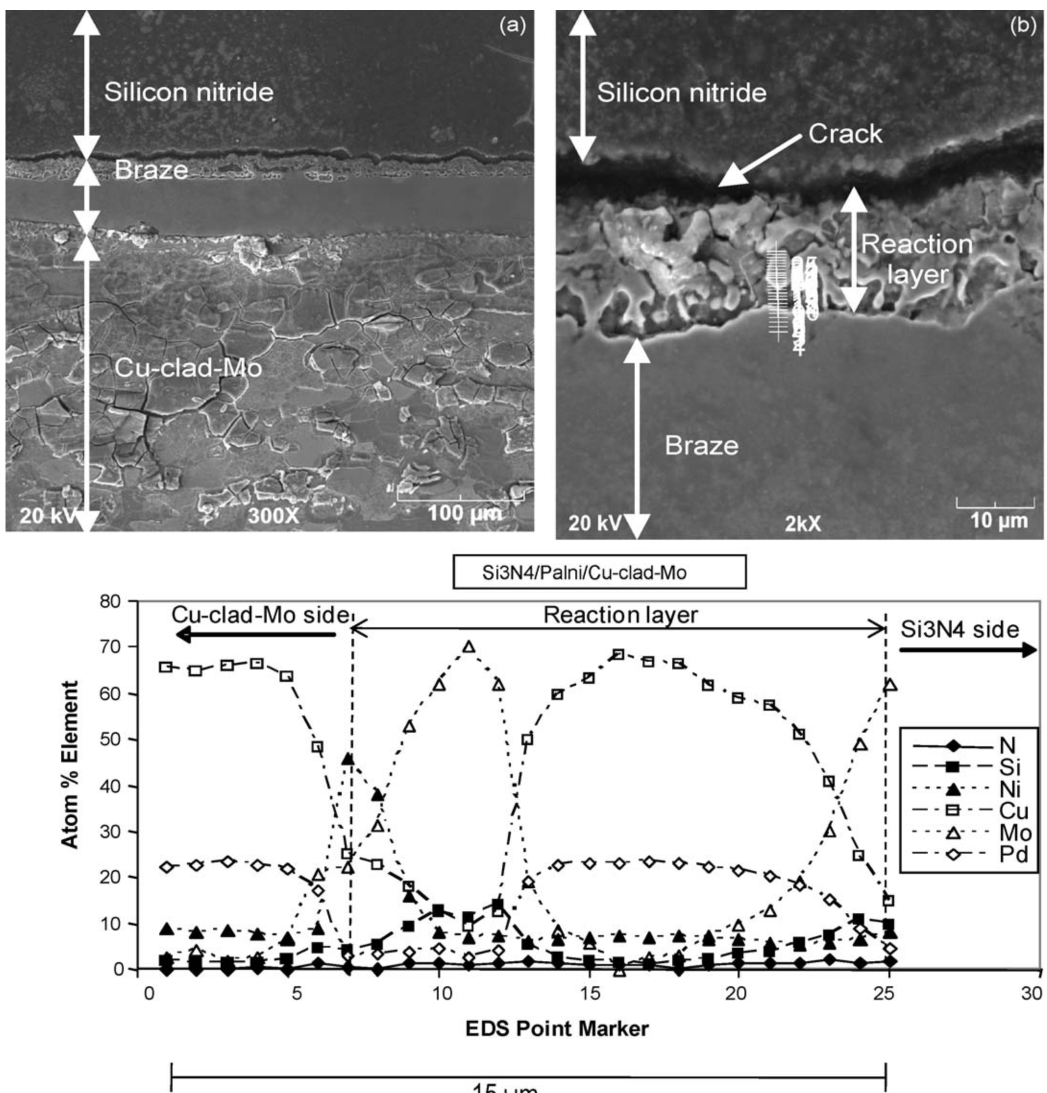

Fig. 3. (a) and (b) Microstructure of a Si_3N_4/Palco/Cu-clad-Mo joint, and (c) relative atomic percentages of alloying elements across the reaction zone at point markers shown in (b).

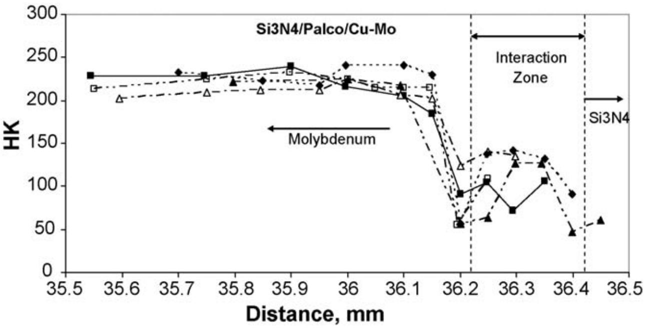

Fig. 4. Knoop microhardness distribution across a Si_3N_4/Palco/Cu-clad-Mo joint; curves marked with symbols represent multiple traces across the joint.

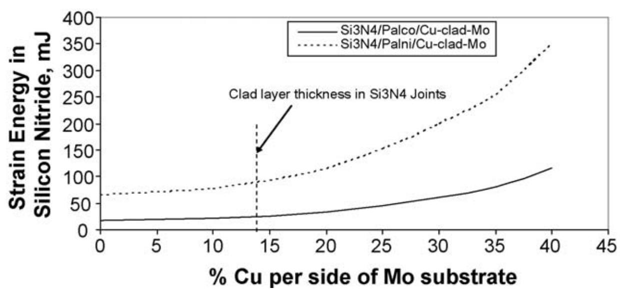

Fig. 5. Calculated strain energy in the ceramic in Si_3N_4 joints made using Palco and Palni.

(43%) ductility and lower ΔT permitted adequate stress relief and formation of crack-free joints in Palco.

The Knoop hardness (HK) profiles across a Si_3N_4/Palco/Cu-clad-Mo joint are shown in Fig. 4. Multiple profiles (identified with symbols) accessed across the joint confirmed the reproducibility of the hardness measurements. The hardness values of the Mo substrate and the interaction zone (including Cu cladding) are ∼200 HK to 240 HK and ∼50 HK to 140 HK, respectively.

Residual stresses that develop due to the CTE mismatch control the joint strength, and joints with large residual stress fracture at low stresses. For well-bonded joints, residual stresses span a distance about three times the thickness of the braze layer [11]. Near the center of the joint far from the free surface, stresses parallel to the interface are tensile in the metal and compressive in the ceramic and exhibit a discontinuity across the interface. Stresses normal to the interface are compressive in the metal and tensile in the ceramic at the free edge where their maximum value is reached. Eager and coworkers [12] present a model to estimate the strain energy in the ceramic in well-bonded ceramic–metal joints. For a small CTE mismatch between the ceramic and the metal substrate, but with a large CTE mismatch between the interlayer and the base materials, the elastic strain energy, U_{eC}, in the ceramic for a disc-shaped joint can be calculated from a knowledge of the yield strength (σ_{YI}) of the braze, the elastic modulus of the ceramic (E_C) and the braze (E_I), the CTE (α) of the ceramic, metal and braze, and the temperature drop ΔT.

Fig. 5 shows the projections of strain energy in the ceramic for Si_3N_4/Palco/Cu-clad-Mo and Si_3N_4/Palni/Cu-clad-Mo joints based on Eager's model. The CTE of Cu-clad-Mo (α_M) depends on clad layer thickness and is taken from Ref. [1]. The following property data were used: $E_{Palco} = E_{Palni}$ = 152 GPa, σ_{YI} = 341 MPa (Palco), σ_{YI} = 772 MPa (Palni), E_C = 318 GPa (Kyocera SN-281), $\alpha_I = 14.3 \times 10^{-6}$/K (Palco), and 15.0×10^{-6}/K (Palni), and $\alpha_C = 3.2 \times 10^{-6}$/K (for SN-281). The strain energy, U_{eC}, in the joints was calculated as a function of the clad layer thickness. The results show that the strain energy values are in the range ∼17 mJ to 116 mJ for Palco joints and ∼64 mJ to 348 mJ for Palni joints for 0–40% clad layer thickness. The strain energy sharply increases with increasing clad layer thickness, and the increase is more pronounced for Palni than for Palco joints. The very large strain energy in Palni joints points toward a considerable weakening of the ceramic. Although the projections are based on simplified calculations that ignore chemical interactions and compositional adjustments in reactive systems, the general conclusions appear to be consistent with the microstructural observations (e.g., joint failure in Palni (Fig. 3) rather than in Palco). Judiciously arranged stress-absorbing compliant layers of controlled yield strength and CTE within the bonded region may relieve the stress and create sound Si_3N_4/Cu-clad-Mo joints using Pd–Ni braze alloys.

4. Conclusions

Pd–Co brazes may be suitable for joining Si_3N_4 to Cu-clad-Mo for moderately high use temperatures in systems where relatively high thermal conductivity is desired. The joints exhibit a prominent reaction layer whose effect on thermal and mechanical properties needs to be assessed. The Pd–Ni brazes were unsuitable for joining because of extensive cracking from ineffective residual stress relief although such brazes also led to strong chemical interactions.

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