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Effects of titanium on some surface properties of nitride ceramics

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The presence of titanium at nitride ceramic–braze interfaces can promote both wetting and bonding. Previously we have added titanium to brazes and examined the effects of segregation to the interfaces but in this study, the ceramic surfaces were precoated with titanium before they were contacted by brazes or solders. Ion assisted coatings were applied to sialon, Si_3N_4 and AlN, and sputter ion platings were applied to sialon. Coating adhesion measured by scratch testing was better for the sputter ion platings than the ion assisted coatings. The platings were also better wetted by an Ag–Cu eutectic braze, and produced joints 50% stronger than those achievable with a commercially developed Ag–Cu–Ti active metal braze.

1. Introduction

Nitride ceramics are emerging as important engineering materials but reliable ways of bonding them must be developed if their full potential is to be realised. Brazing and soldering are attractive techniques for fabricating ceramic–metal components because they are familiar to production engineers concerned with joining metal–metal components, and the ductility of brazes and solders enables some mismatches of workpiece thermal expansion coefficients to be accommodated. However, nitrides are not wetted by the conventional brazes or solders developed for metal–metal joining and without such wetting, the liquid metal cannot form joints by entering the capillary gaps between workpieces. Nitrides are not the only family of ceramics it is difficult to wet, and a number of technical solutions have been developed. Thus, satisfactory wetting can be achieved either by modifying braze alloys to incorporate components such as titanium that can react to cover the ceramic surface with wettable products, or by precoating the ceramics with a metal and then using a conventional braze or low melting point solder.

We have discussed previously the segregation of titanium to ceramic surfaces during the reactive brazing of nitrides [1], but this study has concentrated on the effects of precoating the ceramic surfaces with titanium. A range of techniques are available for coating ceramics, but the products vary in their thickness, microstructure, porosity and adhesion. To promote brazing it is important not only that the coating be wetted but also that it should be structurally sound and adherent. In this work, therefore, attention was focused on two techniques – ion assisted coating and sputter ion plating – noted for their product quality but comparisons were made also with the activation of ceramic surfaces using TiH_2 and with a titanium activated braze alloy.

2. Experimental materials and techniques

2.1. Ceramics and metals

The three ceramics used in the study were AlN, Si_3N_4 and a sialon, Table I, were prepared as 3–5 mm thick square coupons with sides of approximately 10 mm. The surface topographies of the ceramics were characterized, Fig. 1, using a Surfcom 30B stylus instrument and were degreased ultrasonically in acetone for 5 min and dried with a hot air blast before being used in any experimental work.

The tin, Sn–38Pb solder, Ag–28Cu braze, Ag–27.5Cu–2Ti braze and Ni–7Cr–4.5Si–3B–3Fe braze were also degreased before being used in wetting studies. The AG–Cu–Ti braze had been supplied by G.T.E. Wesgo of Belmont (California, USA) and the nickel braze was supplied by Neomet of Stockport (UK) but the other alloys were produced at Harwell by melting mixtures of high purity metals under an argon cover gas. These alloy ingots were then machined into small cylinders, with diameters and heights of approximately 2 and 3 mm, which were melted to produce sessile drops during wetting tests, or were rolled into 0.25 mm thick sheets that were used to manufacture shear strength samples.

2.2. Coating techniques

The two principal methods used in this work were ion assisted coating and sputter ion plating. Ceramics prepared using the first technique were vapour coated with 60 nm of titanium then ion implanted with 10^{15},

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TABLE I Ceramics employed

Ceramic	Source/grade	Nominal composition (wt %)
AlN	ESK[a]/HDALN	65.5Al, 32.3N, 20, 0.2C
Si_3N_4	ESK[a]/Ekasin S	54Si, 36N, $6La_2O_3$, $4Al_2O_3$
Sialon	LCS[b]/sialon 101	solid solution of Al_2O_3 in Si_3N_4

[a] Elektroschmelzwerk Kempten, Munich, FRG.
[b] Lucas-Cookson-Syalon, Solihull, UK.

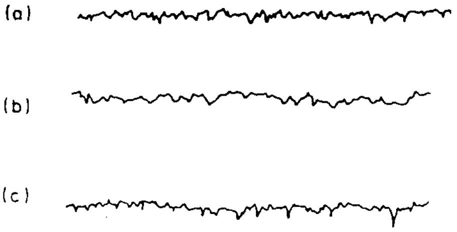

Figure 1 Surface profilometer traces across the ceramics used in the wetting and bonding studies. Vertical magnification 1000 ×, horizontal magnification 40 ×. (a) AlN, $R_a = 0.33$ µm, $\lambda_a = 49.1$ µm. (b) Si_3N_4, $R_a = 0.35$ µm, $\lambda_a = 56.2$ µm. (c) Sialon, $R_a = 0.15$ µm, $\lambda_a = 98.2$ µm.

10^{16} or 10^{17} of N^+ ions accelerated using a 60 keV potential. Most of these ions passed through the coatings to cluster at a depth of 100 nm beneath the ceramic surface, as illustrated in Fig. 2 for AlN and Si_3N_4, but the interfacial disorder created by their passage should have promoted the adhesion of the titanium.

The sputter ion plated coatings of titanium were much thicker, 1000 nm on average, and were applied only to the sialon ceramic at nominally room temperature using an argon glow discharge and source plates biased to 1 kV.

In a few experiments, brushed coatings of TiH_2 powder were applied to the sialon surface using Nicrobraz cement as a carrier. As the samples were heated through the 350–500 °C temperature range during a vacuum brazing cycle, the powder should have dissociated to liberate hydrogen and deposit titanium on to the ceramic surface to a thickness of about 1 µm.

2.3. Evaluation techniques

The qualities of the coatings were assessed mainly in terms of adhesion or of their effects on the wettability of the ceramics, or both. A measure of adhesion was derived using a Revetest scratch tester to determine the load needed to disrupt the coatings. The machine was fitted with an acoustic emission device tuned to a frequency range centred on 10 kHz and with a gain set to give a full scale deflection when a 10 kg load was used to produce a chipped track on uncoated Si_3N_4. The acoustic response of the coated samples was used as a measure of coating adhesion but more attention was paid to subsequent examination of the scratch tracks using optical or scanning electron microscopy or both.

Wetting behaviour was characterized by photographing the profiles of small sessile drops of molten metal resting on horizontal ceramic plaques. If the contact angle identified as θ in Fig. 3 had a value of less than 90° the liquid had wetted and therefore could enter capillary gaps between workpieces. These wetting tests were performed in a vacuum furnace and the samples were heated at 5 K min^{-1} to the experimental wetting temperatures of 450 °C for tin and the Sn–38Pb solder, 900 °C for the Ag–28Cu and Ag–27.5Cu–2Ti brazes, and 1075 °C for the nickel braze alloy once the chamber had been evacuated to less than 1×10^{-3} Pa. The residual gas pressure did not rise above 2×10^{-3} Pa even during the 15 min dwell at the wetting temperature.

For systems which wetted, strength test samples were produced by brazing sandwiches of unequal sized ceramic plaques which were subsequently sheared apart using an Instron 1195 test machine with a crosshead traversing at 1 mm min^{-1}.

3. Experimental results and discussion

Effects of coatings on both the mechanical and wetting behaviour of the ceramics were assessed. In each case, data for uncoated ceramics were generated as well to provide a control.

3.1. Mechanical effects

3.1.1. Scratch tests on uncoated ceramics

The behaviour of sialon and Si_3N_4 was similar in these tests. Smooth shallow scratches were produced using low loads, but high load scratching was associated with significant chipping and by a rapid rise in acoustic emission, as illustrated in Fig. 4. The critical loads,

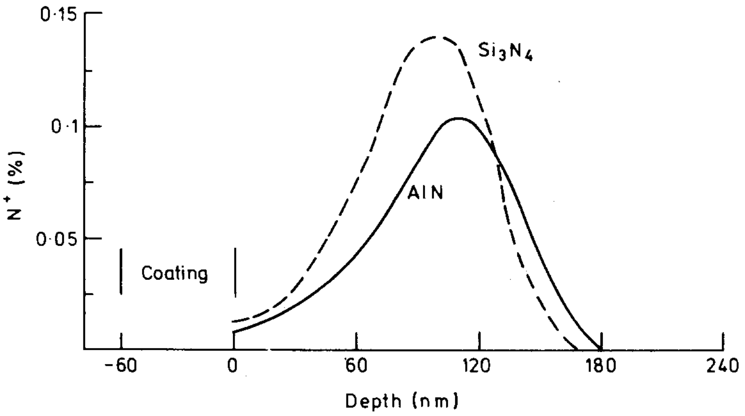

Figure 2 Computed penetration of AlN and Si_3N_4 coated with 60 nm of titanium by 10^{16} atoms cm^{-2} of N^+ ions. The computed curve for sialon is identical to that for Si_3N_4.

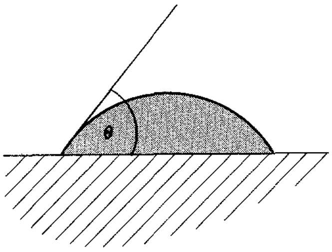

Figure 3 Schematic profile of a sessile drop sample.

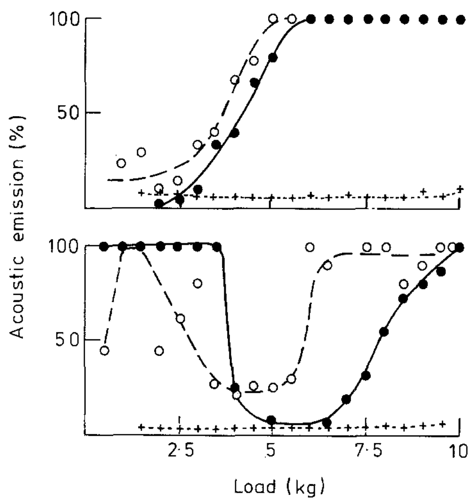

Figure 4 The acoustic emissions generated by scratching three nitride ceramics; top, bare ceramic; bottom, ion assisted coated ceramic. (●) Sialon, (○) Si_3N_4, (+) AlN.

the loads needed to initiate significant chipping were estimated as about 4 kg for both sialon and silicon nitride. However, use of the 50% full scale deflection of the acoustic emission meter to define significant chattering suggests that the critical load for silicon nitride is slightly less than that for sialon, Fig. 4.

The behaviour of aluminium nitride was markedly different, with minor chipping to produce fine dust and modest chattering being caused by even a 0.5 kg load. It was not possible, therefore, to identify a critical load for this ceramic at which damage and fracturing commenced.

3.1.2. Scratch tests on samples with ion assisted coatings

The behaviour of the coated samples was more complex than that of the ceramics in their original state. Thus acoustic emission could be caused not only by fragmentation of the ceramic but by debonding of the metal coatings. As shown in Fig. 4, acoustic emission by coated sialon was high at even the lowest scratching loads used, and subsequently decreased before rising again for a second time as the ceramic chipped. A mid-load trough was exhibited by coated Si_3N_4 as well, but the acoustic emission was modest with the lowest load used. Finally, like the original ceramic, coated AlN generated very little noise except at the highest load. These data were for samples subjected to a dose of 10^{16} atoms cm^{-2}, but varying the dose to 10^{15} or 10^{17} atoms cm^{-2} did not change the general characteristics of the dependence of noise level on scratching load.

Acoustic emission measurements were supplemented by optical and scanning electron microscopy. These showed that the ruptured films were torn but not necessarily removed. At moderate scratching loads, ruptured films could be pushed down into the scratch tracks and become mechanically attached. Complete removal could require significantly higher loads, as illustrated in Fig. 5 for Si_3N_5.

Comparison of acoustic emission data complemented by observations of tearing enable some

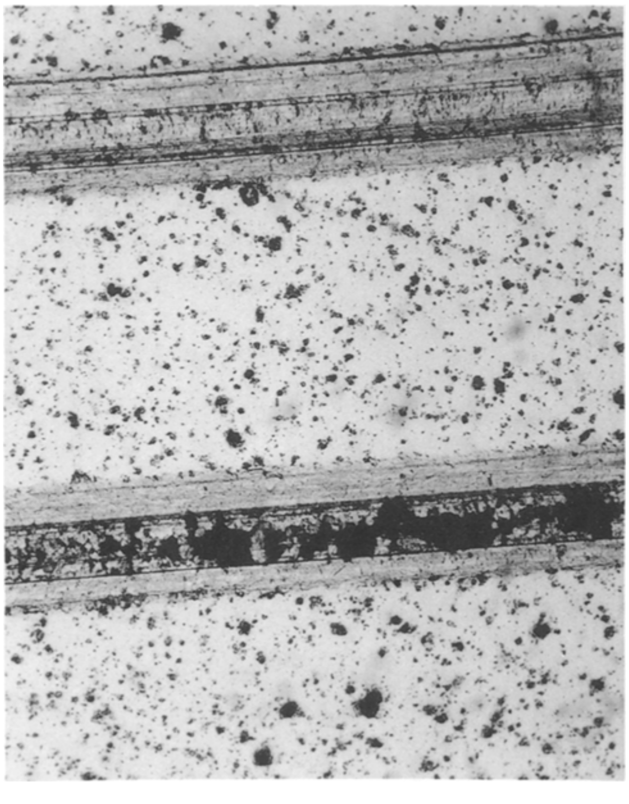

Figure 5 Scratch tracks on titanium coated Si_3N_4 that had been implanted with 10^{16} atoms cm^{-2} of N^+ ions. The left hand track was made using a load of 6.5 kg, and the right hand track was made using a load of 7 kg, but acoustic emission measurements suggested that rupture occurred at a load of 1 kg. Magnification × 270.

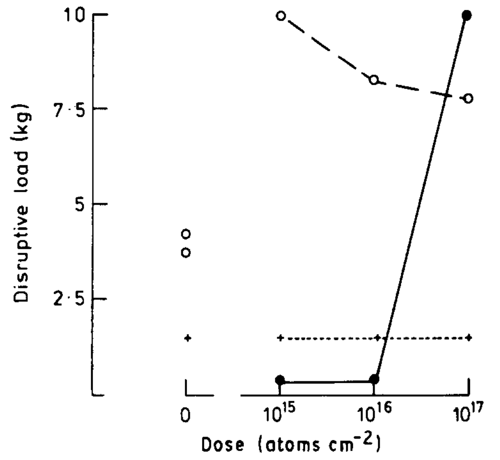

Figure 6 The rupture loads of ion assisted coatings deposited on (●) sialon, (○) Si_3N_4 and (+) AlN.

conclusions to be drawn about the effects of ion implantation on coating adhesion. Thus Fig. 6 shows that the scratch resistance of the coatings on fragile AlN were unaffected by increasing the intensity of ion implantation, while those of coatings on Si_3N_4 were decreased somewhat. The most dramatic effect was the tenfold increase in the disruptive load for sialon samples caused by raising the dose from 10^{16} to 10^{17} atoms cm^{-2} of N^+. These complex observations demonstrate that the influence of ion implantation on coating adhesion is sensitive to both the chemistry and structural integrity of the substrates.

3.1.3. Scratch tests on sputter ion plated sialon

The loads necessary to remove these coatings were higher than the maximum 10 kg available with the test equipment. Even at that load, no significant acoustic emission signals were generated, and hence it was concluded that the coatings were bonded very strongly to their ceramic substrates.

Thus the sputter ion plated coatings were far more adherent than those produced by ion implantation of vapour deposited coatings. However, it is not possible to make direct comparisons that would permit identification of which process was more efficient, because the coating thicknesses differed by 16 × and this will have affected rupture behaviour during scratch testing.

3.1.4. Hardness testing

Vickers diamond hardness tests were performed on both uncoated and ion assisted coated samples. The average hardness values decreased from 2030 (± 52) to 1843 (± 49) for Si_3N_4 but were essentially unchanged for sialon, decreasing only from 2258 (± 47) to 2230 (± 42). Although increasing the dosage of N^+ ions caused some variation in hardness values, these were small and within the experimental scatter. Nor could any trend be discerned in the data for AlN, but the individual values were low, 1500–1600, and rather scattered.

This behaviour was not characterized in detail, but hardness decreases have been observed also for N^+ ion assisted coatings of zirconium on Si_3N_4 [2] and attributed to the effect that plastic deformation of the metal film occurring during indentation has on reducing the tensile stress within the ceramic. Thus bigger impressions can be formed without being distorted by crack nucleation and propagation.

3.2. Wetting and bonding behaviour

Wettability was characterized for the uncoated ceramics using both solders and brazes. Only the active metal braze, Ag–27.5Cu–2Ti, wetted with sessile drops assuming contact angles of 12–17° on all three ceramics. The other alloys and tin assumed contact angles of 130–150° at the experimental temperatures used, as summarized in Table II.

The effects of the coating treatments of sialon substrates were very varied. Sessile drops of the Sn–38Pb eutectic solder failed to wet samples ion assisted coatings or sputter ion platings with contact angles of 145 and 134° being assumed even at 450 °C, a superheat of 267 °C. Experiments with the Ag–Cu eutectic at 900 °C however produced variable results, with contact angles ranging from 154° on samples with ion assisted coatings to 85° on samples with TiH_2 and to only 8° on samples that had been sputter ion plated with 1 μm of titanium. In a further experiment with

TABLE II Wetting and bonding date for sialon

Coating	Melt	Temperature (°C)	Contact angle (deg)	Joint shear strength (MPa)
Bare	Sn	450	134	–
Bare	Sn–38Pb	450	142	–
Ion assisted	Sn–38Pb	450	145	–
Sputter ion plated	Sn–38Pb	450	138	–
Bare	Ag–28Cu	900	135	–
Ion assisted	Ag–28Cu	900	154	–
TiH_2	Ag–28Cu	900	85	45–47
Sputter ion plated	Ag–28Cu	900	8	75–95
Bare	Ag–27.5Cu–2Ti	900	14	56–60
Ion assisted	Ni braze	1075	140	–
Sputter ion plated	Ni braze	1075	18–20	55–60

sputter ion plated sialon, the nickel base braze exhibited a contact angle of less than 20° at 1075 °C.

The wetting combinations were used also to produce brazed sandwiches which were subsequently mechanically tested. TiH_2 coated sialon brazed with the Ag–28Cu eutectic braze had a joint shear strength of 45–47 MPa while sputter ion plated samples brazed with the nickel alloy had shear strengths of 55–60 MPa, as had uncoated samples bonded with the AgCuTi active metal braze. The greatest shear strengths, 85 ± 10 MPa, were produced by brazing sputter ion plated samples with the AgCu eutectic, Table III.

The non-wetting of the coated samples by the solder is noteworthy, and suggests that the titanium surfaces were still oxide coated at 450 °C in a vacuum. At high, brazing, temperatures the solubility of oxygen in titanium is about 30 at % [3], so a 60 nm thick ion assisted coating could dissolve a 10 nm thick TiO_2 film, and a 1 μm thick sputter ion plating could dissolve a 160 nm thick film. The oxide films formed on titanium at room temperature are reported to be only 5 ± 3 nm thick [4] so they should dissolve completely as equilibrium is approached. However, this removal must be achieved within the duration of a braze cycle, and further, oxide film renewal can occur by interaction with residual gas present in the furnace chamber.

At high temperatures, 1150 °C, the residual gas partial pressures have been measured for the particular equipment used [1] as 1×10^{-6} mbar of H_2O, CO_2 and CO, 6×10^{-7} mbar of N_2, 4×10^{-7} mbar of H_2 and 3×10^{-7} mbar of O_2. Since the total pressure did not vary markedly with temperature, it is assumed that neither did the individual partial pressures. The diffusion rate of oxygen in titanium at 450 °C can be estimated as 1.6×10^{-19} $m^2 sec^{-1}$ [5], and hence a 5 nm thick film of TiO_2 could dissolve in less than 3 min. However, kinetic theory [6] predicts that 5.6 nm of TiO_2 could be reformed in our environment due to oxygen impingement during that 3 min, so there should be no net thinning of the surface oxide. Water vapour present in the residual gases could also maintain the oxidized surface, although work with stainless steel suggests that water is a far less efficient oxidizing agent than oxygen [7].

At 900 °C, the temperature used for the Ag–Cu and Ag–Cu–Ti brazing, sufficient oxygen will impinge on the coating surface to create a 22 nm thick film of TiO_2 in 15 min, but the diffusion rate of oxygen in titanium of 1.7×10^{-3} $m^2 sec^{-1}$ is such that even a 1200 nm film of TiO_2 could dissolve in that time. Thus the coating surface should be oxide free provided the coating can absorb (5 + 22) nm thick film of TiO_2. This is easily accomplished by the 1 μm thick sputter ion platings but the 60 nm thick ion assisted coatings will become saturated with oxygen and some TiO_2 should be left on their surfaces.

Thus it is understandable that the Sn–38Pb solder was unable to wet the coatings at 450 °C, and that the Ag–28Cu eutectic braze did not wet the oxide saturated ion assisted coating at 900 °C. However, the sputter ion plated samples should have been oxide free at 900 °C and above, and this accounts for their excellent wetting by the Ag–28Cu eutectic and the nickel braze.

It is noteworthy that sputter ion plating also promoted bonding, producing shear strength values equal to or substantially better than those achieved using the Ag–27.5Cu–2Ti active metal braze. However, the specific reasons for this behaviour are not clear and have not been elucidated in this work. To gain understanding would require detailed knowledge of the interfacial microstructures and stress analyses of the joint configurations.

4. Conclusions

1. The adhesion of 60 nm ion assisted coatings of titanium to sialon are greatly enhanced when the flux is increased to 10^{17} atoms cm^{-2} of N^+. However, fluxes of 10^{15} or 10^{16} atoms cm^{-2} have no noticeable effect, and increasing fluxes progressively degrade the adhesion of the coatings to Si_3N_4 substrates.
2. Thin, 60 nm, ion assisted coatings of titanium on sialon are not wetted in a vacuum by Pb–Sn eutectic solder or Ag–Cu eutectic braze. Thicker, 1 μm, sputter ion platings, however, are wetted by the Ag–Cu eutectic braze, and by a nickel braze, due to their ability to dissolve surface oxide films at high temperatures.
3. Strong bonding, 60 MPa in shear, of sialon can be achieved using an Ag–27.5Cu–2Ti active metal braze or by sputter ion plating titanium and then brazing with a nickel alloy. Even stronger bonding, 85 MPa in shear, can be achieved by sputter ion plating with titanium and then brazing with an Ag–28Cu eutectic alloy.

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