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Title	A Novel Approach To Ceramic/Metal Joining(Physics, Processes, Instruments & Measurements)
Author(s)	Samandi, Masoud; Gudze, Mathew; Ji, Hauxia et al.
Citation	Transactions of JWRI. 1997, 26(2), p. 1-5
Version Type	VoR
URL	https://doi.org/10.18910/9598
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A Novel Approach To Ceramic/Metal Joining †

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Abstract

The joining of ceramics to metals is problematic primarily due to the vastly different atomic bonding in these materials. In an attempt to overcome this problem MEVVA ion implantation of titanium into alumina was performed to modify the physico-chemical properties and microstructure in the near surface region of the ceramic. The brazing of alumina to copper, before and after implantation, was performed using both reactive (titanium containing) and non-reactive Cu-Ag eutectic brazes. It has been established, for the first time, that metallic implantation of ceramic enables joining to metal with non-reactive braze.

Extensive characterisation of faying surfaces was carried out by Rutherford Backscattering (RBS), four point probe conductivity tests, and braze wettability tests. Further, the microstructural evolution of implanted ceramic surfaces was elucidated by detailed cross-sectional transmission electron microscopy (XTEM) in conjunction with nanobeam electron diffraction (NBED). It has been demonstrated that implantation drastically changes the nature of bonding in alumina by forming metallic-like compounds such as TiO_2 thus enhancing the degree of wetting by non-reactive braze compared to the unimplanted alumina.

KEY WORDS: (Joining) (Ceramic/metal) (XTEM) (Implantaion) (RBS) (Wettability) (Brazing)

1. Introduction

High performance ceramics must often be bonded to other ceramics or metals, because certain shapes cannot be made in one piece. There are many reasons for wishing to join particular ceramic and metal components, but the motives can usually be related to design, manufacturing, or economic factors. The main applications of ceramic/metal joining to date are in the electrical and electronic industries and in high temperature structural applications such as ceramic turbocharger blades, swirl chambers in diesel engines, ceramic turbo-molecular pumps, multilayer ceramic capacitors and cutting tool inserts.

The major difficulty in metal/ceramic joining is the dissimilar nature of the atomic bonding of the two materials. The key to a successful joining technology lies in the ability to modify the interface to accommodate the vastly different atomic bonding from the metallic bonding of the metal to the ionic or covalent bond of the ceramic to reduce the electronic discontinuity at the faying surfaces. This is usually achieved by using a graded interface. A gradual change across the interface in metal

ceramic joints is also essential to reduce the thermal mismatch between the two materials. On cooling from the joining temperature, the metal (having high thermal expansion coefficients) will contract more than the ceramic inducing undesirable residual tensile stresses in the ceramic[1].

The technology of joining ceramics to metals has progressed steadily since its beginning in the early 1930s. Many techniques have been proposed to join ceramics to metals but the most common methods for structural applications can be divided into metal brazing, glazing and diffusion bonding.

Brazing is a method of joining by which a low melting point metal foil is placed between the metal and ceramic and foil melts and 'wets' the two surfaces and flows into the capillary gaps. Upon solidification, the braze material joins the two materials. However, some ceramics, particularly oxide ceramics such as aluminum oxide or zirconia, are difficult to wet due to the high stability of the surface. This problem can be overcome by modifying the surface of ceramic using reactive brazes. For instance, titanium is added to the braze material. The high affinity

of titanium results in reaction with the oxygen in the ceramic to form a titanium oxide on the surface which facilitates the wetting of ceramic.

A popular active braze alloy is based on Cu-Ag eutectic with addition of about few wt.% Ti. Copper-silver eutectic braze is extensively used for brazing of metals to metals because of its low melting point, high fluidity and ductility. However, the addition of reactive elements such as titanium increases the melting point, reduces the fluidity and embrittles the alloy with detrimental effect on joint integrity[1]. Further, the excessive amount of titanium can embrittle the interfacial area between the braze and metal. Also, the use of conventional Cu-Ag braze as the basis for reactive braze limits the application of joint assembly to temperatures that can be withstood by the braze ($\approx 500°C$) rather than utilizing the high temperature properties of the ceramic.

In an attempt to overcome the main shortcomings of the reactive metal brazing of ceramic to metal, the metal vapour vacuum arc (MEVVA) ion source was used to implant the reactive element (titanium) directly into ceramic, eg. alumina, prior to brazing to produce a suitable surface that will be wetted by the conventional (non-reactive) copper silver braze. It was envisaged that successful demonstration of this approach would pave the way for developing high temperature brazes without the above-mentioned limitations. The major thrust of this paper is to present the findings of this investigation.

2. Experimental Procedures

The substrate materials used for Ti implantation was a commercially available high purity alumina, 10x10x3 mm, which were polished to a 1μm diamond finish. Titanium ion implantation was carried out using a MEVVA ion source described elsewhere[2)-4)], with an extraction voltage of 40 kV. Implantation was carried out to obtain a range of doses from $2x10^{16}$ to $3.1x10^{17}$ ions/cm^2. The brazing of alumina to copper was conducted using the following methods;

1) brazing using Cu-Ag-Ti(Cusil®-ABA) reactive braze alloy,

2) brazing with non-reactive (conventional) Cu-Ag eutectic alloy, and

3) brazing of titanium implanted alumina with non-reactive Cu-Ag eutectic alloy.

The brazing of titanium implanted and unimplanted alumina to copper was performed by heating the join assembly in a microwave induced plasma[5)] to temperatures above the melting point of Cu-Ag eutectic ($\approx 830°C$). A more detailed description of experimental procedures can be found elsewhere[6)].

Characterization of the implanted surfaces involved Rutherford Backscattering (RBS) using a 2.0 MeV $^4He^+$ beam with a backscattering angle of 169°. Four point probe conductivity tests were performed to monitor the changes in the nature of atomic bonding on the surface of alumina after implantation. The joint integrity and the degree of wetting of the ceramic surface after different brazing procedures was assessed with optical microscopy of the cross-section of the joints.

A detailed description of cross-sectional transmission electron microscope (XTEM) sample preparation has been published elsewhere[7),8)]. First, the implanted surfaces were thinned from the untreated side to a thickness of 1 mm, with the modified surface carefully protected. Then the thinned discs were sliced to give 2 mm wide slabs. These slabs were subsequently sandwiched using G-1 epoxy from Gatan, with the treated surfaces facing each other. The specimen sandwich was then cast into a brass tube of 3 mm outer diameter, using silver epoxy. Discs of 400-500 μm thickness were sectioned from the tube assembly using a slitting wheel. The direction of cutting was perpendicular to the epoxy-bonded joint to minimise loss of the epoxy. A multi-function EDWARDS IBT Auto Model 306 Coater equipped with an ion gun were used for ion-beam thinning of the samples. XTEM and NBED investigations were conducted on a JEOL-2000FX transmission electron microscope at an accelerating voltage of 200 kV. The beam size for NBED was less than 5 nm.

3. Results

The surface appearance of alumina changed drastically as the implantation dose was increased. Generally, as the dose increased, the surface appeared more lustrous and reflective, indicating a change in the electronic structure and bonding of the surface or near surface region.

The concentration profiles of implanted titanium, derived from RBS spectra, are shown in **Fig. 1**. The depth profiles of the Ti appear to be slightly skewed Gaussian distribution. Although the same implantation energy (40 keV) was used for all the samples, the peak concentration of Ti does not occur at the same depth. This is attributed to sputtering which shifts the peak position closer to the surface as the implantation dose increases. However, at the highest dose, almost 50 at.% titanium was retained in a depth of 60 to 70 nm.

Four point probe conductivity tests revealed that the resistance of alumina dropped dramatically as the implantation dose was increased and reached a plateau as dose increased further (**Fig. 2**). It should be pointed out the resistivity of unimplanted alumina, not presented in
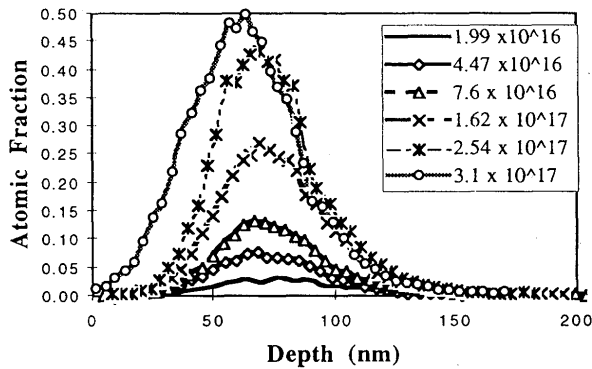
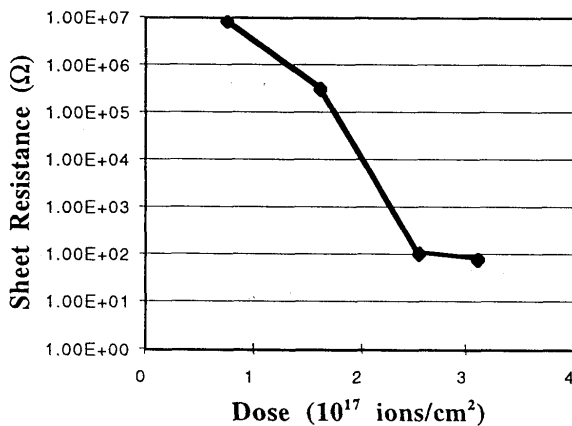Fig.1 Concentration profiles of titanium implanted into alumina for different doses.

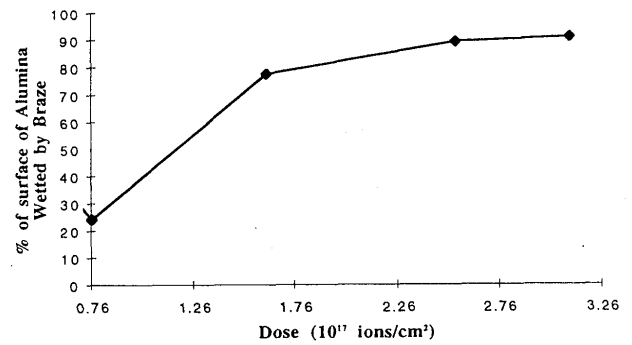Fig.2 Resistance of alumina as a function of implantation dose.

Fig.3 Percentage of the surface of alumina sample covered with non-reactive copper-siliver braze as a function of implantation dose.

defects are mainly vacancies, interstitials and impurities (foreign ions). Corresponding NBED patterns are given as inserts in Fig.4. The pattern from Ti implantation layer is consistent with the hexagonal structure of α-Al_2O_3 in the [$\bar{1}2\bar{1}1$] orientation, identical with the unimplanted Al_2O_3 substarte. This result indicates that the implantation layer depicted in this micrograph is fully monocrystalline with the same orientation as the underlying α-Al_2O_3 grain.

In contrast, **Fig.5** presents a typical XTEM micrograph of high dose (3.1×10^{17} ions/cm^2) Ti implanted alumina. The implanted layer consists of two sublayers, I and II, in outer and inner regions, respectively. Sublayer I is approximately 90 nm thick, whereas sublayer II is about 70 nm thick and contains a high concentration of defects. The NBED pattern from sublayer I consists of
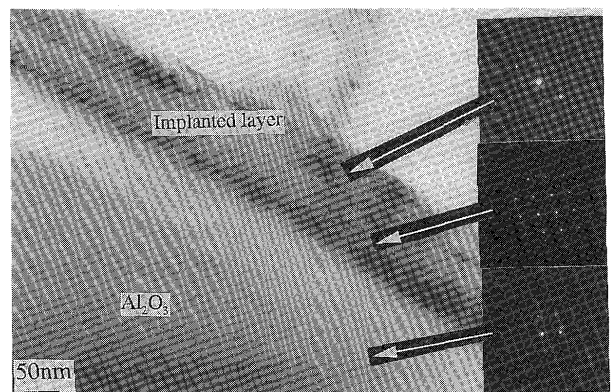
Fig.3, is many orders of magnitude greater than the values obtained on implanted alumina. Further, great care was taken to ensure the reliability of four point probe measurements.

The cross-sectional microscopy examination indicated that the degree of wetting of ceramic by non-reactive braze increased as the implantation dose was increased. At the highest dose almost a complete surface coverage of ceramic by braze alloy took place. Figure 3 is a plot of the percentage of the surface coverage of alumina with the non-reactive braze as a function of dose.

XTEM revealed an obvious implantation layer about 100 nm thick in alumina implanted with low dose of Ti ions. A typical example is shown in **Fig.4**, for the case of alumina implanted with 7.6×10^{16} titanium ions/cm^2. The implantation layer exhibits a high concentration of defects produced by bombardment with Ti ions. The

Fig.4 TEM micrograph taken from alumina implanted with 7.6×10^{16} titanium ions/cm^2 at 40kV, showing implantation layer with inserted diffraction patterns from implantation layer and Al_2O_3 matrix.
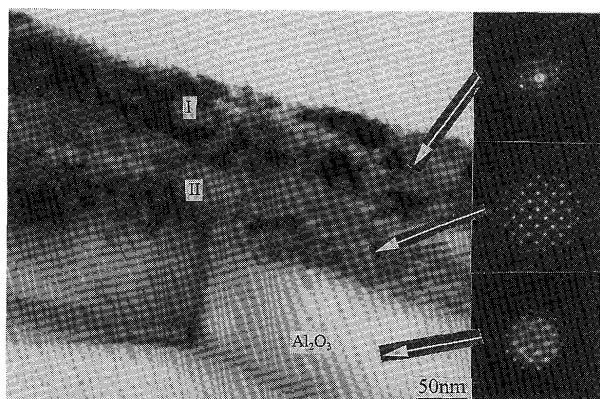
Fig.5 TEM micrograph taken from alumina implanted with 3.1×10^{17} titanium ions/cm^2 at 40kV, showing implantation layer consisiting of sublayer I and II with interted diffraction patterns.

diffraction spots which are extended into nearly complete diffraction rings, indicating that this sublayer is no longer monocrystalline and contains numerous fine precipitates which are identified as TiO$_2$. Sublayer II revealed similar features to the implantation layer produced at the lower dosage. The zone axis of the diffraction pattern from this region is [$\bar{4}401$] and is the same as that from the α-Al$_2$O$_3$ matrix, indicating that sublayer II remains monocrystalline even though a high concentration of defects is present in this region. With increasing fluence and Ti ion concentration, precipitation of fine TiO$_2$ particles is promoted by the compositional changes and high defect density brought about by implantation.

XTEM micrographs and corresponding NBED patterns for Ti ion implanted Al$_2$O$_3$ did not reveal any evidence of amorphisation, as reported by other investigators [9],[10]. We believe the lack of amorphisation in our samples is due to low implantation energy. There are numerous examples (see for instance ref.11) that amorphisation in ceramics is a strong function of the type of bonding (e.g. ionic or covalent) and the implantation energy. For a highly ionic ceramic such as alumina high implantation energy (high fluence at high energy) is required for amorphisation. At fluences below 1×10^{17} ions/cm^2 no amorphisation occurs and at higher implant doses it is inappropriate to regard the material as alumina since the high concentration of dopant results in the formation of new compounds, for example TiO$_2$ in the case of titanium implantation.

4. Discussion

The results presented above unequivocally establish that titanium implantation into alumina results in major

atomic and structural changes in the ceramic which facilitate the wetting of ceramic by non-reactive braze. The enhanced wettability could be due to three effects. Firstly, the wettability would increase owing to the modified alumina surface becoming more metallic, as confirmed by increasing conductivity and more lustrous appearance. This lessens the electronic discontinuity between the metal and ceramic allowing a greater chance for an interface to form.

Secondly, it is not inconceivable that implantation induced defects would increase the surface energy of ceramic. XTEM micrographs for Ti ion implanted Al$_2$O$_3$ (Figs.4 and 5) clearly show significant increase in defect density. This occurs because the atoms have been elevated to a higher energy state due to the deviation from the lower energy lattice sites. Increasing the defects in the near surface region would result in increasing the surface energy which, in turn, may lead to enhanced wetting. Indeed, Inoue[12] has reported that defects such as vacancies, interstitials or impurities atoms caused by argon ion implantation increased the wetting of silica with water.

The third, and arguably the most important, reason for improved wetting is due to the formation of phases with improved conductivity or enhanced wetting characteristics. Daniel et al.[13] have reported the effect of titanium ion implantation on increasing the conductivity of silica. This was attributed to the chemical interaction of Ti with the SiO$_2$ to form conductive compounds rather than just due to the presence of metallic precipitates of Ti. The chemical interaction was found to be essential and implantation with Fe and Cu ions (chosen due to the similar atomic size and therefore similar implantation ballistics), even with doses up to 2×10^{17} ions/cm^2, failed to have any effect on conductivity.

In this work, NBED pattern of titanium implanted alumina unambiguously demonstrated the formation of rutile. According to thermodynamic data the heat of formation of alumina is lower than that of titania, i.e. alumina is more stable than titania. However, it is not clear how the thermodynamic stability of alumina and titania would be affected under implantation condition. It is now widely recognized that metastable formation can be facilitated in the collision cascade which is set up by high energy implantation. Therefore, it is surmised that in this work high energy implanted titanium exhibited greater affinity for oxygen and preferentially reacted with it to form titanium oxide.

Regardless of exact cause of the formation of titania, it is known that titanium oxides enhances the wettability of conventional brazes[1]. It is also possible that other

compounds of titanium with general formula of TiO$_x$ might have formed.

Irrespective of the exact contribution of above mentioned factors on enhanced wetting of alumina, it is quite clear that significant wettability improvement can be realized. This enhanced wettability obviates the need for incorporation of reactive metal into a braze alloy and paves the way for developing advanced brazes tailored specially for enhanced performance (e.g. high temperature application) without detrimental impact on wettability or embrittlement of the joint.

5. Conclusions

In this investigation Ti ion implantation was used as a precursor to brazing of alumina to copper. It has been found that implantation resulted in a characteristic metallic lustre and significant reduction in the resistivity of alumina. Further, titanium implantation resulted in the formation of titanium oxide in the near surface region of alumina. The enhanced wettability of alumina enabled its joining to copper with non-reactive braze. The degree of wetting was similar to those ordinarily achieved by active brazes.

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