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<td>Author(s)</td>
<td>野口, 晴利</td>
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<tr>
<td>Citation</td>
<td>Transactions of JWRI. 26(2) P.1-P.5</td>
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<td>Issue Date</td>
<td>1997-12</td>
</tr>
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<td>Text Version</td>
<td>publisher</td>
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<td>URL</td>
<td><a href="http://hdl.handle.net/11094/9598">http://hdl.handle.net/11094/9598</a></td>
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A Novel Approach To Ceramic/Metal Joining

Masoud SAMANDI*, Mathew GUDZE*, Huaxia JI*, Peter EVANS**, Yukio MAKINO*** and Shoji MIYAKE****

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 TiO₂ thus enhancing the degree of wetting by non-reactive braze compared to the unimplanted alumina.

KEY WORDS: (Joining) (Ceramic/metal) (XTEM) (Implantation) (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.

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

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Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan.
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. Further, the excessive amount of titanium can embrittle the interfacial area between the brazed 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 (≤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, e.g. 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, 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 joint assembly in a microwave induced plasma to temperatures above the melting point of Cu-Ag eutectic (≥830°C). A more detailed description of experimental procedures can be found elsewhere.

Characterization of the implanted surfaces involved Rutherford Backscattering (RBS) using a 2.0 MeV ³He 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. 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 resistivity of implanted 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 $\alpha$-Al$_2$O$_3$ in the [121] orientation, identical with the unimplanted Al$_2$O$_3$ substrate. This result indicates that the implantation layer depicted in this micrograph is fully monocrystalline with the same orientation as the underlying $\alpha$-Al$_2$O$_3$ grain.

In contrast, Fig. 5 presents a typical XTEM micrograph of high dose (3.1x$10^{17}$ 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 [description of TEM micrograph and NBED patterns]

Fig. 4 TEM micrograph taken from alumina implanted with 7.6x$10^{16}$ titanium ions/cm$^2$ at 40kV, showing implantation layer with inserted diffraction patterns from implantation layer and Al$_2$O$_3$ matrix.
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 TiO₂. 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 [440] and is the same as that from the α-
Al₂O₃ 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 TiO₂
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 Al₂O₃ 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 1x10¹⁷ ions/cm² 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 TiO₂ 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 Al₂O₃
(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, Inoue¹²) 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 SiO₂ 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 2x10¹⁷ ions/cm², 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 brazes¹⁴). 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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