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Transient liquid phase bonding of alumina to alumina via boron oxide interlayer

L.-S. Chang*, C.-F. Huang

Department of Materials Engineering, National Chung Hsing University, Taichung, Taiwan, ROC

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Abstract

Alumina bulks coated with 3 μm boron oxide layer were bonded at various temperatures and times in air. The joining strength, interfacial compounds and morphologies of cross-sections and fracture surfaces were investigated by means of four-point bending, X-ray diffraction and scanning electron microscopy. The maximum bending strength is 71 MPa for alumina bonded at 800 °C for 15 h. The layered metastable phase of $3Al_2O_3$–B_3O_3 forms at the beginning of joining at temperature above 700 °C. This interlayer transforms into a whisker structure consisting of $2Al_2O_3$–B_3O_3 and $9Al_2O_3$–$2B_3O_3$ with increasing temperature and time. Models for the growth and morphology of these interfacial compounds are proposed.

Keywords: A. Joining; D. Al_2O_3; B_2O_3; Transient liquid phase bonding

1. Introduction

Fine ceramics are widely used in modern industries due to their special properties, including extreme melting/decomposition temperature, excellent corrosion resistance and high strength and hardness. However, based on these properties, it is difficult to produce a ceramic object with complicated shape or large size. An easier way to achieve this is the application of joining techniques. A complicated or large object can be assembled from joining small parts together. It inspires therefore the improvement of ceramic joining methods not only for strengthening the joint, but also for ensuring that the properties of bonded object are weakly influenced by the joining interface.

The methods for joining ceramics can be classified into two types: one with and another without interlayer. Methods without interlayer include solid-state diffusion bonding, friction joining, laser welding and ultrasonic joining [1]. Their basic principle is the interdiffusion of atoms at the interface. All these methods need to be carried out at high temperature. In contrary to this, moderate temperature is used when joining materials via an interlayer. Adhesion, soldering, brazing and glass sealing are some example well known. High cost always occurs when using methods without interlayer, while some disadvantages, e.g. low joining strength and low operating temperature, are usually accompanying in parts bonded by methods with interlayer.

Recently, transient liquid phase diffusion bonding has been proposed. This method is also called "isothermal solidification process" or "diffusion soldering" in variation, because that in this method a controlled reaction between interlayer and matrix takes place at constant temperature and a high melting compound forms at the interface. The formation of high melting compound makes it possible that the operational temperature can be higher than the joining temperature. This method has been successfully applied for joining some metallic [2–6] and ceramic systems [7–9]. However, materials of interlayer used are metallic. This metallic interlayer restricts the usage environment of a bonded component and reduces its practicability. Using metals with high temperature and oxidation resistance, e.g. Pt, Nb or Au, is a way to improve the joining property, providing that their high costs are acceptable.

In this work another attempt was tried. Instead of metallic interlayer, boron oxide interlayer was used to joining

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* Corresponding author. Tel.: +886-4-22840500; fax: +886-4-22852433.
E-mail address: lschang@dragon.nchu.edu.tw (L.-S. Chang).

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alumina bulks. Glassy boron oxide has a very low melting point of 540 °C. The eutectic point in the B_2O_3–Al_2O_3 system is 470 °C. Two equilibrium incongruent compounds $2Al_2O_3$–B_2O_3 and $9Al_2O_3$–$2B_2O_3$ with melting point of 1035 and 1950 °C are seen in the phase diagram [10]. It is therefore to be expected that these high melting compounds may form at the interface in the Al_2O_3–B_2O_3–Al_2O_3 assembly during heating. The purpose of this work is to find the best joining condition (temperature and time) and to explain it with the composition and morphology of the interface.

2. Experimental

Alumina slurry was prepared by dispersing alumina powder (99.7% α-Al_2O_3, ALCOA A16-SG) in same weighted de-ionized water with 2 wt.% Darvan 7 as dispersant. The slurry was ball milled for 24 h. Pressure slip casting was used to form alumina green cake from slurry. The green cake was dried at 60 °C for 24 h and de-binder at 200 °C for 6 h. Alumina cakes were sintered at 1550 °C for 6 h in a 1700 °C furnace (Thermolyne 46100). The density and the four-point bending strength of the sintered alumina bulk are 3.91 g/cm^3 and 332 MPa, respectively.

The alumina parts being bonded were ground and polished to 1 μm diamond paste. The polished alumina surface ultrasonically cleaned in acetone was coated with boron oxide layer. The used coating process was atmospheric thermal evaporation. Boron oxide powder (99.6%, STREM CHEMICAS) was put into a stainless container and then heated to 300 °C in air. A boron oxide film was formed on the surface of the alumina bulk cooled by water. The growth rate of the oxide layer was approximately 0.1 μm/min. The alumina bulks coated with 3 μm boron oxide layer were bonded in air by facing their coated sides. The experimental conditions, including joining temperatures and times, are listed in Table 1.

Bonded alumina bulks were cut vertically to the joint by diamond saw and the microstructure of the joint was observed by means of SEM (JOEL JSM-5400). 4 mm × 4 mm × 25 mm specimens containing joint in the midpoint were also cut from bonded alumina bulks for the four-point bending test. The fracture surface of the bended specimens was analyzed by small angle (incident angle = 1°) X-ray diffraction to determine the phases in the joint.

Table 1
Experimental conditions: the joining temperatures and times

Fixed parameters		Variant parameters	
Joining time (h)	6	Temperature (°C)	500, 600, 700, 800, 900, 1000
Joining temperature (°C)	700	Time (h)	6, 15, 24, 48
	800		6, 10, 15, 24
	900		2, 6, 10, 15, 24

3. Results

3.1. Microstructure of joint cross-section

Fig. 1a and b shows the SEM pictures of the cross-sections of the joints bonded at 800 and 1000 °C for 6 h. At temperature below 700 °C the boron oxide interlayer remains non-reacted and its thickness is about 6 μm. A denser columnar structure forms in the interlayer and the thickness of this interlayer reduces to less than 5 μm (Fig. 1a) as joining temperature reaches 800 °C. The thickness decreases continuously and the boundary between interlayer and substrate become vaguer with more increasing temperature. At 1000 °C the thickness is approximately 2 and 1 μm, respectively, as shown in Fig. 1b. However, voids appear at joining temperatures above 900 °C and more voids are to be observed at 1000 °C than at 900 °C.

The SEM pictures of the cross-sections of the joints bonded at 900 °C for 2 and 24 h are shown in Fig. 2a and b, respectively. After joining for 2 h the interface be-

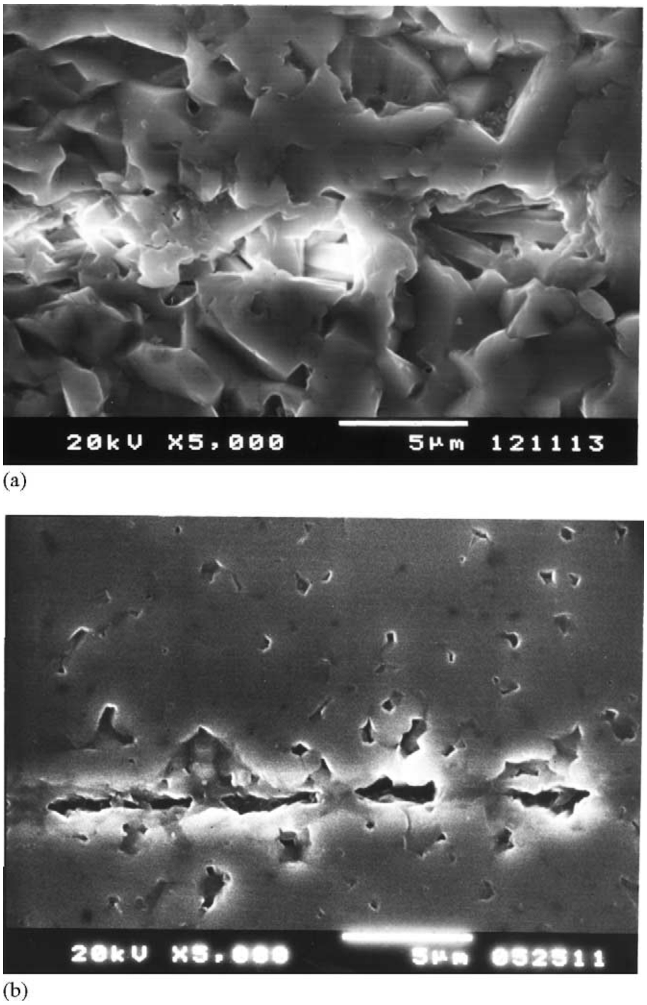


Fig. 1. SEM pictures of the cross-sections of the joints bonded for 6 h at (a) 800 °C and (b) 1000 °C.

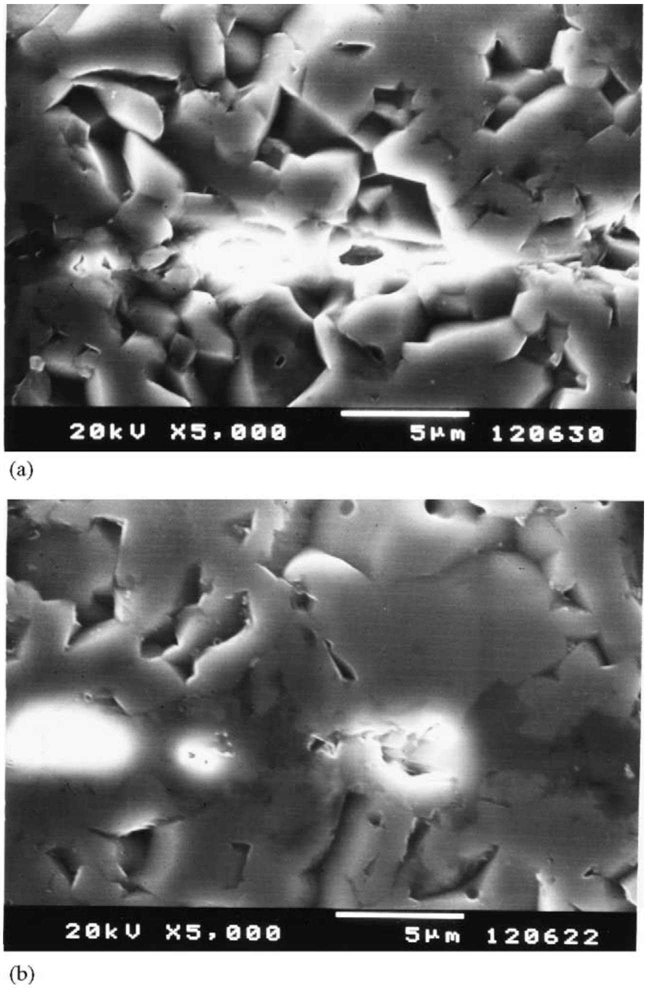


Fig. 2. SEM pictures of the cross-sections of the joints bonded at 900 °C for (a) 2 h and (b) 24 h.

tween alumina are partly filled with some phase and partly remaining unfilled (Fig. 2a). When the joint is heat-treated for longer times, the unfilled region shrinks. In Fig. 2b the portion of void in interface is similar with that in Fig. 2a, although different shapes of void are to be seen.

3.2. Four-point bending test

The relationship between the four-point bending strength of alumina bonded for 6 h and the joining temperature from 700 to 1000 °C is plotted in Fig. 3. The strengths of alumina bonded at 500 and 600 °C are so weak that the two bonded components break apart during cutting. The bending strength starting with 37 MPa at 700 °C goes up to 62 MPa at 800 °C and then down to 47 MPa at 900 °C and 22 MPa at 1000 °C.

Fig. 4 shows the time dependence of the bending strength of alumina bonded at 700, 800 and 900 °C. At 700 °C, as shown in Fig. 4a, the maximum strength found is 64 MPa after joining for 15 h. The strength does not decrease radically for longer joining time. Its value is 56 MPa for 48 h. Analog to the time dependence at 700 °C the strongest bonded alumina at 800 °C is bonded for 15 h. It possesses a strength value of 71 MPa. The strength is 68 MPa as bonded for 24 h. A shorter time is needed for reaching the maximum bending strength observed in the case of joining at 900 °C. Joining must be carried out for more than 10 h to get the best value of 55 MPa.

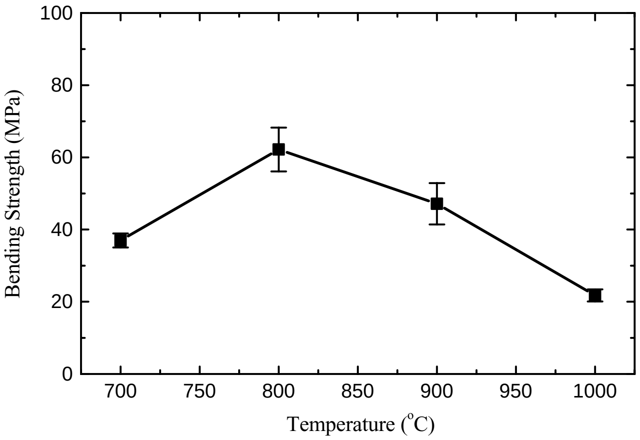


Fig. 3. The relationship between the four-point bending strength of alumina bonded for 6 h and the joining temperature from 700 to 1000 °C.

3.3. Morphology of fracture surface

The SEM pictures of the fracture surfaces of the alumina bonded at 700 and 800 °C for 6 h are shown in Fig. 5a

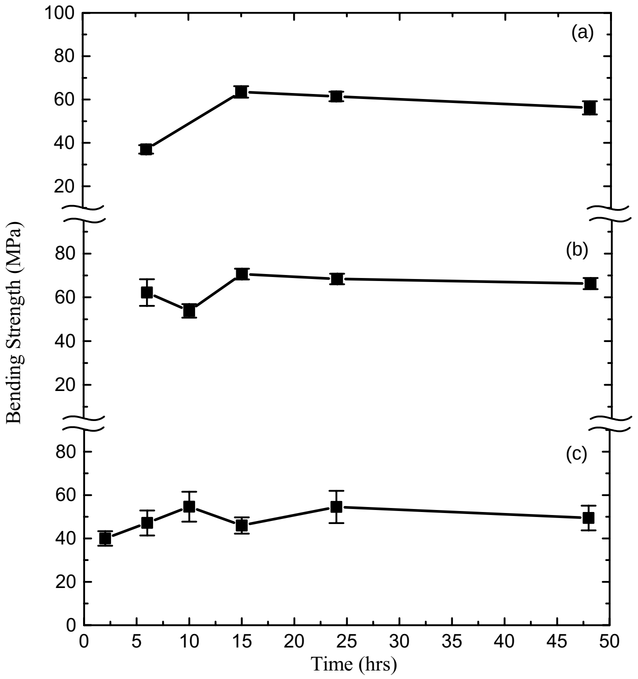


Fig. 4. Time dependence of the bending strength of alumina bonded at (a) 700 °C, (b) 800 °C and (c) 900 °C.

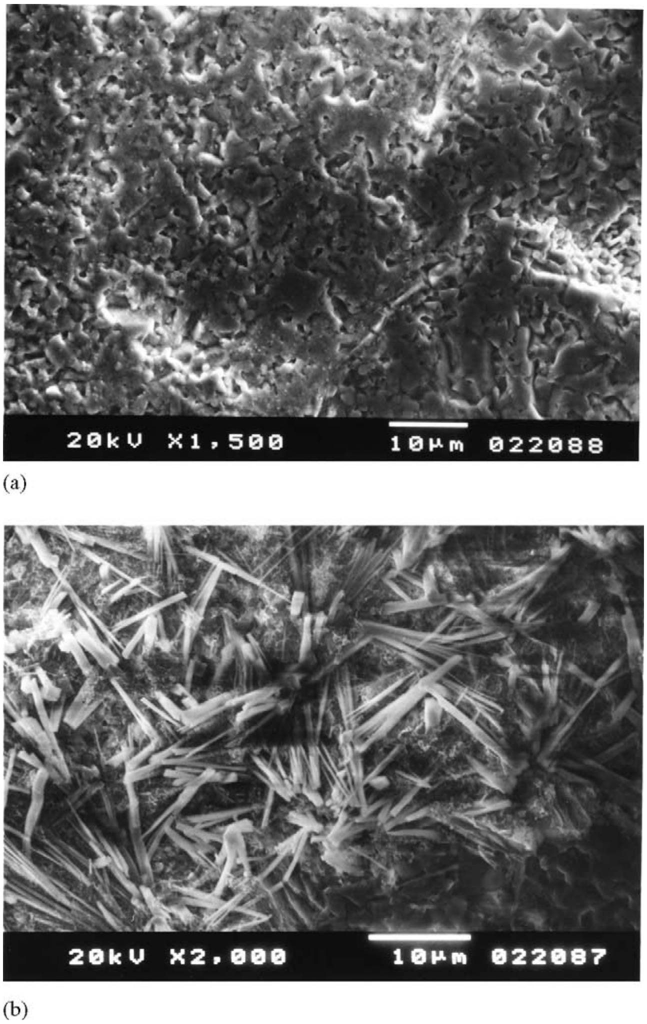


Fig. 5. SEM pictures of the fracture surfaces of the joints bonded for 6 h at (a) 700 °C and (b) 800 °C.

and b. The fracture surface of joint in Fig. 5a is similar to that of alumina bulk; however, it seems to be partly covered by a thin layer. When temperature rises to 800 °C, whisker compounds grow from bulk into interlayer (Fig. 5b). At 900 °C, the fracture surface is mostly dressed with a kind of whisker network. Fissures appear on the fracture surfaces of specimens bonded at 1000 °C and the shape of the whisker network fades.

Various effects of joining time on the morphology of fracture surface are found at 700, 800 and 900 °C. At 700 °C (Fig. 5a for 6 h and Fig. 6a for 24 h) the morphology does not change much with time. No whisker compound was found. Figs. 5b and 6b show the fracture surface of alumina bonded at 800 °C for 6 and 24 h. The whisker compound grows and covers the most area of fracture surface for 24 h. The whole covering time at 900 °C is about 10 h (Fig. 7a). Thereafter, the clear boundary of whisker becomes cloudy and a finer structure appears for 24 h (Fig. 7b).

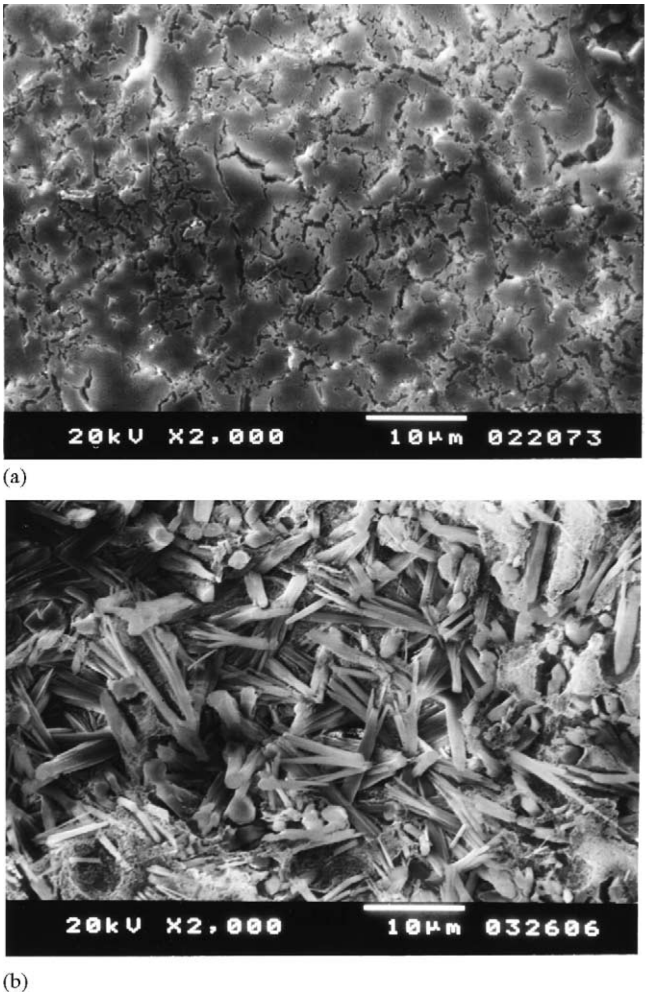
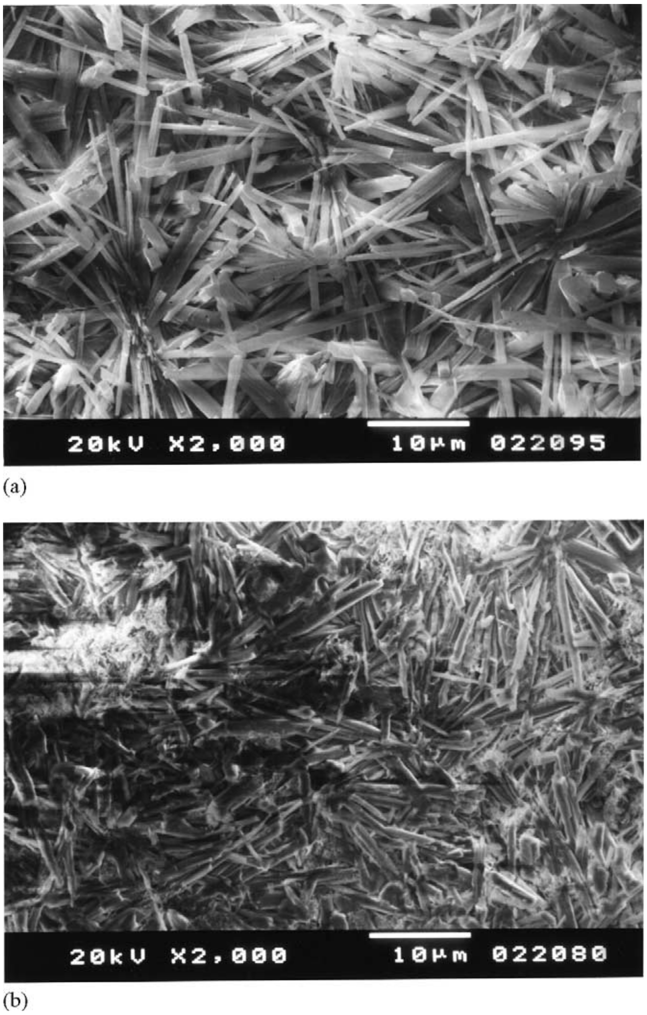


Fig. 6. SEM pictures of the fracture surfaces of the joints bonded for 24 h at (a) 700 °C and (b) 800 °C.

3.4. X-ray diffraction pattern

The X-ray diffraction patterns of fracture surface for specimens bonded at various temperatures for 6 h are shown in Fig. 8. Phases and symbols for characteristic peaks are labeled and indicated in the pattern. The peak at 28° in the X-ray diffraction pattern of the specimen bonded at 700 °C indicates the formation of $3Al_2O_3$–B_2O_3 in comparison with that of pure alumina. The intensity of this peak increases with increasing temperature below 900 °C. At 1000 °C the peak is hardly to be seen. This means the disappearance of $3Al_2O_3$–B_2O_3. The appearance of $2Al_2O_3$–B_2O_3 and maybe also $9Al_2O_3$–$2B_2O_3$ is shown in the pattern of the specimen bonded at 800 °C. Due to the overlap of the characteristic peaks of $9Al_2O_3$–$2B_2O_3$ by those of $2Al_2O_3$–B_2O_3 at 26.5 and 33°, it is hard to tell which of these two phases forms at 800 °C. However, because that the peak at 48° at 800 °C is only contributed by $2Al_2O_3$–B_2O_3, the vanishing of this peak and the existence of the peaks at 26.5 and 33° at higher temperatures point out that the amount of $2Al_2O_3$–B_2O_3 decreases with increasing temperature.



(a)

(b)

Fig. 7. SEM pictures of the fracture surfaces of the joints bonded at 900 °C for (a) 10 h and (b) 24 h.

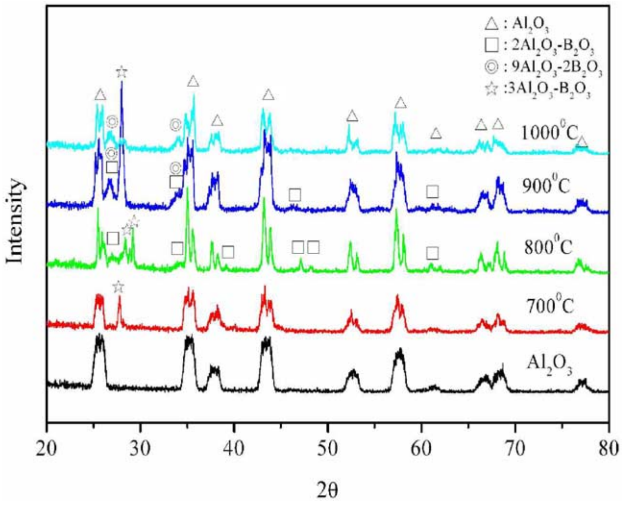


Fig. 8. X-ray diffraction patterns of fracture surfaces of the joints bonded at various temperatures for 6 hrs.

In contrary to the evident effect of joining temperature on the formation of phases, the effect of joining time is quite varying. Fig. 9a–c shows the X-ray diffraction patterns for various joining time at 700, 800 and 900 °C. Phases and symbols for characteristic peaks are labeled and indicated in these patterns. At 700 °C, as shown in Fig. 9a, the composition of interface does not change much with increasing joining time within 48 h, except that the peak at 28° from $3Al_2O_3$–B_2O_3 rises with time. At 800 °C, the $3Al_2O_3$–B_2O_3, $2Al_2O_3$–B_2O_3 and/or $9Al_2O_3$–$2B_2O_3$ co-exist in the joint for 6 h (Fig. 9b). The latest phase seem quite stable at this temperature up to 24 h because that all peaks stand in the XRD pattern. Finally, the moderation of the peak at 48° indicates the preference of $9Al_2O_3$–$2B_2O_3$ at 900 °C (Fig. 9c).

4. Discussion

4.1. *Growth of interfacial compounds*

The stages of the growth of interfacial compounds with joining temperature can be interpreted from the cross-section observation in Fig. 1 and the X-ray diffraction result in Fig. 8. The schema of these stages is shown in Fig. 10a–f. These stages can be described as following:

500 °C: No compound is found. The interlayer remains boron oxide (Fig. 10a).

700 °C: The thickness of interlayer reduces. Only the compound $3Al_2O_3$–B_2O_3 forms (Fig. 10c).

800 °C: Three compounds $3Al_2O_3$–B_2O_3, $2Al_2O_3$–B_2O_3 and $9Al_2O_3$–$2B_2O_3$ coexist and the structure of interface is dense (Fig. 10d).

900 °C: The coexistence of the compounds found at 800 °C was observed. However, the X-ray diffraction signal of the compound $3Al_2O_3$–B_2O_3 vanishes and pores form at the joint (Fig. 10d). The pore formation furthermore results in the reduction of joining strength. The diffusion of boron oxide out of the interface region is probably the reason for the formation of more pores. The volume increase involved in the decomposition of the compound $3Al_2O_3$–B_2O_3 into the mixture of $2Al_2O_3$–B_2O_3 and $9Al_2O_3$–$2B_2O_3$ should have little influence on the formation of pores at the joint, though most pores appear as the compound $3Al_2O_3$–B_2O_3 disappears (Fig. 10e).

1000 °C: More and larger pores arise and the strength decreases. The XRD pattern indicates that only the compound $9Al_2O_3$–B_2O_3 exists at the joint (Fig. 10f).

4.2. *Growth morphology of compounds*

The growth morphology of compounds at the joint is discussed under the joining conditions of temperature 900 °C

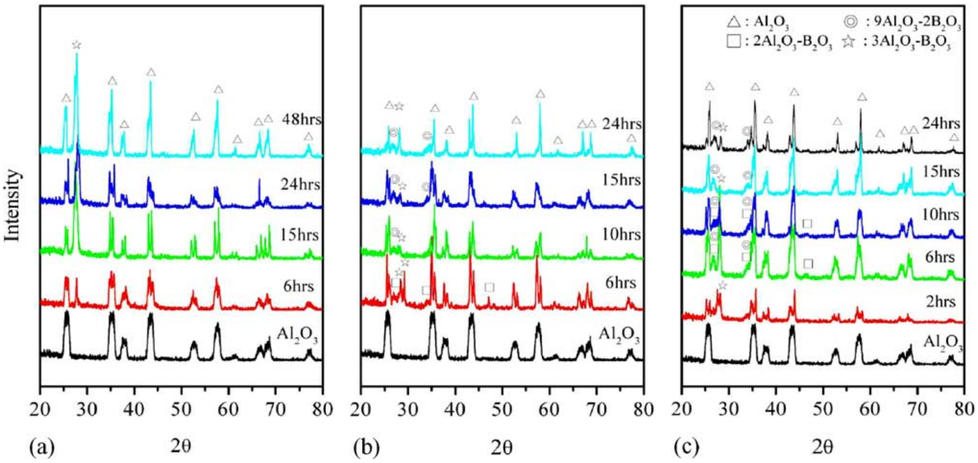


Fig. 9. X-ray diffraction patterns of fracture surfaces of the joints bonded for various joining time at (a) 700 °C, (b) 800 °C and (c) 900 °C.

and various times. The schema of growth morphology of compounds formed at interfaces bonded for 2, 6, 15 and 24 h are drawn as Fig. 11a–d.

The crystal structure of alumina is rhombohedral, while all the compounds $3Al_2O_3–B_2O_3$, $2Al_2O_3–2B_2O_3$ and $9Al_2O_3–2B_2O_3$ are orthorhombic. The structure, density and lattice constants of these compounds are listed in Table 2. The lattice constant of $3Al_2O_3–B_2O_3$ at *c*-axis (4.29 Å) is the one mostly close to that of alumina at *a*-axis (4.76 Å) comparing with those of $2Al_2O_3–B_2O_3$ (5.6 Å) and $9Al_2O_3–2B_2O_3$ (5.66 Å). The compatibility in lattice constants alleviates the interfacial strain and reduces the interfacial energy. This means that less strain energy is raised by the formation of $3Al_2O_3–B_2O_3$ at interface than by that of $2Al_2O_3–B_2O_3$ and $9Al_2O_3–2B_2O_3$ and, therefore, the nucleation of $3Al_2O_3–B_2O_3$ is easier. This explains the lamellar formation of the compound $3Al_2O_3–B_2O_3$ at the beginning of joining (Fig. 11a).

When $3Al_2O_3–B_2O_3$ gets thicker at the interface, higher Gibbs free energy causes the decomposition of the metastable compound and the formation of stable phases, i.e. $2Al_2O_3–B_2O_3$ and $9Al_2O_3–2B_2O_3$. The lattice constants of *a*- and *b*-axis of $2Al_2O_3–B_2O_3$ are larger than twice of that of *c*-axis. This indicates a faster growth rate along the direction of *a*- and *b*-axis and explains the whisker shape of the compound (Fig. 11b). The formation

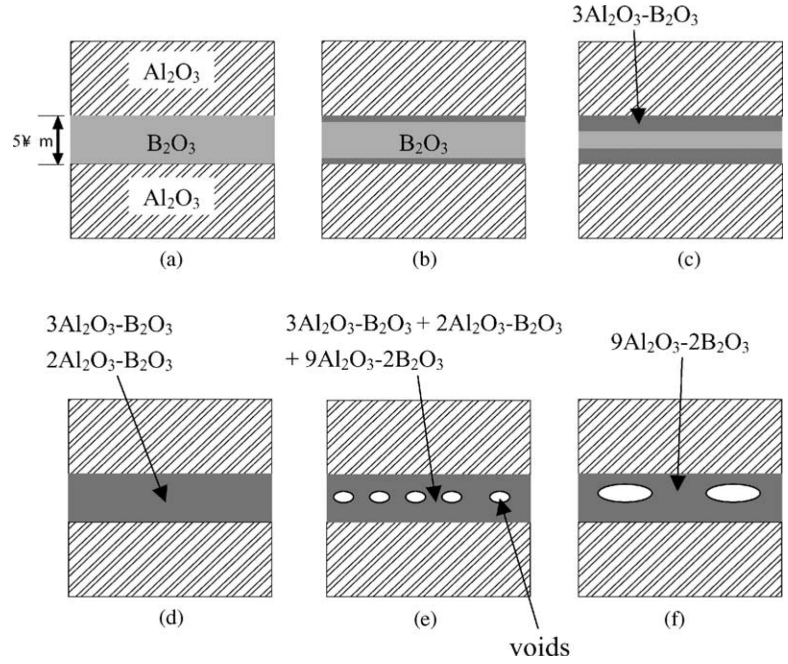


Fig. 10. The schema of the stages of the growth of interfacial compounds with joining temperature: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C and (f) 1000 °C.

Table 2
Crystal structure, density and lattice constants of some compounds composed of Al_2O_3 and B_2O_3

Composition	Crystal Structure	Density (g/cm^3)	Lattice constant (Å)		
			a-axis	*b*-axis	*c*-axis
Al_2O_3	Rhombohedral	3.987	4.76		12.99
B_2O_3	Hexagonal	2.546	4.33		8.39
$2Al_2O_3$–B_2O_3	Orthorhombic	2.904	14.8	15.1	5.6
$3Al_2O_3$–B_2O_3	Orthorhombic		9.51	8.11	4.29
$9Al_2O_3$–$2B_2O_3$	Orthorhombic	2.685	7.69	15.01	5.66

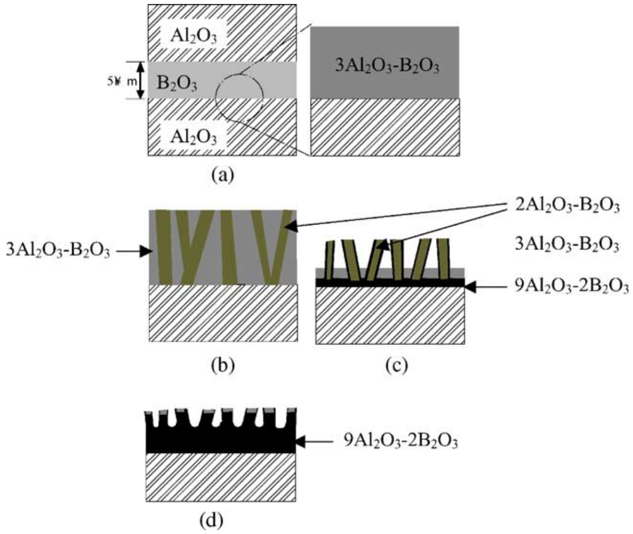


Fig. 11. The schema of growth morphology of compounds formed at interfaces bonded at 900 °C: (a) 2 h, (b) 6 h, (c) 15 h and (d) 24 h.

of compound $9Al_2O_3$–$2B_2O_3$ around $2Al_2O_3$–B_2O_3 with increasing time may be due to the similarity in structure and lattice constants between these two compounds. The boundary between $3Al_2O_3$–B_2O_3 and $2Al_2O_3$–B_2O_3 becomes indefinite (Fig. 11c). More $9Al_2O_3$–$2B_2O_3$ is found and the whisker structure is faded while joining for 24 h (Fig. 11d).

5. Conclusion

The transient liquid phase joining of alumina via boron oxide interlayer evaporatively deposited in air has been studied. We conclude:

1. The maximum joining strength found in this study is 71 MPa at the joining condition of 800 °C and 15 h. The increase of joining temperature to 1000 °C lowers the strength down to 21 MPa. The decrease of strength is caused by the formation of pores.
2. The sequence of compound formation with temperature is firstly the metastable compound $3Al_2O_3$–B_2O_3 followed by that of $2Al_2O_3$–B_2O_3 and $9Al_2O_3$–$2B_2O_3$, and finally the compound $9Al_2O_3$–$2B_2O_3$. The formation of ceramic compound is found at joining temperatures above 700 °C.
3. The growth morphology of $3Al_2O_3$–B_2O_3 is lamellar, while that of $2Al_2O_3$–B_2O_3 and $9Al_2O_3$–$2B_2O_3$ is whisker.
4. The interlayer thickness decreases with increasing temperature.

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