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The high-temperatures bonding of graphite/ceramics by organ resin matrix adhesive

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Abstract

The joining of ceramic materials is one of the key factors that influence its successful application in wider fields. And the joining between different kinds of materials has more values and significances in the realistic society. In this paper, graphite/alumina ceramic joints were achieved by means of bonding method. A high-temperature adhesive was prepared by using phenol–formaldehyde resin as matrix and boron carbide (B_4C) as additive. The graphite/alumina joints were bonded by the above adhesive and treated at different temperatures. The adhesive strength was tested at room temperature. Results showed that the high-temperature adhesive possessed satisfactory adhesive property for the joining of graphite/ceramics (Al_2O_3). The adhesive strength of the joints treated at 600 °C and 800 °C was not satisfactory due to the decline of the cement framework, which was derived from the carbonization of the resin. But good adhesive strength and thermal shock resistance were achieved when the treat temperature was above 1000 °C. As to the test of thermal shock resistance, the adhesive strength of the joints decreased at the beginning and then was stabilized and rose again after experiencing several shock cycles. By means of scanning electron microscope (SEM), the micrograph of bonding interface was investigated and showed that the failure mode of joint was due to the mixing failure. Ceramic substrates could be found on the bonding interface due to the high bonding force.

Keywords: High-temperature adhesives; Ceramics; Bonding; Thermal shock

1. Introduction

With the development of science and technology, many burgeoning fields including aerospace, fusion, metallic and so on are developing rapidly. As a correspondence, the application environments of materials/instruments become much more complex and critical. Many materials have to be applied in high-temperatures, high-pressures, high-speeds or highly- erosive situations. So the demand for improving the joining performances becomes more and more urgent since the quality of joining has a crucial influence on the application of materials or instruments in safety in the above situations.

Ceramic materials are widely applied in high-temperature fields due to its excellent heat-resistance property. But many difficulties are shown in the design, production, machining and assembly of the ceramics materials due to its brittleness. As to some main traditional methods, such as riveting, bolting and threading, it is not suitable to be applied in the joining of ceramic materials for that the stress concentration is an inevitable problem. At present, the main techniques are diffusion bonding, metal brazing, diffusion and friction welding. Besides accurate and complex treatment process, the joints achieved by the above techniques still have certain limitations such as porosity, mismatch of thermal expansion coefficients, and low strength at joining sites. As a result, many works are still focused on the research and development of the high-temperature joining for ceramics. Some new joining techniques, including transient liquid phase (TLP), reaction forming (RF) and so on, were developed recently [1–6]. But as to the above joining methods, accurate heat-treatment process and complex instruments are needed.

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Comparing with the above methods, the most convenient and promising method for high-temperature usage is the high-temperature adhesive [7,8]. The carbon material is also one of the most important materials applied in the high-temperature fields [9]. In our previous works, we have prepared high-temperature adhesives composed of organic resin modified by ceramic fillers with satisfactory bonding properties for carbon materials [10]. The joining between different kinds of materials has more difficulties but values in realistic society. In this paper, the joining of the graphite/ceramic by the high-temperature adhesives is researched, and the selected ceramic material to be joined is alumina for its wide use in our life.

2. Experimental procedures

2.1. Raw materials

The phenol–formaldehyde resin selected as the adhesive's matrix was provided by Tianjin Resin Factory with thermosetting property. Some properties of PF resin are tabulated in Table 1.

As starting materials, B_4C powder with the size of 2.5–3.5 μm and purity of 85% was provided by Mudanjiang Jingangzuan Boron Carbide & Accurate Ceramic Company Ltd.

Some properties of the graphite to be bonded were listed in Table 2. The alumina ceramic to be bonded was the common electrode connectors got from the market with size of 22 × 15 × 12 mm.

2.2. Preparation of high-temperature adhesive, graphite and alumina specimens

The high-temperature adhesive was prepared by using phenol–formaldehyde resin as matrix and using boron carbide as filler [10]. For convenience, the phenol–formaldehyde resin would be abbreviated as PF resin, and the high-temperature adhesive would be referred to as $PF + B_4C$ consequently.

Table 1
Some properties of phenol–formaldehyde resin

Trade	Viscosity (Pa · s)	Solid content (%)	Free phenol (%)	Carbon residue at 900 °C (%)
213#	1.53	80±3	⩽21	46.5

Table 2
Properties of the graphite materials for bonding

Character	Density ($g \cdot cm^{-3}$)	Flexural strength (MPa)	Compressive strength (MPa)
Isotropy	1.8	25	46

The glaze layers covering the surfaces of alumina substrates were removed by using corundum abrasive paper. The graphite materials were cut into cuboids with a size of 10 × 10 × 15 mm.

The surface to be bonded was ultrasonically cleaned in water and then dried. The adhesives were brushed to the graphite and alumina's surfaces. The specimens were bonded together at room temperature. The bonding area was 10 × 15 mm.The bonding model was the same with the Ref. [10]. All the bonded specimens were thermally cured at 200 °C. Then, the cured specimens were placed in the furnace at room temperature, and heat treated at different temperatures ranging from 400 to 1200 °C controlled by PTC-2 type Intelligent Temperature-Control Instrument. Each bonded sample was heat- treated at a given temperature for 2 h. In order to avoid the oxidation of the graphite substrates, all joints are buried in char powders during the heat-treatment process at high temperatures.

In order to investigate the thermal shock resistance of the above joints of graphite/alumina, a thermal shock resistance experiment was carried out. Several different thermal shock resistance cycles were designed. The selected specimens were the joints heat- treated at 1000 °C previously, and the thermal shock temperatures are $\Delta T = 800$ and 1000 °C, respectively. The experimental procedure is described as follows: (1) the muffle furnace was heated to 820 °C or 1020 °C previously; (2) the graphite/alumina joints were directly placed in the muffle furnace rapidly; (3) after being heated at the given temperature for 15 min, the joints were taken out rapidly and cooled in atmosphere naturally. The thermal shock resistance experiment of $\Delta T = 800\,^{\circ}C$ was carried out for 10 cycles, while that of $\Delta T = 1000\,^{\circ}C$ for five cycles. Throughout the thermal shock experiments, no oxidation protection was provided for the joints in order to realize the heat -transfer in a rapid rate.

2.3. Testing and analysis

The adhesive strength of graphite/alumina joints treated at different temperatures was tested by using the universal testing machine at room temperature. The test method of the specimens experienced thermal shock experiment is the same. The testing rate of loading is 1.5 mm/min, and the bonding mode and the test of shear strength were coincident with Ref. [10].

A JSM-6301F scanning electron microscope (SEM) system was employed to investigate the micro-structural morphology of the debonded section of the joints.

3. Results and discussion

3.1. Adhesive strength of graphite/alumina joints

The adhesive strength of the graphite/alumina joints treated at different temperatures is tabulated in Table 3.

Table 3
Adhesive strength of graphite/ceramics treated at different temperatures

adhesive	Adhesive strength treated at different temperatures (MPa)				
	400 °C	600 °C	800 °C	1000 °C	1200 °C
PF + B_4C	12-15.7	3–6.2	2.8–3.5	10–14	10–15

Data in Table 3 show that the adhesive strength of the joints treated at 400 °C and above 1000 °C is satisfactory. Because the PF resin is the matrix of the adhesive and works as the framework of the adhesive cement during the bonding process, the change of PF will have important effects on the bonding properties of the adhesive. When the heat-treatment temperatures are below 400 °C, except for the occurrence of some condensation reactions, the integrity of intertexture structure of PF resin remains rather high because the level of the carbonization or the pyrolysis reactions is relatively low. So the structure of the adhesive cement has a good stability below 400 °C. As a consequence, the adhesive strength of graphite/alumina joints is satisfactory, higher than 12 MPa, due to the outstanding adhesive properties of PF resin.

With further increasing heat-treatment temperatures, an obvious decreasing tendency of adhesive strength is shown in Table 3 in the range of 600–800 °C, which also can be attributed to the influences of the change of resin matrix. When the heat-treatment temperature is above 400 °C, PF resin enters into the carbonization stage, and the carbonization level keeps on increasing at the elevated temperatures. Complex chemical reactions, including condensation, dehydrogenation, re-organization, decomposing, aromatization , and so on occur in the range of 500–650 °C and result in the drastic change of resin [11]. Lots of volatiles are released, which result in the great volume shrinkage. So the bending strength and compressive strength of resin are dropped drastically, and reache its minimum value at nearly 600 °C [12]. Because of the decline of the PF resin, the cohesive force in the bonding cement decreases drastically. Correspondindly, the adhesive strength of graphite/alumina joints is only 3–6.2 MPa when the heat-treatment temperature reach 600 °C, and the broken sites of the joints are located in the interior of bonding cement, namely that the failure modes belong to the cohesive failure.

It is worth noting that the adhesive strength of graphite/alumina joints is obviously different from that of graphite/graphite joints at 800 °C. The adhesive strength of graphite/graphite joints treated at 800 °C is 13.2 MPa [10], while that of graphite/alumina joint is only 2.8–3.5 MPa. The reason for such results might be the mismatch of the thermal physical properties between the adhesive cement and substrates to be joined. In the graphite/graphite joints, certain chemical and physical compatibilities exist between the graphite substrate and adhesive cement because the organ resin converts into amorphous carbon at high temperatures. Once the alumina ceramic displaces graphite, some micro-cracks might be introduced at the bonding interface due to some physical property (e.g. thermal expansion coefficient and elastic modulus) mismatches between the adhesive cement and ceramic substrate (Fig. 1), and result in the further decrease of adhesive strength consequently.

Regarding the heat -treatment above 1000 °C, the carbonization of resin is nearly complete and a amorphous carbon skeleton with certain strength, derived from the carbonization of PF resin matrix is formed. As a result, a carbon/ceramic composite composed of amorphous carbon and ceramic filler (B_4C particles) is formed in the adhesive cement. So the cohesive force of the adhesive cement rises again greatly. Due to the modification effect of B_4C, some boron oxides (B_2O_3) with a favorable viscosity is formed. The conversion of B_4C to B_2O_3 results in 250% volume increase, and the B_2O_3 possesses good wetting-ability and can heal the micro-cracks effectively [10]. Besides, there are some interaction forces at the bonding interface between B_2O_3 and Al_2O_3 substrate in the form of complex compound at higher temperatures, which might be expressed as follows [13]:

$$2Al_2O_3 + B_2O_3 \rightarrow 2Al_2O_3 \cdot B_2O_3,$$
$$2(2Al_2O_3 \cdot B_2O_3) + 5Al_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3.$$

By means of the above changes, the compatibility and joining force between the adhesive cement and alumina substrate are improved effectively. As a result, satisfactory bonding properties are achieved when the graphite/alumina joints are treated above 1000 °C. It can be seen from the SEM micrograph that some alumina substrates are still adhering on the adhesive cement due to the satisfactory bonding force (Fig. 2). The white substance showed on the debonded section can be attributed to the alumina substrate.

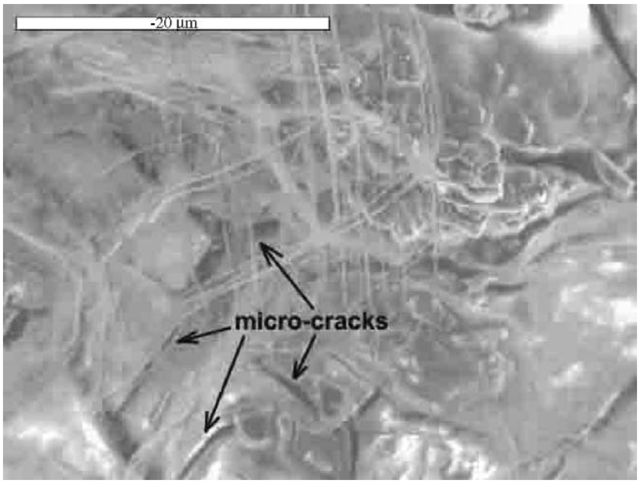

Fig. 1. Micrograph of bonding interface treated at 800 °C.

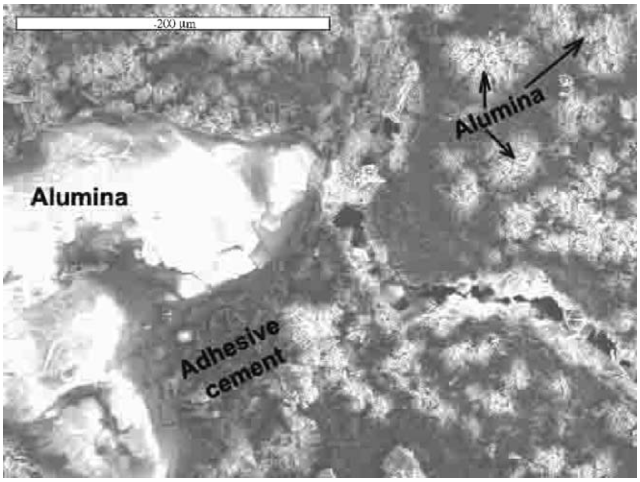

Fig. 2. Micrograph of graphite/alumina joint's boning interface treated at 1000 °C

3.2. The thermal shock resistance properties of graphite/alumina joints

It can be found from Table 4 that there are some differences between the joints experiencing different thermal shock temperatures. Data show that the adhesive strength of the joints shocked with $\Delta T = 800\,^{\circ}\mathrm{C}$ is higher than that of the joints shocked with $\Delta T = 1000\,^{\circ}\mathrm{C}$, indicating the effect of the thermal shock temperature. It also can be found that the times of thermal shock cycles also have an important influence on the adhesive strength. When the first thermal shock is experienced, no obvious decrease in adhesive strength is found in Table 4, while the adhesive strength of joins drops to some extent when the joints experience the second and third cycles. But the re-rising of adhesive strength is shown after more than three times of thermal shock cycles.

It can be seen that after the first thermal shock, the micro-cracks on the debonded interface of the joints shocked at $\Delta T = 800\,^{\circ}\mathrm{C}$ (Fig. 3) are smaller and much less than those of the joints shocked at $\Delta T = 1000\,^{\circ}\mathrm{C}$ (Fig. 4). But both specimens still possess certain joining strength and the failure mode is due to the mixing failure. Some alumina ceramic substrates still can be found on the bonding interface. Such phenomena might indicate that most of the thermal stresses are consumed in the induction of micro-faults, so the micro-cracks are not very serious and cannot lead to the drastic decreasing of adhesive strength.

But accompanied with the increase in thermal shock cycle times, the micro-cracks become larger and more (Fig. 5), and result in the rapid decreasing of joining strength. When the graphite/alumina joints experiences two or three thermal cycles, the micro-faults existing between bonding interface are developed under the impelling of thermal stress.

Table 4
Adhesive strength of the joints after being thermal shocked with different cycles

	Adhesive strength (MPa)					
	0 cycle	1 cycle	2 cycles	3 cycles	5 cycles	10 cycles
ΔT = 800 °C	10–14	10.2–11.3	6.4–10.0	4.4–9.0	—	9.8–10.1
ΔT = 1000 °C	10–14	10.4	5.6–8.4	3.5–5.6	5.7–7.4	—

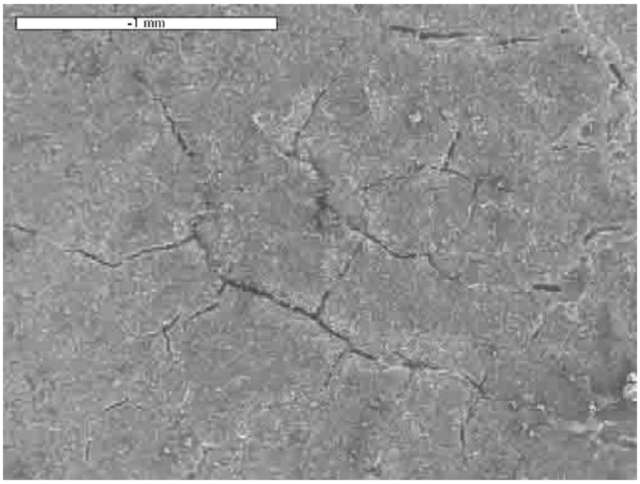

Fig. 3. Micrograph of graphite/ceramics after being thermal shocked once at ΔT = 800 °C

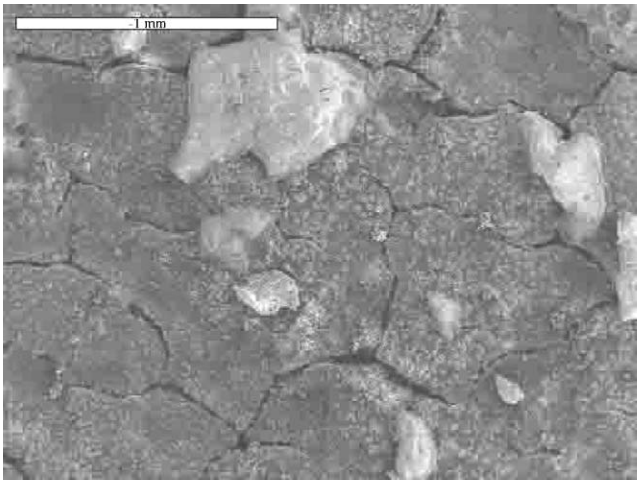

Fig. 4. Micrograph of graphite/ceramics after being thermal shocked once at ΔT = 1000 °C

It is worth noting that the data in Table 3 show that the joining strength rises again after being shocked for more than three times. As to the graphite/alumina joints shocked with $\Delta T = 800\,^{\circ}\mathrm{C}$, the adhesive strength returns to nearly 10 MPa. Because of the drastic oxidation of the graphite, the thermal shock test of the joints shocked with $\Delta T = 1000\,^{\circ}\mathrm{C}$ is only carried out for five cycles. But the re-increasing tendency of the adhesive strength is also shown. From the SEM photo of debonded interface of the

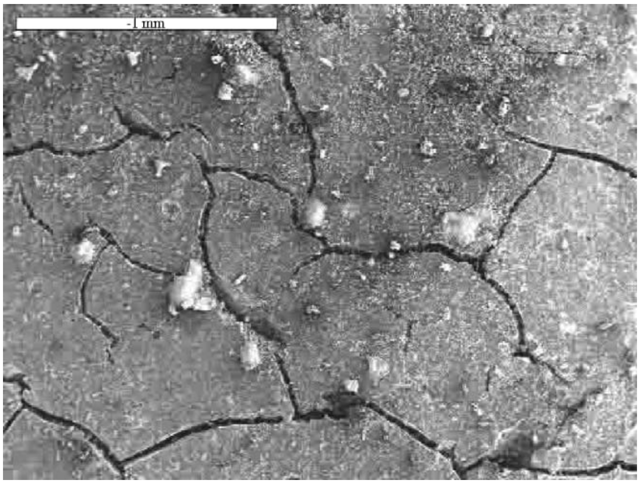

Fig. 5. Micrograph of graphite/alumina after being thermal shocked twice at $\Delta \mathrm{T} = 800\,^{\circ}\mathrm{C}$

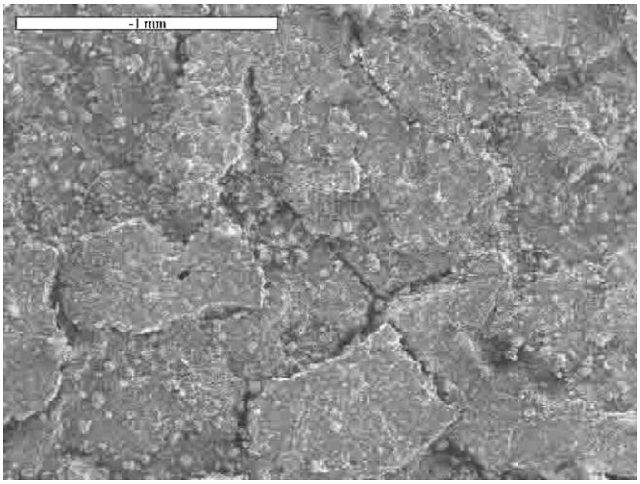

Fig. 6. Micrograph of graphite/alumina after being thermal shocked ten cycles at $\Delta \mathrm{T} = 800\,^{\circ}\mathrm{C}$

joints which experience 10 times thermal shock cycles at $\Delta T = 800\,^{\circ}\mathrm{C}$ (Fig. 6), some cracks are healed to some extent and the morphology of debonded interface is coarse, which might indicate that the stress transfer is complex and the failure route is flexuous. This result might be due to the release of the residual stress after cycling for many times [14].

4. Conclusion

The high-temperature adhesive composed of phenol-formaldehyde resin and boron carbide possesses satisfactory properties for the bonding of graphite and alumina ceramic.

1. Satisfactory adhesive strength is achieved when the joints are treated below 400 °C or above 1000 °C. The failure mode is mixing failure. Some alumina substrate can be found on the bonding interface.
2. The adhesive strength of the joints treated at 600 °C is not satisfactory due to the decline of resin matrix. Because of the mismatch in properties of thermal physics between adhesive cement and alumina ceramic substrate, the joining strength is also not satisfactory at 800 °C.
3. The joints possess certain thermal shock resistance performance after being treated at 1000 °C previously. A decreasing tendency of the joining strength is shown at the beginning of thermal shock cycles. With further consequent cycles, the re-rise of the joining strength is shown.

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