

Microstructure and strength of zirconia/stainless steel joints prepared by pressureless active brazing

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ZrO₂ ceramic/stainless steel joints were fabricated by pressureless brazing using a Ag-Cu filler metal and a TiH₂ powder pre-coating. The microstructure and microchemistry of the joint cross section were characterized and analyzed by means of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The effects of brazing conditions on the joint shear strength were also investigated. The results showed that there existed three zones with distinct microstructural differences crossing the brazing interlayer. A reaction layer and a Ti-rich sublayer were formed at the ZrO₂/filler interface. The influence of the brazing temperature on the joint strength was more remarkable than that of the holding time. In the experimental condition ranges, the joint strength first increased, and the maximum shear strength was over 90MPa with the optimized condition. Most of the joint fractures developed in the ceramic matrix near the ceramic/filler interface.

Key words: Brazing, Zirconia, Microstructure, Interface, Mechanical Properties.

Introduction

Advanced structural ceramics mainly include oxides, carbides, nitrides and composite ceramics of them. Oxides, in particular alumina and zirconia, dominate industrial applications of advanced ceramics. Compared to alumina, zirconia exhibits better mechanical properties (strength and fracture toughness) and chemical stability, and it is also a good ionic conductor at elevated temperatures. For these reasons, zirconia can be found in applications ranging from wire drawing dies, cutting and machining tools, to oxygen sensors and fuel cells [1].

The joining of ceramics to metals or ceramics could overcome the drawbacks of most of advanced ceramics, which are involved in brittle and poor in machinability, as well as difficulties in the fabrication processes of complex-shaped and large-sized components [2, 3]. The techniques for joining ceramics for high-temperature applications include a sintering metal powder process, active metal brazing and diffusion bonding, etc. Active metal brazing is the most appropriate technique for zirconia ceramic taking into account the structural reliability and economical industrialization. For the reason that the addition of Ti to some alloys promotes lower contact angles and hence wetting, joining of zirconia to metal or ceramic has been investigated using Ag-Cu(-Sn)-Ti [1-14], Ag-In-Ti [15], Cu-Ga-Ti [16, 17] and Au-Ni-Ti [18] filler metal, etc. Presently, the addition of Ti is mainly adopted in two

methods: smelting before brazing and fusing during brazing with these alloys. Most of these studies have adopted the former method. However, for the latter, Ti vapor coatings [9, 10], Ti foil [11], TiH₂ [12, 13] and TiH powder [16] were used.

The main aim of this study is to investigate the joint microstructure, and to obtain a higher joint strength between two materials (zirconia and stainless steel) with a large difference in their coefficients of thermal expansion (CTE) by a pressureless brazing technique.

Experimental Procedures

Partially stabilized zirconia (PSZ) containing 3 mol% Y₂O₃ was used. Its porosity, density and bending strength was 0.5%, 5.95 g·cm⁻³ and 850 MPa, respectively. The sizes of PSZ pieces used for brazing were Φ17 × 6 mm. The metallic component was a commercial stainless steel (AISI 304, S-S), and its dimensions were Φ10 × 5 mm. A 72Ag-28Cu (wt.%) alloy filament was used as the brazing solder with a diameter of Φ0.8 mm. Commercial TiH₂ powder was used, and its meso-diameter D₅₀ is 2.785 μm after milling.

The three solid materials (PSZ, Ag-Cu alloy and S-S) were carefully cleaned. The adjusted TiH₂ paste was applied on the brazing surface of ceramic specimens with a writing brush, and then air-dried. A thin Ni layer on the brazing surface of the stainless steel was coated by electro-plating using Watts' solution. The brazing of PSZ to S-S were executed in a vacuum furnace (vacuum: about 8 × 10⁻³ Pa, furnace model: High-multi 5000, Japan). In the first stage, the temperature of furnace was taken

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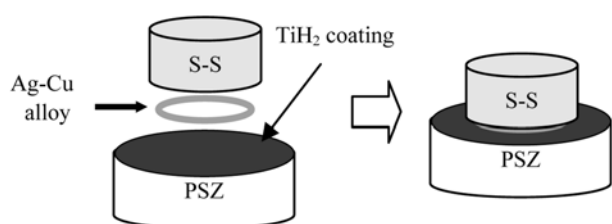


Fig. 1. Chart of assembling the brazing parts.

to 400 °C within 40 minutes and maintained for 30 minutes. Subsequently, the temperature was raised to 750 °C over 50 minutes and kept for 10 minutes. Then the temperature was taken to the brazing temperature (820-860 °C) at a speed of 5 K·minutes⁻¹ and held for 10-50 minutes. Finally, gradually cooling at a rate of less than 10 K·minutes⁻¹. The three brazing parts were assembled as shown in Fig. 1.

Some PSZ/S-S joints were cut along the cross section and polished. The microstructure of joint cross sections was characterized by SEM (Model Quanta-2000, Philips-PET, Ltd., Holland). EDS (Model Oxford INCA, British) was also adopted to determine elemental compositions of the characteristic microstructures. The joint strength was tested by a shear-load method using an Instron-1195 testing machine. The loading speed was 0.5 mm·minutes⁻¹. The mean value of joint strength under each brazing condition was the arithmetical average of five joint samples.

Results and Discussion

Microstructure

Backscattered electron (BSE) images of the PSZ/S-S joint cross section are shown in Fig. 2. Three main zones (I, II and III) with distinct microstructural differences were formed in the brazing interlayer shown in Fig. 2(a). Their thickness was about 30-50, 60-80 and 10-25 μm, respectively. In the temperature rising stage, the organics in TiH₂ coating were first evaporated, and then the TiH₂ was decomposed to form a loose Ti layer on the PSZ surface. When it reached the eutectic temperature, the Ag-Cu alloy started to melt and penetrated into the loose Ti layer, and reactions of Ti/ZrO₂ and Ti/Ag-Cu alloy occurred almost simultaneously, forming the zone I. At the same time, the neonatal active Ti and the Ni (mainly originated from the Ni coating on the S-S surface) diffused into the middle melting Ag-Cu layer from both sides. Reacting, dissolving and precipitating processes took place continuously. As a result, zone II was formed. Furthermore, some melting Ag-Cu alloy entered onto the rough surface of the S-S, then the zone III came into being by their fusion. It may be seen from Fig. 2(b) that zone III mainly consisted of a Ag-rich phase, which is displayed as a bright belt.

A double-layer structure including a black layer about 1 μm thickness and a gray layer about 1.5 μm thickness is shown in Fig. 2(c). From EDS analysis, they were

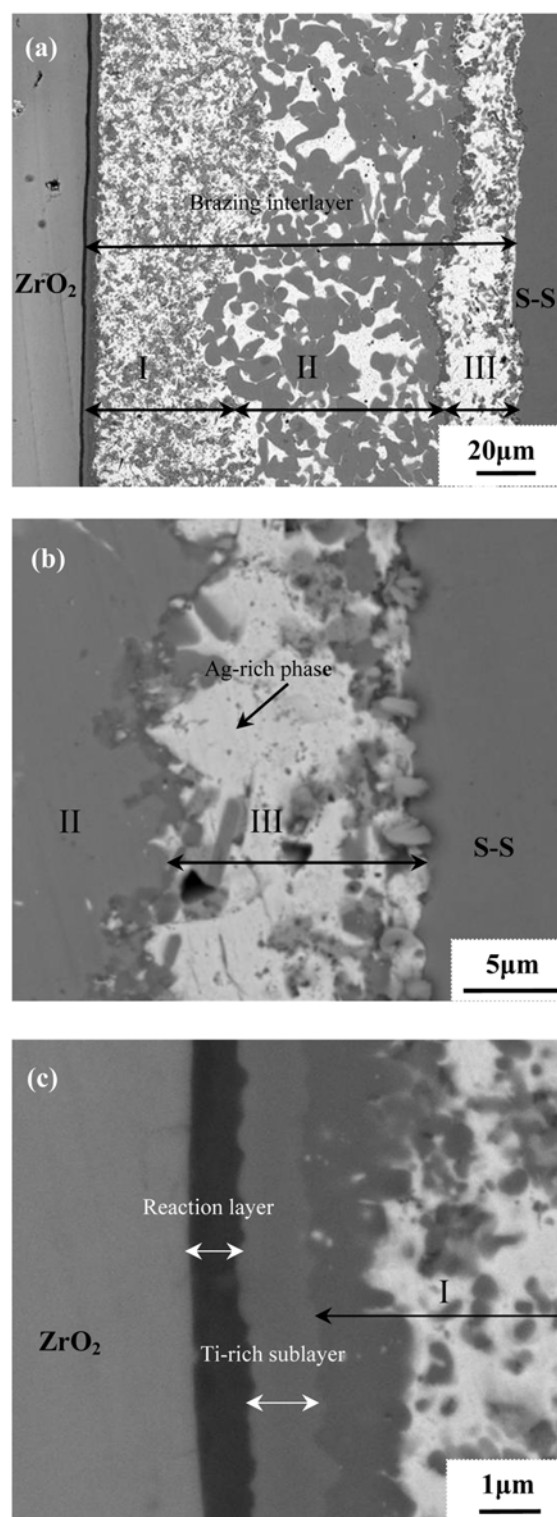


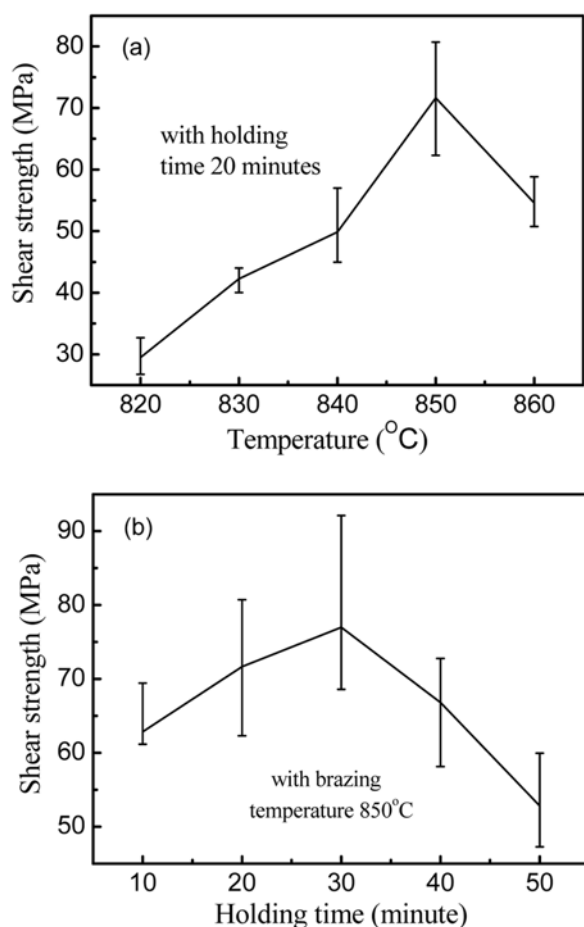
Fig. 2. BSE images of the joint cross section: (a) PSZ/filler/S-S; (b) Filler/S-S; (c) PSZ/filler.

identified as reaction layer and a Ti-rich sublayer. The elemental compositions of the reaction layer and Ti-rich sublayer are shown in Table 1. Besides Ti, the sublayer contained Cu, oxygen and a minor amount of Zr. Furthermore, in the brazing interlayer, the white region was mainly Ag-rich phase, i.e. the Ag-Cu eutectic structure.

Table 1. Elemental compositions of reaction layer and Ti-rich sublayer

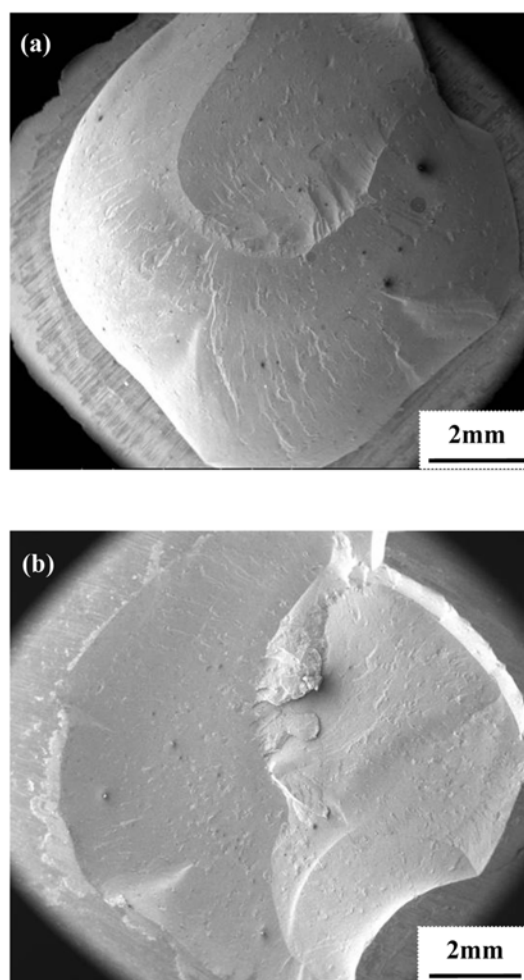
Element	Wt.%	At.%	Element	Wt.%	At.%
(Reaction layer)			(Ti-rich sublayer)		
O	25.78	61.68	O	9.96	26.16
Ti	18.88	15.09	Ti	68.19	59.84
Zr	55.34	23.23	Cu	19.60	12.97
			Zr	2.24	1.03

The black layer in zone II was a phase mainly containing Cu, Ti and Ni. In addition, from EDS analysis across the whole seam by line-scanning, the Ti diffused into the whole brazing interlayer, and the oxygen diffused from the ZrO_2 side to a limited distance of about 30 μm . A number of Ni atom mainly existed in zone II rather than zone III, and minor amount of Ni was found in zone I, although most of the Ni originated from the Ni coating on S-S surface. A reasonable explanation was that the high activity of Ti attracted Ni to diffuse a long distance into zone II and even zone I. So diffusion and enrichment of diversified elements acted as a key role in the formation of the brazing interlayer.

**Fig. 3.** Joint shear strength at different (a) brazing temperatures and (b) holding times.

Mechanical Properties

The effects of brazing temperature and holding time on joint shear strength are shown in Fig. 3. It could be shown from Fig. 3 that the brazing temperature gave a more noticeable influence on the joint strength than the holding time. In the ranges of brazing temperature and holding time investigated, the joint strength first increased. The maximum shear strength was over 90 MPa, and the average was about 75 MPa at a brazing temperature of 850 °C for 30 minutes. With an increase in brazing temperature or holding time, the neonatal active Ti originates from the TiH_2 would react with the ZrO_2 ceramic and filler metal more fully, therefore a firm reaction layer with a good bonding was formed. By contrast, when the temperature was too high or holding time was too long, the neonatal active Ti reacted excessively with the ceramic and the alloy, and more brittle intermetallics were formed near the interface and in the brazing interlayer and the interface was weakened. Furthermore, the residual stress in the brazing joint became accumulated as those brittle products thickened. Both the weakened interface and the large residual stress led to a lower joint strength when the temperature raised

**Fig. 4.** Shear broken joint fractured in the ceramic matrix: (a) metal side; (b) ceramic side.

above 850 °C or the holding time exceeded 30 minutes.

Most of the joint fractures developed in the ceramic matrix near the ceramic/filler interface, as shown in Fig. 4, because the maximum residual stress in the ceramic matrix appeared at a position under the interface at a certain distance related to the joint size. Only a few samples fractured along the reaction layer and gave a lower strength. The lower the temperature or the shorter holding time was, the higher was the possibility of joint fracture along reaction layer.

Conclusions

ZrO₂ ceramic/stainless steel joints were fabricated by a pressureless active brazing technique. Three zones with distinct microstructural differences crossing the brazing interlayer were formed. A reaction layer and a Ti-rich sublayer was also produced at the ZrO₂/filler interface. In the range of brazing conditions studied, the brazing temperature gave a more noticeable influence on the joint strength than the holding time. The joint strength increased at first, and the maximum strength of over 90 MPa, and an average of about 75 MPa were attained at a brazing temperature 850 °C for 30 minutes. Most of the joint fractures developed in the ceramic matrix near the ceramic/filler interface. Diffusion, enrichment and interreaction of the diverse elements, act as key roles in the formation of the brazing interlayer, and finally affected the joint mechanical properties.

Acknowledgement

This work was supported by the National Basic Research Program of China (2006CB601200).

References

1. W.B. Hanson, K.I. Ironside and J.A. Fernie, *Acta Mater.* 48[18-19] (2000) 4673-4676.
2. C.G. Zhang, G.J. Qiao, Z.H. Jin, *J. Eur. Ceram. Soc.* 22[13] (2002) 2181-2186.
3. G.J. Qiao, C.G. Zhang, Z.H. Jin, *Ceram. Int.* 29[1] (2003) 7-11.
4. D. Sciti, A. Bellosi and L. Esposito, *J. Eur. Ceram. Soc.* 21[1] (2001) 45-52.
5. M.L. Muolo, E. Ferrera, L. Morbelli and A. Passerone, *Scripta Mater.* 50[3] (2004) 325-330.
6. O. Smorygo, J.S. Kim, M.D. Kim and T.G. Eom, *Mater. Lett.* 61[2] (2007) 613-616.
7. T.H. Chuang, M.S. Yeh and Y.H. Chai, *Metall. Mater. Trans. A* 31A[6] (2000) 1591-1597.
8. A.J. Moorhead and H. Keating, *Weld. J.* 65[10] (1986) 17-31.
9. J.P. Hammond, S.A. David and M.L. Santella, *Weld. J.-Weld. Res. Suppl.* Vol. 67[10] (1988) 227-s-232-s.
10. M.L. Santella and J.J. Pak, *Weld. J.-Weld. Res. Suppl.* 72[4] (1993), 165-s-172-s.
11. L.D. Wang, Y.H. Wang, W.Z. Li, H.D. Li and T. Ok, *Acta Metall. Sini.* 33[7] (1997) 756-762.
12. Y.Q. Wu, L.Q. Gao, and M.H. Hu, *Vacuum. Electronics*(in Chinese). [4] (1995) 1-7.
13. J.Y. Kim, J.S. Hardy and K.S. Weil, *J. Mater. Res.* 20[3] (2005) 636-643.
14. X.-L. Wang, C.R. Hubbard, S. Spooner, S.A. David, B.H. Rabin and R.L. Williamson, *Mater. Sci. Eng. A* 211[1-2] (1996) 45-53.
15. X.M. Xue, J.T. Wang and Z.T. Sui, *J. Mater. Sci.* 28[9] (1993) 1317-1322.
16. A.V. Durov, B.D. Kostjuk, A.V. Shevchenko and Y.V. Naidich, *Mater. Sci. Eng. A* 290[1-2] (2000) 186-189.
17. A.V. Durov, Y.V. Naidich and B.D. Kostyuk, *J. Mater. Sci.* 40[9-10] (2005) 2173-2178.
18. M. Singh, T.P. Shpargel and R. Asthana, *Int. J. Appl. Ceram. Technol.* 4[2] (2007) 119-133.