JOURNAL OF MATERIALS SCIENCE **40** (2005) 3693–3701

Joining of SiC fibre reinforced borosilicate glass matrix composites to molybdenum by metal and silicate brazing

J. JANCZAK-RUSCH, D. PIAZZA
Laboratory for Joining and Interface Technology, Swiss Federal Laboratories for Materials Testing and Research (EMPA), 8600 Dübendorf, Switzerland

A. R. BOCCACCINI*
Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, UK
E-mail: a.boccaccini@imperial.ac.uk

The brazing of SiC fibre reinforced borosilicate glass matrix composites with Mo plates has been investigated. Molybdenum was chosen as the metallic partner under consideration of system requirements, e.g. thermomechanical stability at temperatures of interest (500–750°C), and physical properties, e.g. coefficient of thermal expansion close to that of the glass matrix composite. Two brazing filler materials were investigated: a glass braze (Schott G018-174) and an active filler metal (Incusil ABA, brazing temperature = 740°C). When using the glass braze the surface of the metal had to be roughened to ensure a bond of significant strength. Vacuum brazing with the active filler metal resulted in joints with high strength, which allows to fully utilise the mechanical competence of the glass matrix composite when the joint configuration is adapted to the relevant loading conditions. A novel design of a tool for hot glassware handling, made of glass matrix composite/Mo joints, is presented.

1. Introduction

Glass and glass-ceramic matrix composites are lightweight structural materials exhibiting excellent mechanical, thermal and chemical properties for applications in energy conversion systems, gas turbines and other specialised areas requiring high oxidation and corrosion resistance at elevated temperatures [1]. These materials are also of interest for a wide range of applications in conventional technologies, i.e. at low to moderate temperatures and under low to moderate stresses, for example for components in vacuum pumps, automotive parts and construction of special machinery [2, 3]. However, suitable manufacturing and joining technologies are required in order to assemble complex components and to expand the application possibilities of glass and glass-ceramic matrix composites [4]. Our previous review of the available technical literature on these materials [5] revealed that the development of suitable joining techniques is one of the main challenges for the future development of these composite materials.

Only a few of the procedures developed for joining traditional ceramics or glasses are directly transferable to composites. In addition to common problems which usually appear when joining ceramics with metals, such as poor wetting behaviour of ceramics and differences in physical and thermal properties of metals and ceramics, other issues arise with composites. For example, the different wetting behaviour of the composite constituents (e.g., fibre and matrix), and the compatibility of the joining process with the composite fabrication technique have to be taken into account when joining ceramics or glass matrix composites with metals. Among different joining processes like mechanical interlocking, diffusion bonding and joining by preceramic polymers, the brazing technology has been widely used in the joining of monolithic ceramics to metals and to other monolithic ceramics [6–12]. This technique has been proposed to be suitable also for a wide range of ceramic-matrix composites (CMCs) [13]. Joining of SiC based ceramic composites to similar SiC/SiC composites or to high temperature alloys has been reported extensively in the literature [14–17], however, there is very little information concerning joining of ceramic composites with oxide matrices, including silicate matrix composites, to metal parts [18–22].

In one of the few studies published on silicate matrix composites, Dixon [19] reported on brazed joints of silicon nitride fibre reinforced cordierite glass-ceramic with titanium and stainless steel parts. Different

*Author to whom all correspondence should be addressed.

interlayer materials were used in order to minimise residual stresses and to prevent the damage of fibre-matrix interfaces in the composite.

In the present study, the brazing of a commercially available SiC fibre reinforced glass matrix composite with molybdenum counterparts was investigated assessing different joining configurations. The performance of the joints was qualitatively evaluated using bending strength tests. The type of joints investigated is relevant for the actual use of the composites in tools for the handling of hot glassware and non-ferrous metals at working temperatures of ∼500–750°C, which is one of the current commercial applications of the composites [23].

2. Experimental

2.1. Materials

The composite investigated was a borosilicate (Duran®) glass matrix composite unidirectionally reinforced with Nicalon® NL 202 SiC fibres. The composite was manufactured by the sol-gel slurry and hot-pressing method [24] (Schott Glaswerke, Mainz, Germany). The fibre content in this material is 40 vol%; the fibres have an average diameter of 0.015 mm. The material was received in the form of rectangular test bars of 50 mm length and 4 × 3.85 mm^2 in cross section. Relevant properties of the composite material are summarised in Table I. This composite system has been fully investigated in terms of thermomechanical behaviour [25, 26] and it has reached commercial exploitation for example in the area of hot glass and non-ferrous metal handling [23]. There is however very little knowledge about the joining of this composite to refractory metal parts. Thus the evaluation of adequate, cost-effective and reproducible joining methods will increase the application possibilities for this composite.

Molybdenum was chosen as metallic joining partner not only due to its good mechanical stability at the temperatures of interest (500–750°C) but also due to the relatively low difference of its thermal expansion coefficient with that of the glass matrix composite, as shown in Table I.

The main criteria for the choice of the brazing filler materials were the brazing temperature and the wettability of the glass matrix composite constituents (borosilicate glass, SiC fibre).

The maximal brazing temperature was in principle limited by the transformation temperature of the glass matrix, which is 550°C [26]. For this temperature range (RT-550°) there are no metallic alloy fillers wetting borosilicate glass. The only brazing filler materials ensuring wetting of the glass matrix composite at such relatively low temperatures are glass brazes. As it is well-known, technical glasses are successfully used to join glasses by silicate brazing, for example bulk silicate-glass components such as cathodic ray tubes. A commercially available composite glass braze (Schott G018-174), which has a working temperature of 430°C, was chosen under consideration of the processing temperature and properties of the materials to be joined. This glass braze is recommended for joining of materials with thermal expansion coefficients of ∼5 × 10^{-6} 1/K. The chemical composition of the glass braze used is given in Table II and the thermal expansion coefficient of this glass in the relevant temperature range is 4.3 × 10^{-6} 1/K, measured according to norm DIN 52328.

Furthermore an active filler metal (Incusil ABA) with a moderate brazing temperature (740°C) was also considered. The chemical composition of the metallic alloy filler, available as a foil, is summarised in Table III and its thermal expansion coefficient is 19.7 × 10^{-6} 1/K. The working temperature of this filler is significantly higher than the glass matrix transformation temperature. This would give the possibility to increase the application temperature of the composite/metal joint component if degradation of the properties of the glass matrix composite during the brazing process can be avoided. It is known from previous investigations [25, 26], that SiC fibre/borosilicate glass matrix composites may be exposed to oxidising environments for short times (up to ∼20 h) even at temperatures of 700°C without major degradation of their mechanical properties.

2.2. Methods

Two joint configurations were investigated, as shown in Fig. 1, which are labeled configurations (a) and (b). Configuration (a) corresponds to joints brazed on sections parallel to the fibres' direction, while in configuration (b) joints are brazed on sections normal to the fibres' direction. Configuration (a) has a higher practical relevance, whilst configuration (b) allows the application of standardized mechanical tests to assess the joint strength. Both configurations are of scientific interest when investigating the suitability of the brazing technique to join glass matrix composites to metals. The morphology of the interfaces between the composite

TABLE I Mechanical and physical properties of the joining partners

Material	E (GPa)	α(RT-600°C) (10^{-6}/K)	Tensile/Bending Strength (MPa)
SiC fibre reinforced Duran® matrix composite	117	3.2	700 (in the fibre direction)
Mo	324	5.3	585

TABLE II Composition of the glass solder

Glass solder	B_2O_3 (wt%)	CaO (wt%)	CaF_2 (wt%)	TiO_2 (wt%)	ZnO (wt%)	PbO (wt%)
G018-74	1–10	1–10	0.1–1	10–50	1–10	>50

TABLE III Composition of the brazing filler materials

Brazing filler	Ag (wt%)	Cu (wt%)	In (wt%)	Ti (wt%)
Incusil ABA	59	27.25	12.5	1.25

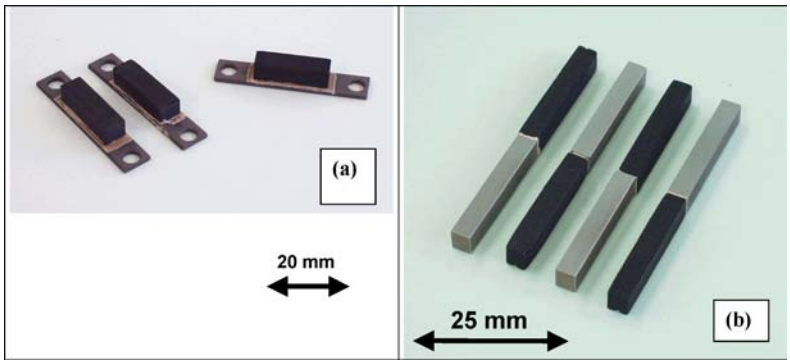


Figure 1 Configurations of investigated joints of SiC fibre/glass matrix composite to Mo plates: configuration (a) in sections parallel to SiC fibre direction, and configuration (b) in sections perpendicular to SiC fibre direction.

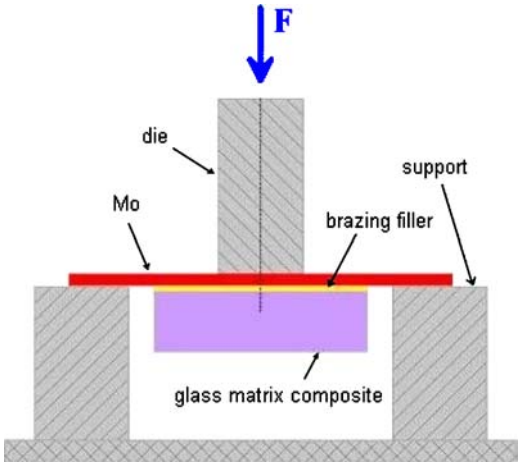


Figure 2 Macrograph showing the rig used for bending tests on joints in configuration (a).

material and the metallic counterpart are different in both configurations, which will influence the wetting as well as the surface reaction behavior (e.g., possible degradation of the glass composite). Configuration (a) corresponds to a typical load configuration in which the favorable thermomechanical properties of the glass matrix composite can be exploited, for example in components for handling of hot glassware [23].

Both filler materials (glass braze and filler metal alloy) were used to manufacture joints of configuration (a). Three specimens were produced with each brazing material. The performance of the joints was then evaluated using a bending test, as shown in Fig. 2. The more suitable filler material was selected considering the results of this test and the accompanying failure analysis.

The joints with glass brazes were performed in an electric furnace in air atmosphere. The parameters used were $T = 430°C$, time = 30 min. A pressure of 1.1×10^{-2} MPa was mechanically applied on the joints. When using the active brazing filler metal, the joints were produced in a TORVAC vacuum furnace, whereby the process pressure was always lower than 10^{-5} mbar. The processing parameters were $T = 740°C$, $t = 10$ min. Samples for active brazing were chemically cleaned and then out-gassed in a vacuum oven prior to the brazing operation. Out gassing took place at the following conditions: for SiC fibre/glass matrix composite: $T = 740°C$, $t = 10$ min and for Mo plates: $T = 800°C$, time = 45 min.

Because the preliminary results from wetting tests showed a significant influence of the substrate roughness on the bonding behavior when using the glass braze, the surface roughness of the Mo plate was altered: for two specimens the Mo surface was sand blasted (grit 80), while for one specimen the smooth surface of the as-delivered material was kept.

For the joints of configuration (b) only the filler metal alloy (Incusil ABA) was applied, which had been evaluated for joints of configuration (a) as being a more

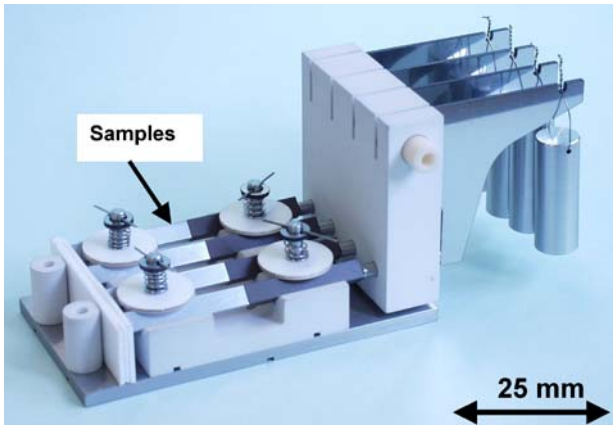


Figure 3 Facility for brazing specimens in configuration (b).

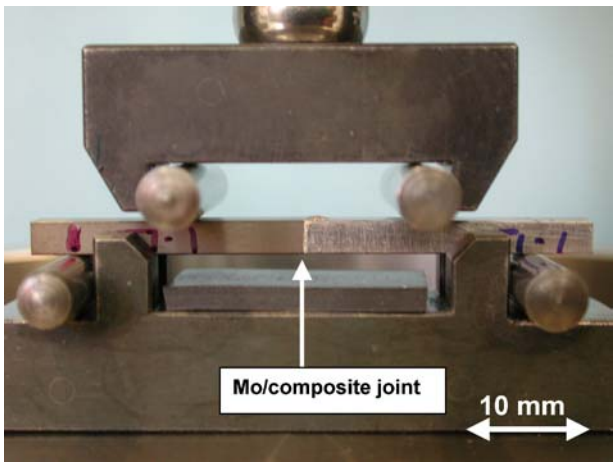


Figure 4 Four-point bending test rig to test joints in configuration (b).

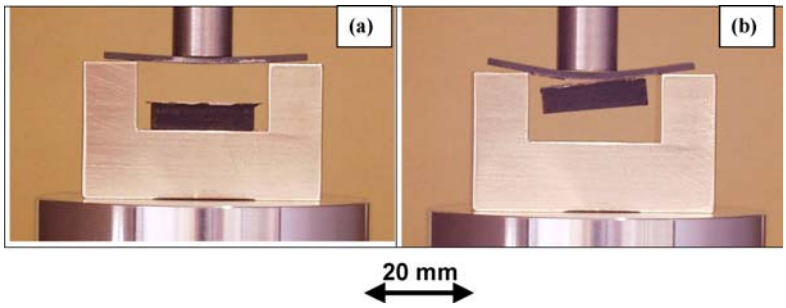


Figure 5 Fracture behaviour of glass braze joints for different surface preparation state of the Mo substrate during early stage of the bending test: (a) Mo plate in as-delivered state (smooth surface); failure at low loads. (b) Mo plate with sand blasted surface; high load capacity.

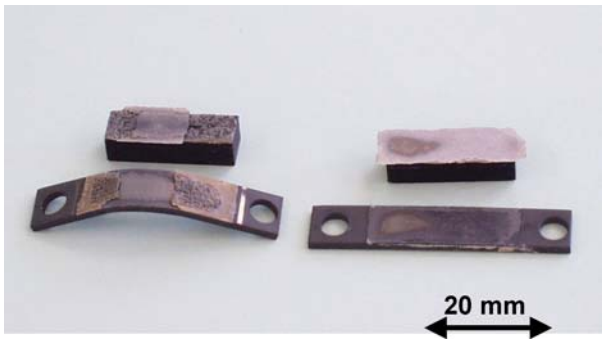


Figure 6 Fracture behaviour of glass braze joints for different surface preparation state of the metallic substrate at the end of the bending test. Right: Mo plate in as-delivered state (smooth surface), left: Mo plate with sand blasted surface.

suitable filler material than the glass braze (see Section 3.2).

For brazing joints of configuration (b), a special jig which assured the proper alignment of the specimens and a constant joint clearance was used, as shown in Fig. 3. Four specimens were simultaneously produced in vacuum. The brazing temperature was 740°C, the brazing time 10 min. Two brazing foils of 0.05 mm in thickness were applied.

The joints in configuration (b) were characterised in a four-point bending test, as shown in Fig. 4.

3. Results

3.1. Joints in configuration (a)

3.1.1. Joints using glass braze

The joints in which molybdenum plates of smooth surface finish were used failed at very low loads during bending tests. On the contrary, brazed specimens where sand blasted molybdenum plates were used showed significantly higher fracture strength, as qualitatively confirmed by the bending tests carried out, documented in Figs 5 and 6.

The comparison of results indicates that the quality of bonding of the glass matrix composite to molybdenum plates performed using the glass braze is determined by mechanical interlocking. For smooth surface of the metallic partner, the composite peeled away from the metallic substrate at very low load in the bending configuration tested. The glass braze remains on the glass composite surface, as seen in Fig. 6. On the

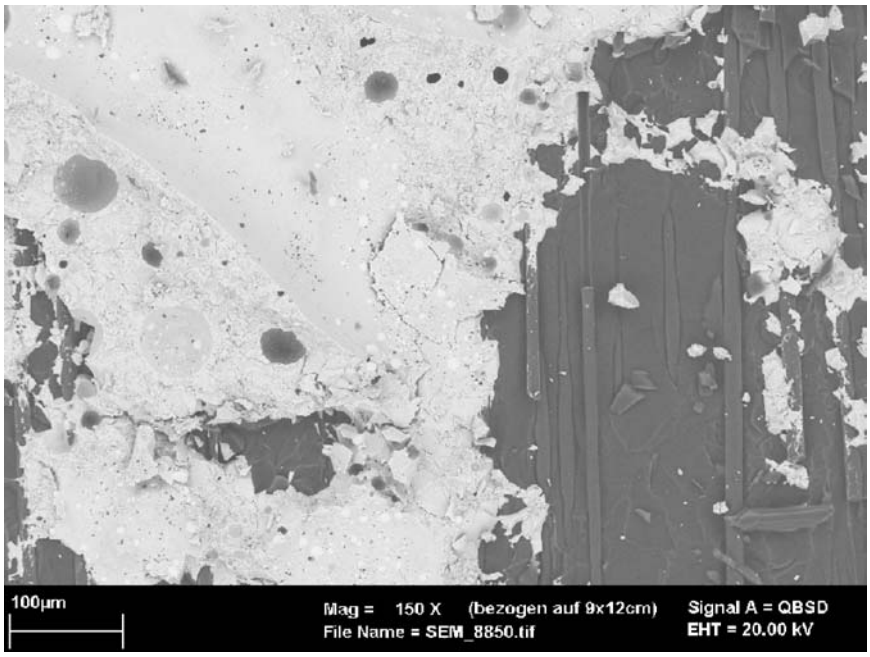


Figure 7 SEM images of the fracture surface of glass matrix composite-Mo joints obtained using glass braze. The glass braze remained adherent on the glass matrix composite surface.

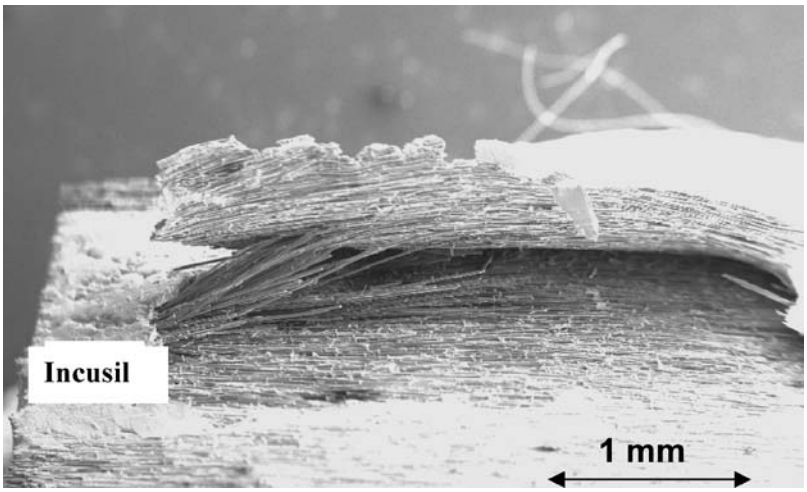


Figure 8 SEM image showing delamination of the glass matrix composite bonded to Mo by Incusil ABA (manually loaded specimens).

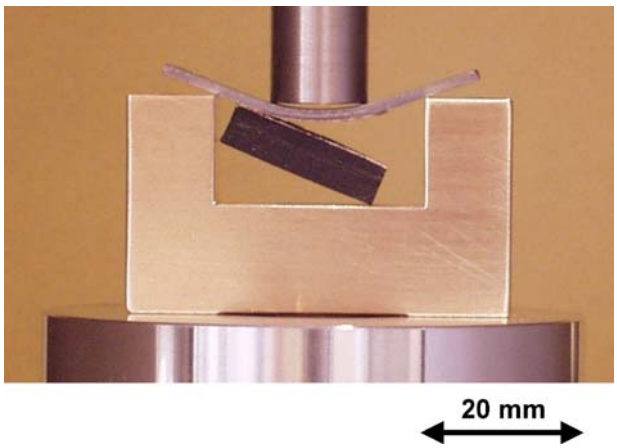


Figure 9 Image showing the deformation capacity of the joints produced with Incusil ABA (qualitative bending test).

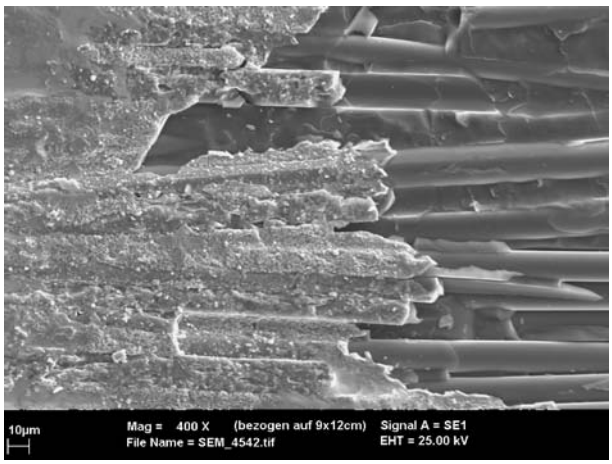


Figure 10 SEM image of the fracture surface of a glass matrix composite—Mo joint in configuration (a), brazed using Incusil ABA, indicating failure by delamination of the composite.

contrary, the joints with sand blasted surface of the metallic partner showed a significant deformation capacity. The failure occurred partially at the metal-glass braze interface, especially in the middle zone and partially at the glass composite-glass braze interface (edge zone), as shown in Fig. 7. According to these results, the brazing zone represents the weakest link of the joints and for this reason the mechanical competence of the SiC fibre reinforced glass matrix composite cannot be fully utilised.

3.1.2. Joints with incusil ABA

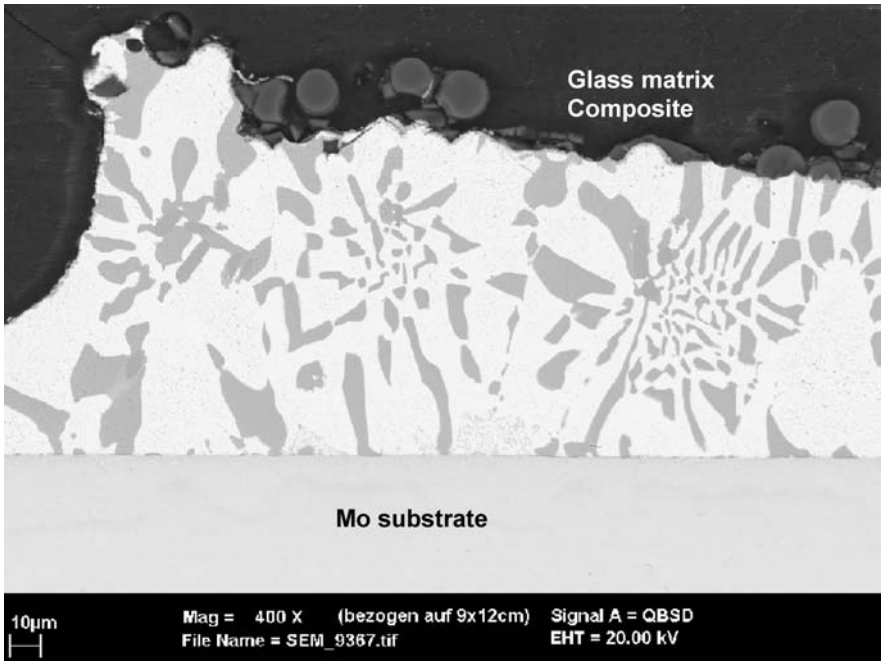
The wetting test indicated a high bonding strength of joints performed with the metallic brazing filler. This was confirmed by the manual test trying to remove the molten brazing filler from the substrate, which resulted in glass composite delamination, as shown in Fig. 8. This indicates that the joint's bond strength is higher than the interlaminar strength of the glass matrix composite. The subsequent qualitative tests on joints of configuration (a) confirmed this behaviour. The joints showed a high loading capacity, much higher than the joints made with glass braze, as it is evident in Fig. 9 (compare with Fig. 5).

Failure always occurred through the glass matrix composite by significant delamination, as the fracture surface in Fig. 10 indicates. The brazing zone as well as the Mo substrate remained intact. Moreover, no degradation of the glass matrix composite material due to thermal effects during the brazing process was observed.

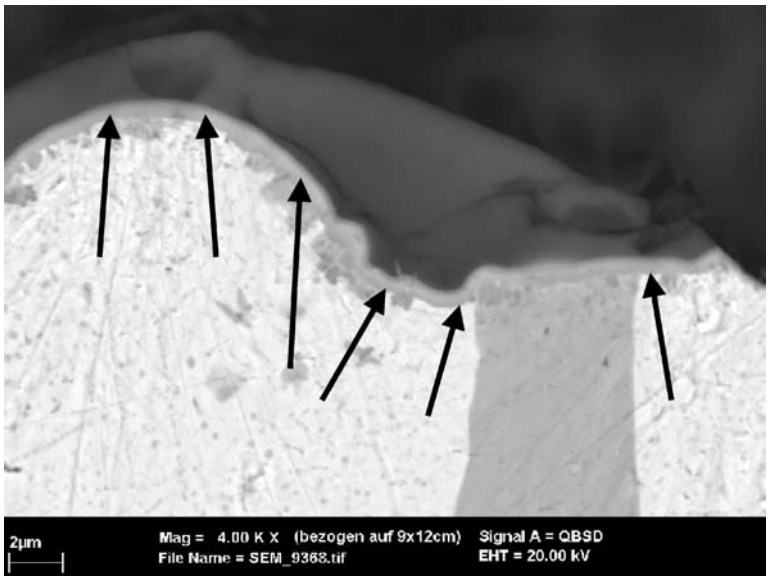
The SEM investigation showed the formation of a thin (ca. 1–2 μm) reaction zone (composed of titanium silicides and nitrides) between the Duran® borosilicate glass matrix and the Incusil ABA brazing filler, which provides a good bonding strength of the joint. The reaction zone is shown in Fig. 11a and b. The Incusil ABA contains as active filler metal 1.25 wt% titanium. It is suggested that a melt with significant Ti content should primarily react with SiO_2, which is the most abundant component of the borosilicate glass matrix material. On the other hand there should be only negligible chemical reaction between Ti and the SiC based fibres (Nicalon®) at the relatively low temperature of the brazing process.

3.2. Joints in configuration (b)

The investigation on configuration (a) indicated that the metallic filler is more suitable for the production



(a)



(b)

Figure 11 SEM micrographs showing the microstructure of the glass matrix composite/Mo joints in configuration (a), at low (a) and high (b) magnifications. A thin reaction zone at the interface between the brazing filler metal and the borosilicate glass matrix is observed, marked by arrows in (b).

of glass matrix composite—Mo joints than the glass braze. Therefore only the metallic filler was used for producing joints of configuration (b).

An average bending strength of 85MPa was measured for the joints of configuration (b) brazed in sections normal to the fibre direction. However, the failure behaviour was completely different to that observed in case of configuration (a). The joints failed at the brazing filler-glass matrix composite interface, as seen in Fig 12. Glass matrix composite delamination was not observed, fracture occurred by brittle failure at the interface. SEM micrographs of a typical fracture surface at different magnifications are shown in Fig. 13a and b. The SEM investigation on the joint cross section confirmed that there was an intact bonding between the borosilicate glass matrix and the Incusil ABA. This joint was of even better quality than the bonding achieved

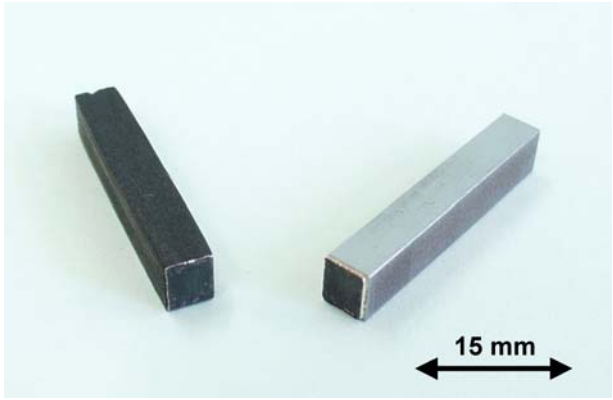


Figure 12 Glass matrix composite—molybdenum specimens of configuration (b) brazed with Incusil ABA after the bending test. Brittle failure occurred through the glass composite-brazing filler interface reaction zone.

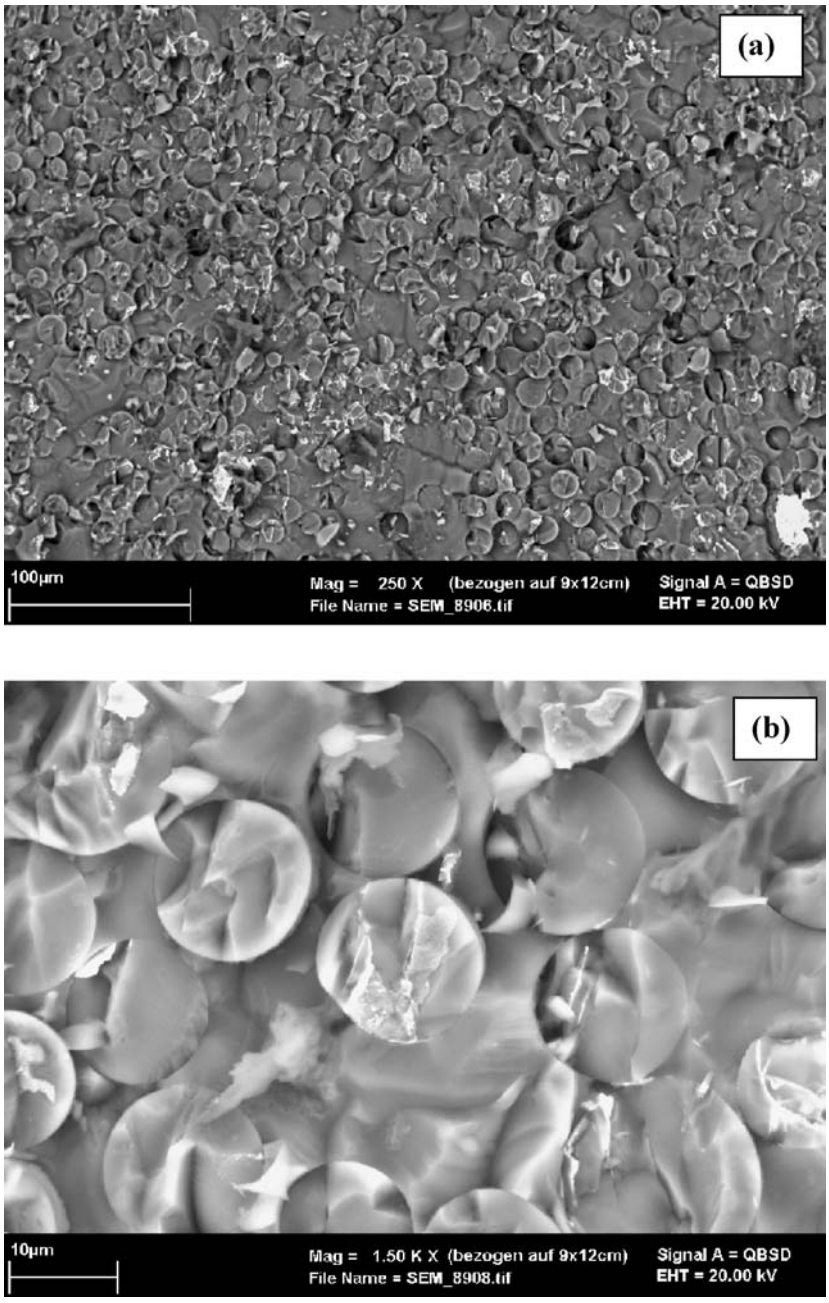


Figure 13 SEM images of the fracture surface of the specimen of Fig. 12 at (a) low and (b) high magnifications, indicating brittle fracture at the interface.

between Incusil ABA and the molybdenum plate, where small defects were detected, as marked by arrows in Fig. 14.

The detailed SEM investigation led to identification of a similar microstructure of the interface between the glass matrix composite and the Incusil ABA filler, as seen in Fig. 15. A thin reaction zone between the borosilicate glass and the Incusil ABA was found.

4. Discussion

Glass brazes and metallic active fillers have been investigated in their suitability to join a SiC fibre reinforced glass matrix composite to Mo plates. The most significant result of the present investigation is that metallic brazing fillers needing a working temperature higher than the glass transition temperature of the composite matrix can be used for joining the glass matrix

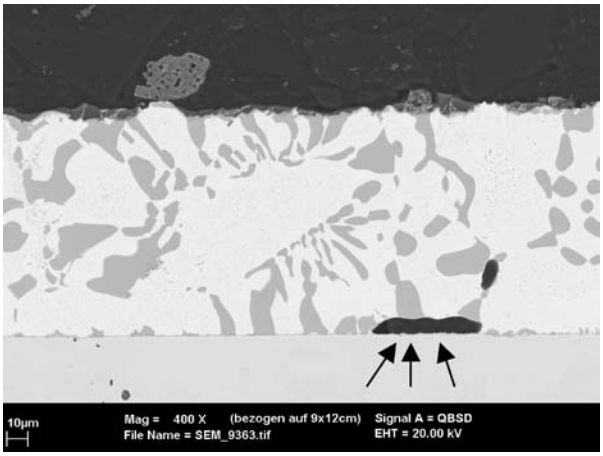


Figure 14 SEM micrograph of the joint profile in configuration (b). Lower layer: Mo substrate, middle section: Incusil ABA, upper layer: borosilicate glass matrix composite. The arrow indicates defects at the Mo/Incusil ABA interface.

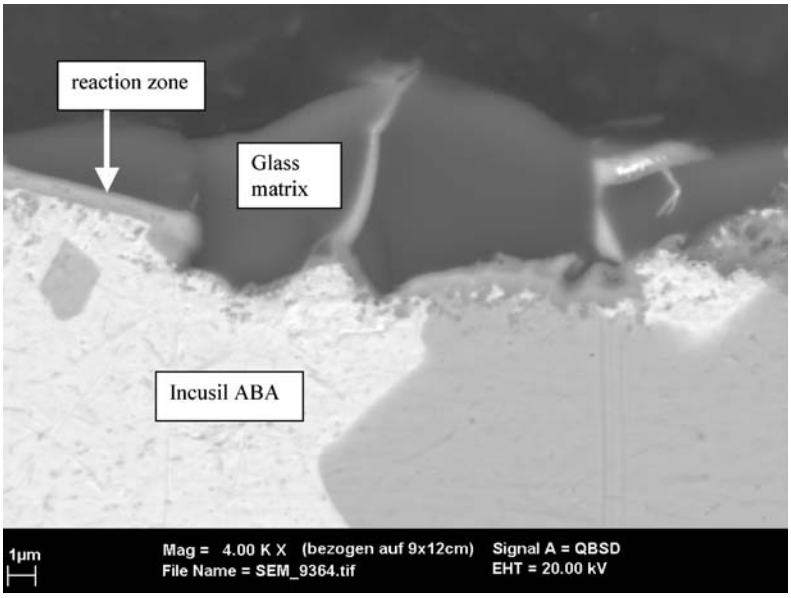


Figure 15 SEM image of the brazing zone in configuration (b) showing the thin reaction zone at the interface region between the brazing filler and the borosilicate glass matrix.

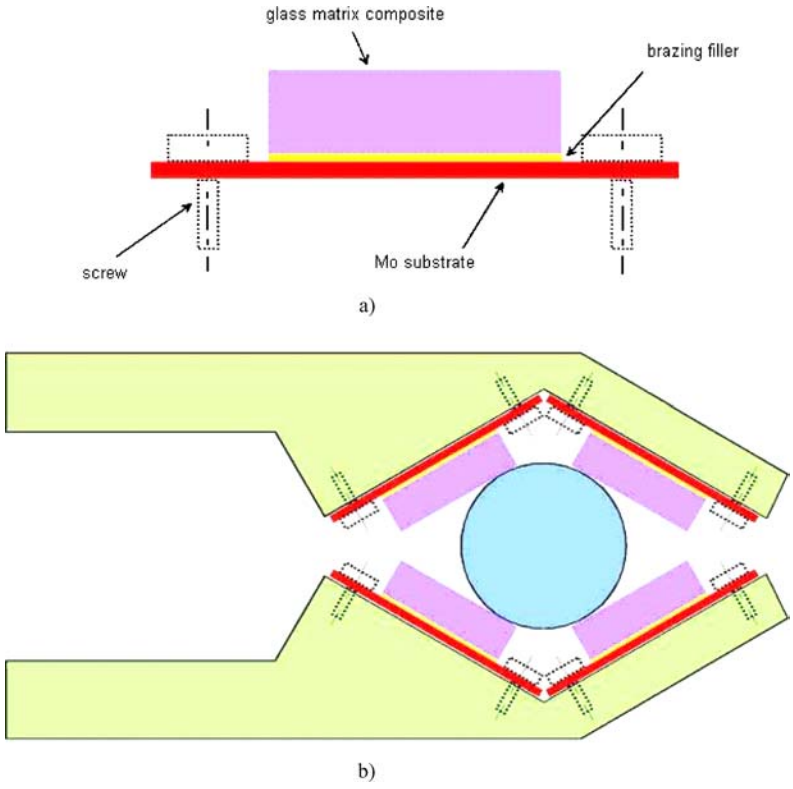


Figure 16 Possible application of the SiC fibre reinforced glass matrix composite in combination with metal parts: schematic diagram of the design of a tong for hot glassware handling.

composite to Mo. No degradation of the glass composite material was observed. The use of these fillers (e.g., Incusil ABA proposed in this study) results in joints with higher strength than that achieved using the glass braze.

In configuration (a) the properties of the glass composite can be fully utilised, as the strength of the glass composite/Mo joint is higher than the delamination stress of the composite. These joints allow application of the composite in components and parts for tools (e.g., tongs for high temperature applications) in which the glass composite must be combined with refractory metal parts [23]. A possible design of such a tool, where SiC fibre reinforced glass matrix composite-Mo joints are featured, is presented in Fig. 16. The maximum bending stress which can be applied in this configuration is limited by the interlaminar shear strength of the glass matrix composite and not by the joint strength.

In configuration (b), the load capacity of the glass matrix composite in parallel to the fibre direction could not be fully exploited. The brazing zone is the weakest link of the joint. A brittle reaction layer between the

borosilicate glass matrix and the Incusil ABA brazing filler was found in the brazing zone. No reaction between the SiC fibre and the filler metal was observed, what also indicates a weak bond between the fibre and the filler. Moreover it can be assumed that the composite/filler metal bond strength in this configuration is determined primarily by the strength of the bond between the glass matrix and the filler (which accounts for ∼60% of the cross section area) and to a lesser extent by the bond between the SiC fibres and the metallic filler (∼40% of the cross section area). Accordingly, the glass matrix will carry a load proportionally higher than that carried by the fibres, which is unsatisfactory. It is also questionable whether or not loads could be transferred to the fibres, which in this case are not well bonded to the brazing material. This result confirms what was observed in case of configuration (a) in that Incusil ABA is a suitable filler metal for joining borosilicate glass matrix composites to Mo in an appropriate configuration, in particular when the glass composite-brazing material interface consists mainly of the glass matrix-filler interface and not SiC fibres-filler interfaces.

5. Conclusions

Brazed joints of SiC fibre reinforced borosilicate glass matrix composite with Mo plates were produced, in which the favourable mechanical properties of the glass-matrix composite can be fully utilised. The active filler metal Incusil ABA was shown to be a suitable brazing material which performed better than a commercially available glass braze. A novel design of a tool for hot glassware handling, made of glass matrix composite/Mo joints, has been presented.

Acknowledgements

Prof. W. Beier and Mr. R. Liebald (Schott Glas, Germany) are gratefully acknowledged for provision of the glass matrix composite samples used in this investigation.

References

1. K. M. PREWO, The Development of Fibre Reinforced Glasses and Glass-Ceramics, in "Mat. Sci. Research Vol. 20: Tailoring Multiphase and Composite Ceramics," edited by R. E. Tressler, G. Messing, C. Pantano and R. Newnham (Plenum Press, New York, 1986) p. 529.
2. R. D. RAWLINGS, *Composites* **25** (1994) 372.
3. I. W. DONALD, *Key Eng. Mat.* **108–110** (1995) 123.
4. H. KUCKERT, G. WAGNER, U. SCHLICKER, E. ROEDER and E. EIFLER, Simulation and Reduction of Residual Stresses in Ultrasonically Welded Glass/Metal Joints, in "Proc. 5th ESG Conference: Glass Science and Technology for the 21st Century," edited by A. Helebrant, M. Maryska and S. Kasa (Czech Glass Society, Prague, 1999) p. C2–72.
5. A. R. BOCCACCINI and R. D. RAWLINGS, *Glass Technol.* **43C** (2002) 191.
6. H. L. NING. Z. T. GENG, J. S. MA, F. X. HUANG, Z. Y. QIAN and Z. D. HAN, *Ceram. Int.* **29** (2003) 689.
7. R. ARROYAVE and T. W. EAGAR, *Acta Mat.* **51** (2003) 4871.
8. S. Y. CHANG, Y. T. HUNG and T. H. CHUANG, *J. Mater. Eng. Perform.* **12** (2003) 123.
9. A. GUEDES, A. M. P. PINTO, M. VIEIRA and F. VIANA, *Mater. Sci. Eng. A* **301** (2001) 118.
10. S. D. PETEVES and M. G. NICHOLAS, *J. Am. Ceram. Soc.* **79** (1996) 1553.
11. W. TILLMANN, E. LUGSCHEIDER, R. XU and J. E. INDACOCHEA, *J. Mater. Sci.* **31** (1996) 445.
12. B. WIELAGE, F. HARTUNG, D. ASHOFF and M. TÜRPE, *Metall* **45** (1991) 454.
13. J. D. CAWLEY, *Ceram. Bull.* **68** (1989) 1619.
14. M. SINGH, *Key Eng. Mater.* **164**(1) (1999) 415.
15. M. FERRARIS, C. BADINI, M. MONTORSI, P. APPENDINO and H. W. SCHOLZ, *J. Nucl. Mater.* **215** (1994) 1613.
16. M. SINGH and E. LARA-CURZIO, *J. Eng. Gas Turbines Power, Trans. ASME* **123**(2) (2001) 288.
17. J. J. ZHANG, S. J. LI, H. P. DUAN and Y. ZHANG, *Rare Metal Mater. Eng.* **31**(Suppl 1) (2002) 393.
18. M. NAKAMURA, M. MABUCHI, N. SAITO, Y. YAMADA, M. NAKANISHI, K. SHIMOJIMA and I. SHIGEMATSU, *Key Eng. Mater.* **164**(1) (1999) 435.
19. D. G. DIXON, *J. Mater. Sci.* **30** (1995) 1539.
20. R. A. HABER and V. A. GREENHUT, Aluminum/alumina Joining in Proc. Metal-Ceramic Joining Symp. (TMS Fall Meeting, Warrendale, USA 1991) 119.
21. K. SAKATA, K. OGAWA, K. HOMMA and K. NLL, *ISIJ-Int.* **30** (1990) 1124.
22. S. WEIL, G. YANG and M. PAXTON DEAN, Joining of Mixed-Conducting Oxides to Heat Resistant Metals, in Proc. of Joining of Advanced and Specialty Materials, ASM, USA (2001) 69.
23. W. BEIER, J. HEINZ and W. PANNHORST, *VDI Berichte* Nr. **1021** (1993) 255.
24. W. PANNHORST, M. SPALLEK, R. BRÜCKNER, H. HEGELER, C. REICH, G. GRATHWOHL, B. MEIER and D. SPELMANN, *Ceram. Eng. Sci. Proc.* **11**(7–8) (1990) 947.
25. A. R. BOCCACCINI, H. KERN, J. JANCZAK-RUSCH, C. B. PONTON and K. K. CHAWLA, *Key Eng. Mat.* **164/165** (1999) 345.
26. A. R. BOCCACCINI, A. STRUTT, K. S. VECCHIO, D. MENDOZA, K. K. CHAWLA, C. B. PONTON and D. H. PEARCE, *Composites Part A* **29** (1998) 1343.

Received 12 July
and accepted 6 December 2004