Alumina–glassceramic composites[†]

SARASWATI VENKATARAMAN

Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad 500 058, India

Abstract. Alumina–glassceramic composites show good densification and uniformly distributed fine-sized particle microstructure owing to the liquid phase of the glassceramic at the sintering temperatures. The flexure strength decreases with increase in the glassceramic content. This is attributed to the dissolution of alumina at the interface resulting in a changed crystalline phase, glass coating around the matrix grains and the difference in thermal expansion. These aspects have been confirmed through expansion coefficient measurements.

Keywords. Composites; alumina matrix; glassceramics.

1. Introduction

Ceramic matrix composites are versatile and can have varied properties and applications from advanced heat engines to microelectronic substrates. In the composites the desired properties are usually tailored through the filler or the second phase—by adjusting the composition, shape, size and volume fraction of the crystallites. But the presence of second phase, especially when it is a whisker or a fibre with different aspect ratio, hinders the normal sintering and densification process owing to the inadequate packing arising from distribution in size and morphology of particles. This can be overcome by using a liquid phase in the sintering by incorporating additives melting at low temperatures (Kingery 1959). The densification behaviour with glass as filler in alumina has been studied by Ewsuk and Harrison (1990). We have studied the strength aspects of few glassceramics as fillers in alumina matrix.

Alumina–glassceramic systems have the advantage of (i) the dispersed phase itself becoming the liquid phase at sintering temperatures, (ii) weight saving as glassceramics are lighter in density (2.5–2.8 g/cc) and (iii) high insulation resistance useful for microelectronic packaging.

2. Materials and experimental methods

Initially, the glassceramics (gc) were made using the glass melt techniques described earlier (Saraswati *et al* 1992). The glassceramics are numbered as per the code we had used earlier in our preparation. Depending on the composition, the melting points of glasses were between 1400 and 1500°C and on heat treatment formed either calcium or magnesium aluminosilicates. They were mostly particulates except for diopside, which formed long whiskers. Alumina was micronized powder, wet-milled, dried and used for both as control and for the composite matrix. The glassceramics were powdered, mixed with alumina, milled and dried. The weight fraction of the dispersed phase was between 3 and 30%. Rectangular tiles of $5 \times 2 \text{ cm}^2$ were compacted and sintered at temperatures between 1450 and 1650°C. The properties studied were density, XRD phases, FTIR absorption, hardness, flexure strengths and microstructure.

[†] Paper presented at the poster session of MRSI AGM VI, Kharagpur, 1995

The densities were measured by water displacement method. X-ray powder diffraction yields lines for both the matrix and the second phase. Care was taken when the filler-induced phases were recorded especially when their weight fraction was low. Infrared absorptions were studied in the transmission mode in KBr discs using a Bomem Michelson 100 spectrometer. Leitz microhardness tester was used for estimating Vickers hardness numbers. Flexure strengths were determined by three-point method in rectangular bars 20 to 40 mm span, about 6 to 10 bars per composite material. For one composite C9, the flexure strengths have been measured as a function of second phase addition, in weight percent. SEM and EDX analysis have been done at several grain areas to evaluate the presence of ions not appearing directly in XRD or IR groups. These probably enter the silicate glass network. XRD had not shown an amorphous phase or presence of silicate in composites with spinel as the only filler phase. But IR has shown Si–O stretch modes and EDX analysis reveal presence of Si around the grains.

3. Results

Table 1 lists several properties of composites measured. The densities of composites changed with the sintering conditions e.g. for 2 h sintering at 1450°C the density for C9 was 3.32 whereas for 60 min at 1600°C it was 3.56. Hence sintering temperatures are

Table 1. Some properties of sintered composites.

	Density (g/cc)	Sinter temp. (°C)	Flex. strength (MPa)	Extra XRD phase
a/MGC (70:30)	3.2	1450	85	spinel
a/CMS (85:15)	3	1550	96	anor. spinel
a/K (70:30)	3.26	1400	110	anor, geht
a/H (70:30)	3.3	1500	90	anor, geht
a/C9 (90:10)	3.3	1450	130	spinel
a/C9 (95:5)	3.75	1600	280	spinel
a/B3 (90:10)	3.38	1600	110	Sr silicate
a/17m (70:30)	3.09	1400	110	spinel
a + M + S (84 + 8 + 8)	3.33	1600	150	spinel
10.a	3.74	1600	295	a

a alumina; MGC, CMS, C9, 17m, K, H, B3 are glassceramics; a + M + S is alumina + magnesia + silica i.e. addition of ceramics; anor, anorthite; geht, gehlenite; spinel MgAl_2O_4 .

Table 2. IR vibrational modes in composites (wavenumbers $\pm 4 \text{ cm}^{-1}$).

a/MGC	1094	788	656	614	566	466
a/CMS	1093	785	652	603	562	465
a/K	1092	—	657	615	—	466
a/H	1097	795	656	613	560	467
a/C9	1093	793	655	618	564	468
a/B3	1094	790	654	609	—	462
a/17 m	1096	792	658	608	561	461
mode	Al-O6	Si-O	Al-O4	Al-O4	Al-O6	Si-O

Figure 1. XRD in composites a/17 m, a/C9 and a/MGC. Some characteristic d spacings of spinel phase are marked.

mentioned in the table. The crystalline phases of glassceramics change after sintering because at the sintering temperatures above 1450°C they melt, dissolve some alumina of the matrix and recrystallize to a different phase on cooling. Spinel, MgAl_2O_4 , is the recrystallized phase for mica-based glassceramics, MGC, C9 and 17 m. In composites of K, H and B3, which had quartz phase had gehlenite and anorthite phases after sintering.

Table 2 gives the FTIR data and identification of the respective vibrational modes. In the glassceramics, which are essentially silicates, the IR absorption modes arise from SiO_4 molecular groups. In the composites, as the matrix volume is alumina, Al-O modes dominate. It is significant that absorptions at $650, 615 \text{ cm}^{-1}$ from tetrahedral AlO_4 groups are present. They show Al substituting for Si in the glass network i.e. solubility of alumina in the glass. Figures 1–3 show the XRD in some composites and

Figure 2. XRD in a/K and a/B3. K has anorthite and gehlenite phases whereas B3 has strontium silicate.

Figure 3. XRD in a/H and a/CMS. Some d spacings are marked.

figures 4 and 5 display the IR patterns in the glassceramic and the composites for comparison. The microstructures are shown in figures 6, 7. The EDX analysis is discussed in the text. The flexure strength variation with additive fraction is as shown in figure 8. The Vickers Hardness numbers at 200 g load were almost the same in the range 1200 to 1300 kg/mm² for the composites. A dilatometer was used for recording the linear thermal expansion up to 950°C in the composites and the expansion coefficients vary with temperature as given in figure 9.

4. Discussion

From the results we note that (i) composite densities improve when glassceramic is added, (ii) microstructure is uniformly good, (iii) crystalline phases in the glassceramics

Figure 4. FTIR in composites—*a/17m*, *a/C9*, *a/MGC*, *a/H* and *a/CMS*.

change owing to the reaction, dissolution of alumina in the liquid phase and reprecipitation, (iv) flexure strengths of almost all composites are lower than pure alumina and (v) in *a/C9* when the addition is less than 5 w% the strength is higher.

(i) to (iii) show the influence of liquid phase sintering. (iv) and (v) arise from the interface properties. In a composite with spinel MgAl_2O_4 as the filler phase, a higher strength is expected when the densification is good and microstructure uniform. But composite strength was low, almost equivalent to the filler glassceramics.

Several reasons could be ascribed to this. The clustering of matrix or filler particles can weaken the system. But as milling procedure was adopted a good homogeneous mixing was realized and we see a uniform microstructure (figures 6, 7). When the glassceramic melts at sintering temperatures above 1500°C it is in contact with alumina and it reacts. In general a silicate melt is a good solvent. Aluminium being a modifier ion in the glass network it has good solubility (Mcmillan 1979). On cooling recrystallization

Figure 5. FTIR in glassceramics 17m, C9, MGC and B3.

results in an altered phase (MGC has mica phase but a/MGC has spinel). The silicate could still remain as a glass coating around alumina grains. It is indeed so as shown in EDX by the presence of silicon around some alumina grains. Difference in the shrinkage rates of alumina and glass can create cracks and weaken the material. When there is adhesion of the second phase the matrix is prevented from stretching and so the composite is less resistive to crack propagation once it is initiated. A weaker bond helps in deflecting or arresting cracks through pullouts.

Thermal expansion mismatch of the phases creates stresses. Spinel has almost similar expansion coefficient as alumina. But the remnant glass and other glassceramic phases depending on their composition can have large coefficients. Figure 9 shows the expansion coefficient variations in alumina and the composites. MGC, H, K and 17m have the same mixing fractions. In a/MGC and a/H the expansion coefficient deviates very much from alumina. These composites have very low strengths. But the strengths

are better in a/K and a/17 m. Their expansion coefficients are closer to alumina. Thus we see that when thermal expansion coefficients are close the strengths are better. This is expected because in ceramic matrix composites thermal strains are proportional to thermal expansion coefficient differences of the filler and matrix. Further, we prepared a compact of alumina, magnesia and silica of almost similar proportion to a/MGC and

Figure 6.

Figure 6. Scanning electron micrographs of carbon-coated fractured surface in composites a/CMS, a/17m, a/MGC, a/H.

sintered at 1600°C. This did not have a liquid phase at the sintering temperature. The microstructure showed well-formed uniform grains (figures 6, 7). This had a similar, filler phase, spinel. The flexure strength was about 150 MPa, higher than glassceramic composites. Thus we note that the absence of the liquid phase while sintering has improved the strength.

Our observations have some significance. Often silicates are used as additives for improving the densification of ceramics. We observe that though liquid phase helps densification and microstructure the presence of glass weakens the matrix when the filler phase is above 5 w%. It is probable that the problem could be overcome through coating.

Figure 7.

Figure 7. SEM in alumina, AMS and glassceramics B3 and C9.

5. Conclusions

Alumina–glassceramic composites have good density and uniformly fine microstructure because of the liquid phase sintering. But the strength decreases with increase in filler content above 5w%. Without the liquid phase the strength of ceramic is reasonable. The weakening is due to the reaction of alumina with the silicate melt and bonding to the glass phase.

Figure 8. Flexure strength variation with C9 addition to alumina.

Figure 9. Thermal expansion coefficients in composites.

Acknowledgements

The authors are grateful to the Director, DMRL for his kind support and encouragement. The help of Mr Venkatrao in recording the expansion data is also acknowledged.

References

- Ewsuk K G and Harrison L W 1990 in *Sintering of advanced ceramics* (eds) C A Handwerker, J E Blendell and W A Kaysser (Ohio: Amer. Cer. Soc. inc.)
Kingery W D 1959 *J. Appl. Phys.* **30** 301
Mcmillan P W 1979 *Glassceramics* (London: Academic Press)
Saraswati V, Anjaneyulu K V S R and Visweswarrao N V 1992 DMRL TR 92159