Enhancement in strength and toughness of Al_2O_3 due to dissolution of carbon

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Abstract. An improvement in fracture toughness and strength is observed in carbon atmosphere sintered alumina on reheating the sintered samples in air at 1200°C. SEM photographs show the presence of secondary precipitate particles at grain boundaries of the sintered samples, which disappear after reheating in air. Infrared spectroscopy indicates that the C–O bond intensity increases on reheating in air. An AES/XPS study reveals that carbon enters the alumina lattice on reheating. These results lead to the conclusion that the enhanced fracture toughness and strength are related to the dissolution of precipitates and consequent dissolution of carbon in alumina lattice.

Keywords. Alumina; carbon; fracture toughness.

1. Introduction

Use of ceramics for structural applications is limited because of their low fracture toughness. Several methods are used to improve the fracture toughness of such ceramics. In case of alumina, two of the more important approaches are addition of zirconia particles or the whiskers of silicon carbide. Different mechanisms operate in the two cases leading to an appreciable enhancement in the fracture toughness. It would be obviously desirable to improve the fracture toughness of alumina further.

The properties of Al_2O_3–C system have been investigated by several workers. This system is of interest, for example, in use of Al_2O_3 as a refractory (Foster *et al* 1958) and in the production of aluminium by carbothermal reduction of Al_2O_3 (Lihrmann *et al* 1989). A small amount of free carbon is also usually present in the Al_2O_3–SiC whisker composites (Homney *et al* 1990). However, the effect of dissolution of small amount of carbon on the mechanical properties of alumina has not been documented.

In an earlier work done in our laboratory (Ramaswamy and Agrawal 1987), it was found that ZrO_2 sintered in 10^{-6} Pa oxygen pressure (which existed in the graphite furnace used for sintering) contained a high concentration of oxygen vacancies. This led to a decrease in the lattice parameter, a lower activation energy for electrical conduction and, interestingly, in a partial stabilization of the cubic phase of ZrO_2. The lattice parameter increased on reheating to 800° C in air due to diffusion of oxygen into zirconia.

The above observations suggested the possibility of enhancing the fracture toughness of alumina by incorporating in it oxygen deficient zirconia and subsequently removing the oxygen deficiency so that increase in the lattice parameter of zirconia

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would generate compressive stresses. During the course of this work it was noted that the fracture toughness of Al_2O_3 increased when subjected to a post sintering reheating treatment. The present paper deals with mechanical properties of alumina sintered in a graphite furnace and the change in these properties after subsequent reheating in air at a lower temperature. It is seen that the mechanical properties are significantly affected both by the sintering atmosphere as well as by the reheating treatment. However, unlike zirconia these changes cannot be attributed to oxygen vacancies but are believed to arise due to the presence of carbon in the sintering atmosphere.

2. Experimental

Submicron alumina powders (Sumitomo Chemical Co., Japan $0.3\,\mu m$ average size) were pressed into pellets $25\,mm\,\phi \times 3\,mm$ high and sintered at $1575°\,C$ for $1\,h$ under flowing nitrogen (99%, $30\,l\,h^{-1}$) in a furnace having resistively heated graphite elements. Heating and cooling rates were $5°\,C\,min^{-1}$. At the temperature of sintering any oxygen in the furnace atmosphere reacts with the carbon from the heating elements, reducing the partial pressure of oxygen to below $10^{-6}\,Pa$. The furnace atmosphere in this case is termed here as 'carbon atmosphere'. Some of the carbon atmosphere sintered samples were reheated in air at $1200°\,C$ for times ranging from $10\,min$ to $8\,h$.

Some samples were also sintered in air at the same temperature and at the same heating and cooling rates.

The fracture strength and fracture toughness were measured on polished rectangular bars of size $15 \times 3 \times 1\,mm$ in three-point bending. The fracture toughness, K_{IC}, was measured by single edge notched beam method on notched bars using ASTM standard test procedure (Brown and Srawley 1966). The notch was cut using a $0.5\,mm$ thick diamond blade and its depth varied between 0.35 and 0.55 of the depth of the bar. The lattice parameter of the alumina samples was measured by X-ray diffraction using a Ni-filtered Cu–Kα radiation in a diffractometer (Iso Debyeflex 2002, Rich Seifert). Infrared spectra were obtained using a Perkin Elmer 580 IR Spectrophotometer.

Characterization of alumina samples was also performed by auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) using a Perkin–Elmer, Physical Electronics, ESCA/SAM model 550. Electrons of 5 KeV and MgKα–X-rays of 300 watts energy (15 KV, 20 mA) were used as excitations for AES and XPS respectively. Relative amounts of carbon and oxygen with respect to aluminium in the as sintered and heat treated samples were determined after sputtering away the surface layers.

3. Results

Figure 1 shows the fracture toughness and flexural strength of the alumina samples as sintered in the carbon atmosphere and after reheating in air at $1200°\,C$ for various times. The fracture toughness and fracture strength of alumina samples increase by more than 50% upon reheating in air for 8 h. The lattice parameter decreases at first but then increases with increasing heating time (figure 2).

The relative density of the as sintered (carbon atmosphere) samples is about 0.9 and the average grain size is $6\,\mu m$. The fracture is intercrystalline. A remarkable observation is the presence of precipitate particles of about $0.5\,\mu m$ size at the grain boundaries
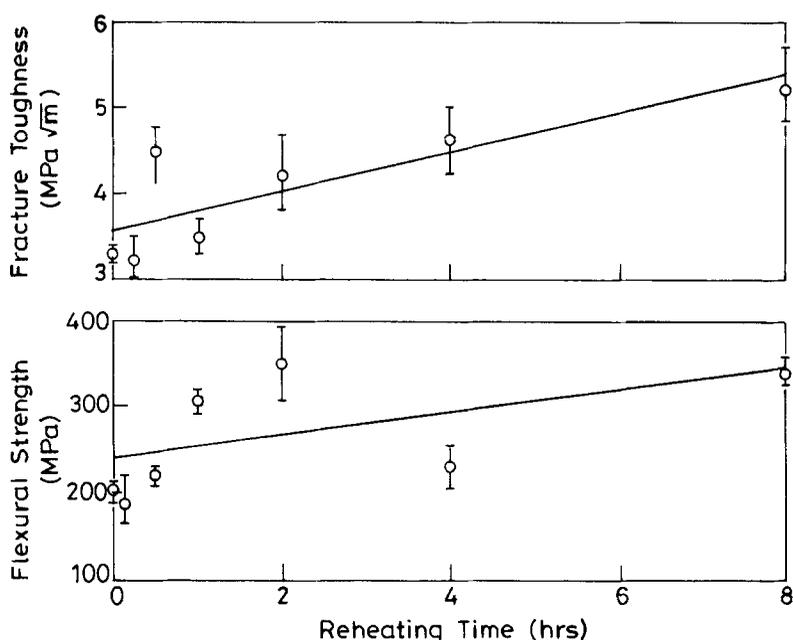
Figure 1. Changes in the fracture toughness K_{IC} and fracture strength of alumina samples on reheating in air at $1200°$ C.
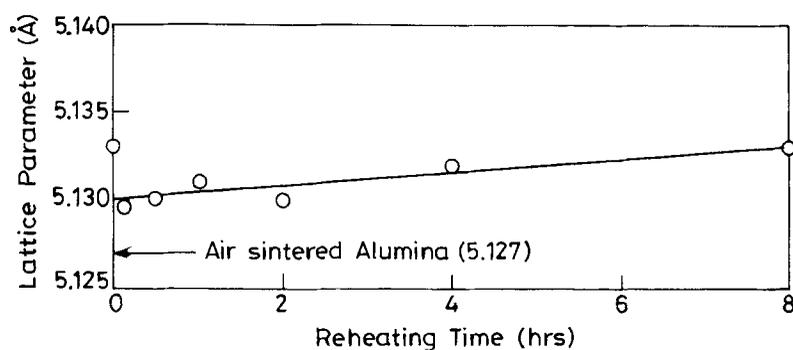

Figure 2. Changes in the lattice parameter of alumina on reheating in air at $1200°$ C.

of the as sintered samples (figure 3a). These precipitate particles are removed on reheating in air (figure 3b) but the density and grain size of the alumina samples did not change on reheating.

The infrared spectra of the carbon atmosphere sintered alumina samples shows a distinct peak at $9.0 \, \mu$m which is identified with C–O bond stretching (figure 4a). The strength of this peak clearly increases on reheating the samples in air for a long time (480 min) (figure 4b).

The AES data were analyzed to evaluate the peak to peak height ratios of two prominent transitions, namely C(KLL) and O(KLL) with respect to Al(KLL). There is virtually no difference in the O/Al peak height ratios between the air sintered sample (control sample), carbon atmosphere sintered samples (A_0) and on reheating the latter
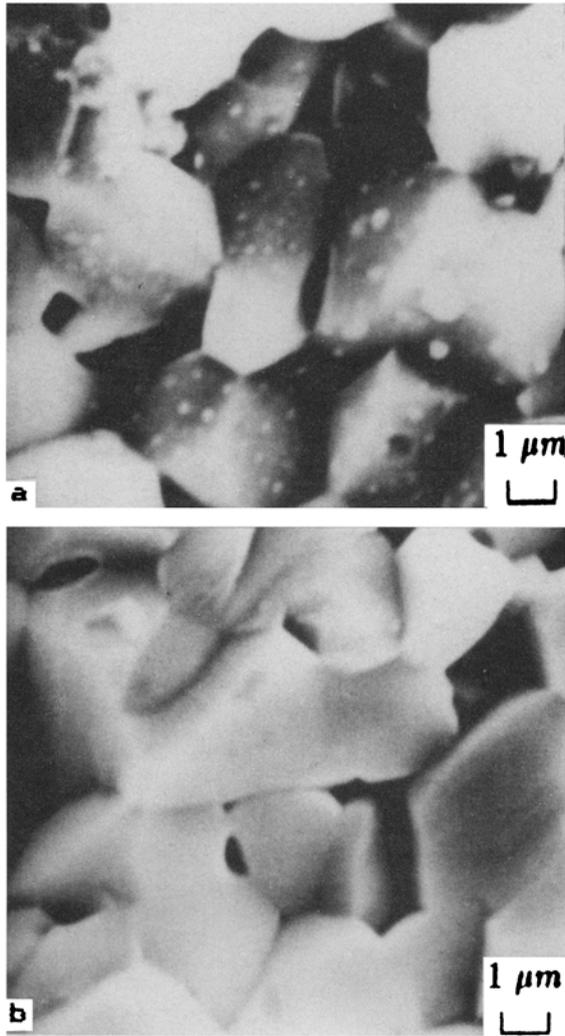
Figure 3. Scanning electron micrographs of the fracture surface of alumina samples (a) as sintered and (b) reheated at 1200° C for 8 h.

samples for 480 min in air at 1200° C (A_0). The C/Al ratios show that the concentration of carbon is slightly more in the carbon atmosphere sintered samples than in the air sintered samples (table 1). However, the ratio (C/Al) increases very significantly on reheating the nitrogen atmosphere sintered alumina samples in air at 1200° C for 480 min (table 1).

4. Discussion

The fracture toughness and strength of the air sintered and the carbon atmosphere sintered alumina are nearly the same (3, 3·2 MPa m$^{1/2}$ and 200, 240 MPa). On reheating the carbon atmosphere sintered samples in air at 1200° C, the fracture toughness and fracture strength increase by about 50%. It is this change in mechanical properties

Table 1. Peak to peak height ratio after sputter etching 200 Å from the surface of the samples.

Sample treatment	Peaks			
	O(KLL)/Al(KLL)		C(KLL)/Al(KLL)	
	Mean	S.D.	Mean	S.D.
Sintered in air (control sample)	2·37	0·13	0·19	0·04
Sintered in carbon atmosphere (sample A_0)	2·19	0·11	0·24	0·03
Sintered in carbon atmosphere and reheated in air at 1200° C for 8 h (sample A_{480})	2·06	0·15	0·47	0·04

which is quite interesting. Some of the phenomena which might occur due to sintering in a carbon atmosphere as used in the present experiments are (i) creation of vacancies, (ii) formation of one or more Al–O–C phase and (iii) incorporation of carbon in the lattice of alumina.

The slightly higher lattice parameter of the carbon atmosphere sintered alumina as compared to the air sintered alumina indicates that no significant enhancement in the oxygen vacancy concentration occurs due to the effect of the sintering atmosphere. This is supported by the result of Coble (1962) who found that alumina containing 0·25 wt% MgO sinters to theoretical density in both oxygen as well as hydrogen atmospheres. Creation of anion vacancies should lead to a relaxation of the lattice and to a decrease in the lattice parameter as observed in the case of zirconia (Ramaswamy and Agrawal 1987). In the present experiments, the lattice parameter of carbon atmosphere sintered alumina is found to increase slightly as compared to the air sintered alumina. A more direct evidence indicating that no anion vacancies are created is provided by the AES data (table 1).

These results show that oxygen concentration does not change appreciably in Al_2O_3 samples upon changing the sintering ambient from air to nitrogen and oxygen vacancies are not created upon heating the alumina samples in oxygen-deficient atmosphere.

The following phases have been reported to form in the Al–O–C system (Foster *et al* 1958; Cox and Pidgeon 1963): Al_2OC, Al_4O_4C and Al_4C_3. Out of these, the formation of Al_4O_4C is most rapid and occurs according to the reaction:

$$2Al_2O_3 + 4CO = Al_4O_4C + 3CO_2.$$
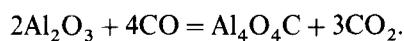
Formation of aluminium carbide due to the direct reaction:

$$Al_2O_3 + 3C = Al_4C_3 + 3/2O_2,$$
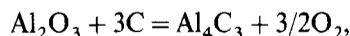
does not occur. Thus the second phase particles found at the grain boundaries (figures 3a, b) appear to be an aluminium oxycarbide, most probably Al_4O_4C. However, this could not be confirmed by X-ray due to the amount of the phase being smaller than that detectable by X-rays.

The disappearance of the second phase particles at the grain boundaries on reheating of the samples in air is accompanied by an increase in the C–O bond stretching peak in
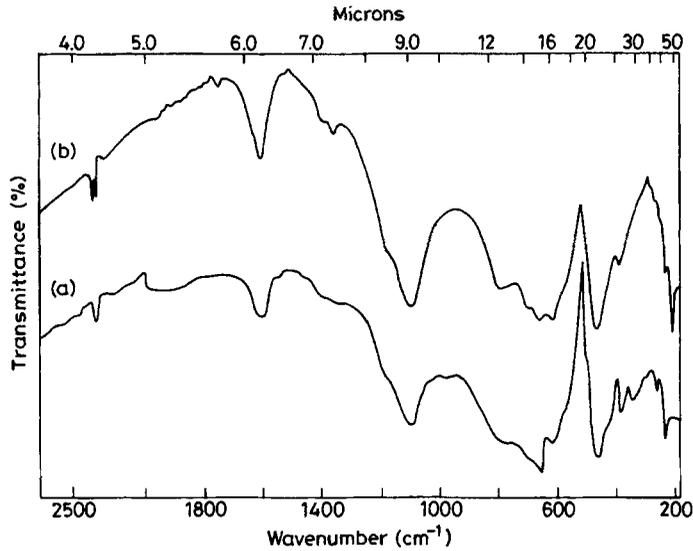
Figure 4. Infrared spectra of alumina showing C–O stretching (a) sintered in carbon atmosphere and (b) reheated in air at 1200° C for 8 h.

the infrared spectra (figure 4), and an increase by more than a factor of 2 in the C/Al ratios in the AES results (table 1).

The possibility of carbon atoms entering the alumina lattice was investigated. The results from AES on peak to peak height ratio for C/Al show that the concentration of carbon is slightly more in the carbon atmosphere sintered samples than in the air sintered samples. However, surprisingly, the concentration of carbon very significantly increases on annealing the samples in air at 1200° C for 8 h (table 1). The contribution to the carbon peaks is expected to come both from the oxycarbide phase at the grain boundaries as well as from any carbon dissolved in the lattice. Thus, as the oxycarbide phase disappears upon annealing, the C/Al peak height ratio is expected to decrease. An increase can only mean that the amount of dissolved carbon increases upon annealing. This is a surprising result. It shows that the oxycarbide precipitate is removed by a mechanism involving dissolution in the lattice.

In view of the above discussion, the enhancement in K_{IC} and strength can be attributed to the removal of the oxycarbide phase from the grain boundaries and the increased dissolution of carbon in the Al_2O_3 lattice. This is corroborated by an appreciable broadening of the X-ray peaks on reheating the carbon atmosphere sintered samples (figure 5). This indicates that the alumina lattice is strained due to the dissolution of carbon atoms in the lattice. The strain in the lattice probably results in a compressive stress in the samples thereby increasing the toughness. The behaviour is similar to that for surface strengthening of alumina due to generation of compressive stress (Kirchner et al 1968).

The enhancement in fracture toughness and strength by sintering in a carbon atmosphere and subsequent annealing in air is not limited to alumina only. We have found that such enhancement occurs in Al_2O_3–ZrO_2 composites also, over and above that due to ZrO_2 alone (Bhattacharyya 1988). Nihara (1992) also found enhancement in the strength of Al_2O_3–SiC composites by annealing in air at 1300° C.
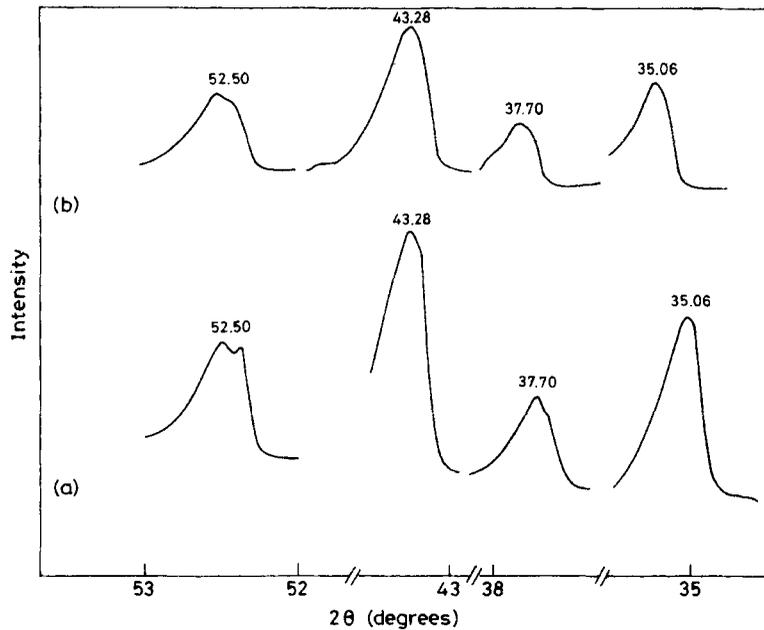
Figure 5. X-ray peaks of alumina (a) as sintered and (b) reheated in air at 1200° C for 8 h.

5. Conclusions

Alumina samples sintered in a carbon atmosphere have a precipitate phase at grain boundaries which disappears on reheating in air. The fracture toughness of alumina sintered in carbon atmosphere increases from 3 to $\geqslant 6\,MPa\,m^{1/2}$ on reheating the sintered samples in air at 1200° C. Concurrently the strength also increases with reheating time. The peak toughness and strength are obtained after 8 h of reheating. The alumina lattice is strained on reheating in air as evidenced by X-ray diffraction. AES and XPS studies indicate an increase in the concentration of C in the alumina lattice on reheating. The inclusion of C appears to be responsible for an increase in toughness and strength of alumina.

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