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DC resistivity of alumina and zirconia sintered with TiC

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Abstract. Pure alumina and zirconia powders were sintered separately with increasing amount of TiC up to ~ 65 vol.%, as a conducting second phase with an aim to prepare conducting structural ceramics which can be precisely machined by EDM technique. TiC did not help in sintering the parent phase but it decreased the d.c. resistivity of the composite to 1 ohm.cm at ~ 30 vol.% loading. The conductivity is explained by the effective media and percolation theories.

Keywords. Alumina; zirconia; titanium carbide; composite; electrical conductivity; electrical resistivity.

1. Introduction

Attempts have been made in different directions to improve the mechanical properties of the structural ceramics. Promising among them is a second phase reinforcement in the parent matrix. The ceramics of superior mechanical properties in turn give rise to time consuming finishing processes which are quite expensive. As a solution to this problem, a newer technique of finishing the components at a faster rate and at a relatively reduced cost viz. electro discharge machining (EDM) technique, has been applied in some cases. The technique essentially needs the components to be electrically conducting (resistance < 100 ohm-cm). The electrically conducting and compatible second phase materials such as nitrides (TiN), borides (TiB_2), carbides (TiC) and silicides ($MoSi_2$, Ti–Si), the electrical resistivity of which are in the range of 13–50 × 10^{-6} ohm-cm, may impart conductivity to the matrix. The reinforcing second phase may also improve mechanical properties of the material. The electrical conductivity of the matrix is directly dependent on the size and amount of the conducting second phase grains, in general (Pierson 1996).

Research in this direction was carried out mainly with engineering ceramics like Si_3N_4, SiC etc (Matkin *et al* 1972; Bellosi *et al* 1989; Mclachlan *et al* 1990; Sawaguchi *et al* 1991; Nakayama and Kuroshima 1992). Si_3N_4 when sintered with SiC nanoparticle (Sawaguchi *et al* 1991) reduced the resistivity of the composite—the effect was remarkable above 10% SiC. Resistance with 25% SiC was found to be ~ 1×10^7 Ω cm and the composite behaved like a semiconductor. The critical volume of SiC at the boundaries of sintered Si_3N_4 grains was 17% and the electrical behaviour of the composite followed the percolation theory. Up to 10% SiC increased the fracture toughness of the composite. Si_3N_4 sintered with TiN (Nakayama and Kuroshima 1992) without any other additive reduced impedance of the composite from ~ 1×10^7 Ω cm to ~ 1×10^3 Ω cm when measured in the presence of moisture. A lot of work was done on SiC based material as the use of SiC in electrical/electronic devices is wide, e.g. making heating elements, semiconductors, sensors, varistors, etc. Al_2O_3 and ZrO_2 are two other common structural engineering ceramic materials. Scanty reports are available on increasing electrical conductivity of the materials (Guicciardi 1992; Buerger 1994; Krell *et al* 1995; Mao *et al* 1998; Wang *et al* 1998) or in the related field. Mao and co-workers (1998) worked on cobalt coated Al_2O_3–TiC composite and measured only the abrasion resistance of the composite. They showed that the role of cobalt coating was important and it was responsible for wear damage. Buerger (1994) used up to 50 wt.% TiC with Al_2O_3. DC resistivity decreased from 1×10^{12} to ~ 1×10^{-3} Ω cm with 45% TiC. The conductivity was explained by the model of connectivity of TiC particles. TiC, up to 30 wt.%, increased flexural strength of the composite. Krell and co-workers (1995) used 30% TiC with ZrO_2 with or without TiH_2. TiH_2 changed the stoichiometry of TiC in the sintered matrix. The grains were free from amorphous phase; the strength and toughness of the composite was similar to 3Y-TZP. Bellosi and co-workers (1989) studied in detail the Al_2O_3 based composites. They used 20 and 30 vol.% of TiC/TiN or TiB_2 and measured the CTE, E-modulus, Vicker's hardness at 500 g load, fracture toughness, flexural strength up to 800°C, oxidation resistance and d.c. electrical resistivity. The effect of TiN on the above mentioned properties is more compared to the others. However, oxidation resistance of the composites is poor above 800°C. DC resis-

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tivity decreases to ~ 10^{-3} ohm·cm with 30 vol.% TiN and the threshold percolation volume is below 20 vol.%. They inferred that the composite may be machined by EDM technique. Wang and co-workers (1999) reported on d.c. resistivity of Si_3N_4–TiC composite and their mechanical properties. They explained the conductivity through percolation theory and calculated the threshold loading of TiC for conductivity to be 18·5 vol.%.

An attempt has been made in this work to study the d.c. electrical behaviour of pure Al_2O_3 and ZrO_2 with addition of TiC and also to optimize the amount of TiC addition. Relevance of decrease of d.c. resistivity of ZrO_2 and Al_2O_3 with TiC was explained with the help of effective media and percolation theories.

2. Experimental

Pure Al_2O_3 (HTM30, 99·5%, avg. particle size, 5 μm, Indian Aluminium Co., Kolkata), pure ZrO_2 (99·9%, avg. particle size, 10 μm, Indian Rare Earths Ltd., Thiruvananthapuram) and TiC (99·0%, avg. particle size, 16 μm, H.C. Starck, Goslar, Germany) were taken for preparation of the composites. Each composition (table 1) was mixed in pure isopropyl alcohol for 3 h. The pellets of 18 mm diameter were dry pressed uniaxially at 300 MPa and sintered at 1600°C in pure argon in a graphite resistance heated furnace for 10, 30, 90 and 180 min. Bulk density of the sintered pellets were measured by water displacement method. X-ray diffractograph of the samples were taken to detect the major phases and to know if there was any reaction. The samples with low porosity were polished progressively with 60 μm, 10 μm, 6 μm, 3 μm and 1 μm diamond paste for microstructural study. The ground pellets were coated with silver paint, cured and their d.c. resistivity was measured with a precision ohm-meter (Hewlett Packard Resistance Tester) at room temperature.

3. Results and discussion

3.1 *Sintering*

Sintered density of both Al_2O_3 and ZrO_2 composites with varying percentages of TiC was measured and is plotted in figure 1. The density is compared with the theoretical density of the composites calculated using mixture rule. Sintered density of the composites achieved in the case of Al_2O_3 (0% TiC) based composition is 78% (max. 80%) while that in the case of ZrO_2 (0% TiC) is 73% because of poorer sinterability of ZrO_2 compared to Al_2O_3 at 1600°C (even in 180 min). Sintering of alumina with TiC addition is, however, poor and the average density reduces to 67% compared to the theoretical value at 55 vol.% TiC. The average sintered density in the case of ZrO_2–TiC composites measured over the whole range of TiC addition is ~ 73% while that with Al_2O_3 drops down slowly with increase of TiC content and achieves an average value of 67% at 55 vol.% TiC content in the composites. TiC in both cases acts as an inert phase and it does not react with the parent phase. TiC acts detrimentally with alumina in forming the composites. The SEM photomicrographs of the composites with 25·68 vol.% TiC–alumina and 33·75 vol.% TiC–zirconia are shown in figures 2a and b. The second phase was seen to be evenly dispersed in the matrix. XRD result shows no reaction between the matrix and the second phase.

3.2 *DC electrical resistivity*

Figure 3 shows the reduction of d.c. resistivity of the composites with amount of TiC. The fall of resistivity of the composites is similar in nature which reaches a plateau after a critical percolation volume of TiC. The composites sintered for 180 min had the critical volume of inflexion of resistivity (j_c) at 34·0 and 26·3 vol% for ZrO_2 and Al_2O_3, respectively. The fall in d.c. resistivity is sharp for the composites sintered for shorter time and the critical percolation volume is also low compared to the others. Sintering within such a short time is very poor and the fine TiC particles are also well distributed in the matrix, while the composites sintered for longer time shows more coagulation of TiC in the matrix. Hence the critical percolation volume is more although the matrix is denser than the former. From the microstructures of Al_2O_3–TiC it is obvious that TiC is more dispersed in the matrix and the effect is reflected in the j_c values. The d.c. resistivity reduced to 1 Ω cm which is favourable for machining the matrix by EDM technique.

Table 1. Batch composition.

Sample	Wt.% Al_2O_3	Wt.% TiC	Vol.% TiC	Sample	Wt.% ZrO_2	Wt.% TiC	Vol.% TiC
A_0	100	0	0	Z_0	100	0	0
A_1	90	10	8·17	Z_1	90	10	11·72
A_2	80	20	16·67	Z_2	80	20	23·02
A_3	70	30	25·68	Z_3	70	30	33·75
A_4	60	40	34·99	Z_4	60	40	44·32
A_5	50	50	44·67	Z_5	50	50	54·43
A_6	40	60	54·77	Z_6	40	60	64·19

The d.c. resistivity of the composites may be explained with the help of percolation theory which explains the conductivity of a composite medium near a metal–insulator transition region. This theory applies, in a strict sense, only when conductivity of the low conducting phase is zero or resistivity of the high conducting phase is zero (Wang *et al* 1999) ideally. In a real case, the general effective media (GEM) equation has been postulated (Mclachlan 1988) where conductance of both media (s_h and s_l) is finite occurrence thus overcoming the limitation of the percolation theory. The equation fits accurately the conductivity for a large number of binary composite media.

In a continuous medium, comprising of an insulating medium as the parent matrix and an electrically conducting second phase, percolation theory predicts that near a conductor–nonconductor transition of the matrix, the resistivity will be given by the percolation equation

$$r_m = k\,\{(1 - j)/j_c\}^t, \tag{1}$$

where r_m is the total resistivity of the composite, j the volume fraction of high conductivity phase, j_c the criti-

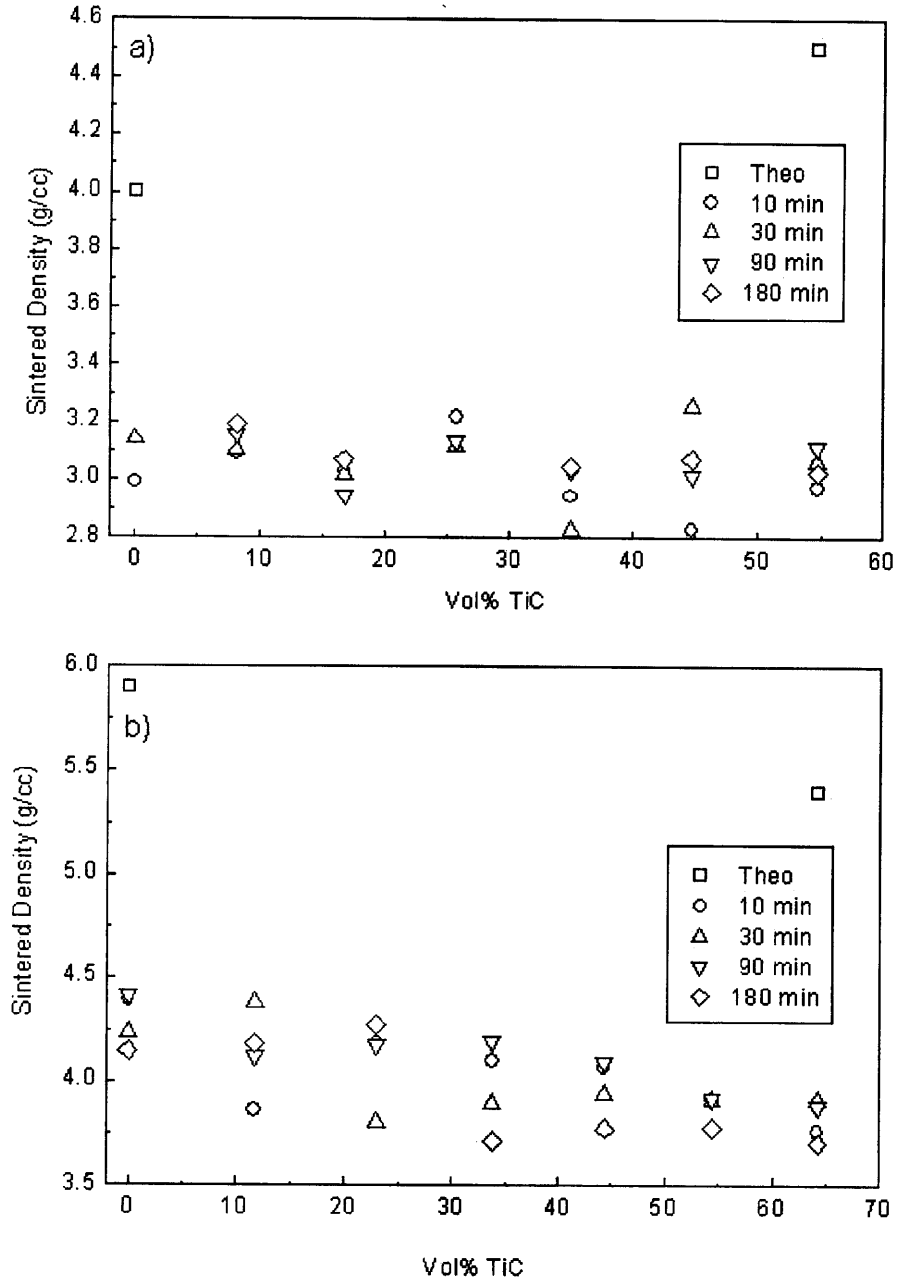

Figure 1. Variation of sintered density of (**a**) Al_2O_3–TiC and (**b**) ZrO_2–TiC with amount of TiC sintered at 1600°C at different soaking times.

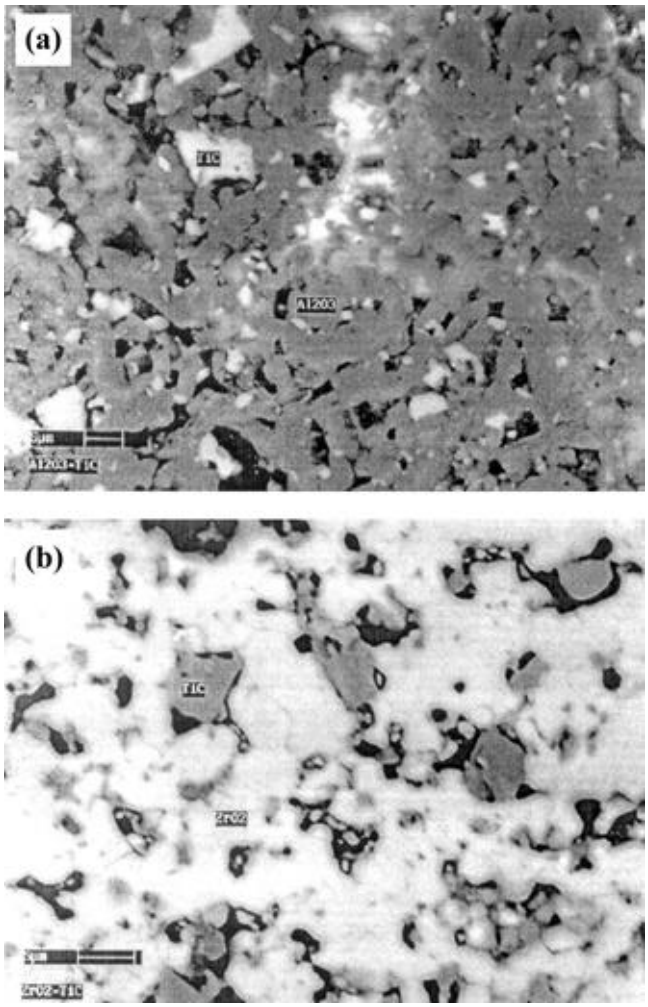

Figure 2. SEM micrograph of (**a**) 74·3 Al_2O_3–25·7 vol.% TiC composite and (**b**) 66·25 ZrO_2–33·75 vol.% TiC composite.

Table 2. Values of threshold percolation volume (j_c) and t of the composites.

Parent phase	Sintering time (min)	Threshold TiC vol. (j_c)	Value of 't'
ZrO_2	10	31·2	0·52
	90	33·5	0·10
	180	34·0	1·78
Al_2O_3	180	26·3	1·60

cal (percolation) volume fraction for the high conductivity phase and t the resistivity exponent whose values range between 1·65 and 2·00 (Balberg 1987).

Equation (1) can be written as

$$\log r_m = \log k + t \log \{(1 - j)/j_c\}, \quad (2)$$

where k is the proportionality constant.

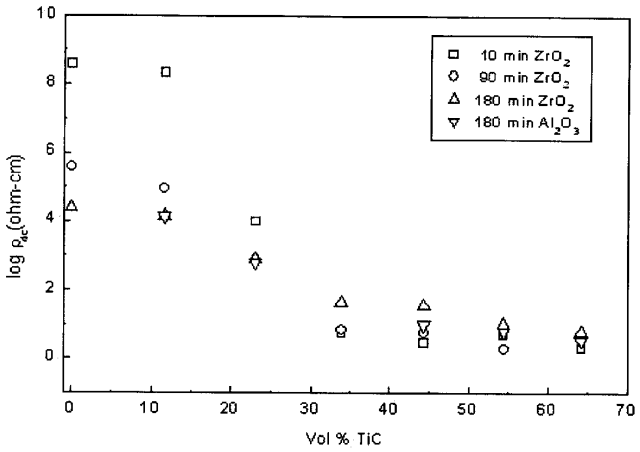

Figure 3. Variation of d.c. resistivity of Al_2O_3 and ZrO_2 composites with TiC.

The compositions of the matrix for microstructural studies were so selected that they are close to the threshold of the critical percolation volume of the systems to have an idea of the matrix. The threshold volume for such percolation in the systems are, however, dependent on the grain size and amount of the parent and the conducting second phases, shape, size and amount of the pores present in the matrix. The value of j_c seems to be on the higher side in both cases mainly because of the larger particle size of the conducting phase and the presence of pores in the matrix (table 2).

4. Conclusions

(I) TiC was of no help in sintering of alumina and zirconia at 1600°C. Sintered density of alumina, however, increased while that of zirconia decreased with addition of TiC.

(II) The minimum percolation volume of TiC in 180 min sintered alumina was 26·3 vol.% and that of zirconia, 34·0 vol.%. This volume decreased when the composites were sintered for shorter time because of non-coagulation of TiC and finer Al_2O_3.

(III) The d.c. resistivity of both composites were sufficiently low and there is a possibility of machining them by EDM technique as addition of 30 vol.% TiC also improves mechanical properties of the sintered composites, in general.

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