

High and Room Temperature Mechanical Evaluation of SiC Ceramics with Alumina and Rare Earth Oxides Additions

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Abstract. In this work, the mechanical properties of SiC samples with (5 wt%) alumina and (5 wt%) rare earth oxides (REO) additions were investigated at room and high temperatures. The possibility of using REO instead of pure yttria could bring cost reductions to obtain sintered SiC ceramics. The powders were mixed, milled, sieved and hot-pressed at 1800°C in argon atmosphere. Hardness and fracture toughness were evaluated at room temperature. The compressive creep behavior was carried out under stress range from 150 to 300MPa and temperatures of 1300, 1350 and 1400°C. After creep tests, the surface analysis of the samples by XRD and SEM showed indications of oxidation reactions, cavity and cracking. The possible creep mechanisms activated in this system were diffusion, grain boundary sliding and cavitation

Introduction

Liquid phase sintered silicon carbide with oxide additives has a good match of chemical, mechanical and thermal properties, which make this material a promising structural ceramic for high temperature applications[1-2]. The oxides additives used can be Al₂O₃-Y₂O₃:[3-8] Y₃Al₅O₁₂ (YAG);[9] AlN-Y₂O₃:[1] AlN-Lu₂O₃:[1] and Al₂O₃-AlN-Y₂O₃.[10]

Backhaus-Ricoult used hot-pressed and hipped SiC polycrystals with and without carbon and boron additions. The compressive creep tests were investigated from 1500 to 1700°C, under stress range from 100 to 1100 MPa. The achieved strain rates were between 10⁻⁹ and 10⁻⁷ s⁻¹ with stress exponent from 1.5 ± 0.3 to 4.0 ± 0.5 and activation energy from 364 ± 40 to 629 ± 30 kJ/mol. For n = 1.5 and activation energy 353 and 453 kJ/mol in a low stress range (up to 500 MPa), the creep mechanism is cavitation and for n = 3.5-4 under higher stress levels, the creep is controlled by a dislocation mechanism[11]. Biswas *et al.* used SiC ceramics with Y₂O₃-AlN and Lu₂O₃-AlN sintered under N₂ atmosphere and pressure of 10MPa at 2100°C. Four-point bend creep tests were performed in air, at temperatures from 1200 to 1500°C with stress varying from 50 to 300 MPa for 60 h. The strain rates obtained were about 10⁻⁹ (Y₂O₃-AlN, 1400°C and 100 MPa) and 10⁻¹⁰ to 10⁻⁹ s⁻¹ (Lu₂O₃-AlN, 300MPa); stress exponent of 1.3 and 1.7; activation energy up 310 to 410 kJ/mol, respectively. They concluded that creep is controlled by grain boundary sliding accommodated by grain boundary diffusion.[12]

Schneider *et al.* studied creep on SiC ceramics with Y₂O₃-AlN sintered in N₂ atmosphere at 1920-1970°C by hot isostatic pressing at 2000°C. Four-point bend tests were conducted in air, at temperatures ranging from 1300 to 1500°C, under stress of 100MPa. They obtained strain rates between 10⁻⁹ and 10⁻⁸s⁻¹. The stress exponent was 1 and the activation energy is about 400 kJ/mol. According to the authors, the linear flow-stress dependency and activation energy suggest that creep process is controlled by the grain-boundary phase.[13] Gallardo-López *et al.* sintered SiC using a proprietary (Hoecht AG) transient liquid phase with yttria and alumina additions. Compressive creep tests were carried out at temperatures between 1575 and 1700°C, under stress from 90 to 500 MPa, in argon atmosphere. The obtained results were: strain rates from 3 x 10⁻⁸ to 10⁻⁶s⁻¹, stress exponent of 1.6 ± 0,1 and activation energy of 840 ± 100 kJ/mol. They concluded that climb-controlled dislocation glide and grain boundary sliding accommodated by lattice diffusion are the operating creep mechanisms.[14] Castillo-Rodrigues *et al.* studied compressive creep in α-SiC ceramics with yttria and alumina additives sintered for 1 and 7 hours, in argon atmosphere, resulting on density of 98.8 ± 0.6 % and 94.9 ± 1.0 %, respectively. The creep tests were carried out in argon atmosphere, at temperatures from 1450 to 1625°C, under stress from 25 to 450MPa. The strain rates reached 4.2 x 10⁻⁸ to 1.5 x 10⁻⁶ s⁻¹, activation energy 680 ± 35 kJ/mol and stress exponent 2.4 ± 0.1 e 4.5 ± 0.2 (for 1 h sintering). For 7 h sintering, activation energy was 710 ± 90 kJ/mol and stress exponent 1.2 ± 0.1 e 2.4 ± 0.1. They concluded that creep mechanisms were grain boundary sliding and glide and climb of dislocation, both accommodated by bulk diffusion.[5]

Experimental Procedure

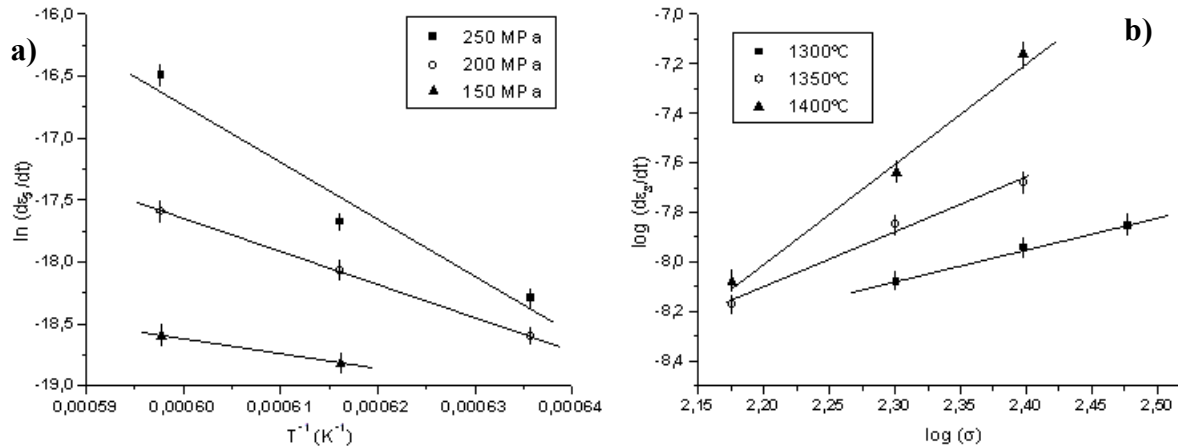
The powders used were SiC (H.C. Starck – BF12), Al₂O₃ (Alcoa – A1000) and concentrate rare earth (NUCLEMON - INB). This concentrate was calcined at 1000 °C for 1 h to obtain rare earth oxides (REO). The composition of REO after calcinations is: 75.88 Y₂O₃; 12.10 Dy₂O₃; 4.04 Er₂O₃; 1.94 Ho₂O₃; 1.32 Tb₂O₃; 0.97 Yb₂O₃; 0.86 Gd₂O₃ (wt%) and others rare earth oxides in lower concentrations. A mixture of 90 wt% SiC, 5 wt% Al₂O₃ and 5 wt% REO was milled in high-energy milling, for 1 hour. This mixture was sieved and sintered in argon atmosphere by hot-pressing under 20 MPa, with heating rate of 20°C/min until 1800°C [15] and final step of 30 min. Sintered samples density were determined by the Archimedes method. Fracture toughness (K_{1C}) and Vickers hardness were measured by indentation techniques, and K_{1C} was calculated by equation proposed by Antis *et al.*[16] The samples were cut on parallel bars (3 x 3 x 6 mm³) and polished, followed by uniaxial compressive creep tests. The creep tests were performed in air, at stress from 150 to 300 MPa, temperatures of 1300, 1350 and 1400°C, and tested during 72 h. After creep tests, the sample surfaces were investigated by XRD (Philips X'Pert – PW1380), using Cu K_α radiation and SEM (LEO-435 VPi), with backscattered electron mode, to observe contrast relative to atomic number. EDS analysis was also performed.

Results and Discussion

The sintered ceramics presented equiaxial grains morphology and micrometric grain size average. The relative density was 99.7 % of theoretical density, with Vickers hardness and fracture toughness of 23.4 ± 0.4GPa and 3.95 ± 0.07 MPa.m^{1/2}, respectively. The strain rates increased as function of the temperature and stress (Table 1). These results are compatible with reported results of SiC-based ceramics.[1,13] The activation energy (Q_c) and stress exponent (n) can be calculated using Figure 1. These results are listed on Tables 2 and 3.

Table 1 – Strain rates as function of temperature and stress.

| σ (MPa) | $d\epsilon_s/dt$ [s^{-1}] | | |
|----------------|---------------------------------|---------------------------------|--------------------------------|
| | 1300°C | 1350°C | 1400°C |
| 150 | - | $(6.7 \pm 0.5) \times 10^{-9}$ | $(8.3 \pm 0.8) \times 10^{-9}$ |
| 200 | $(8.3 \pm 0.5) \times 10^{-9}$ | $(14.1 \pm 0.8) \times 10^{-9}$ | $(2.3 \pm 0.1) \times 10^{-8}$ |
| 250 | $(11.4 \pm 0.8) \times 10^{-9}$ | $(2.1 \pm 0.1) \times 10^{-8}$ | $(6.9 \pm 0.2) \times 10^{-8}$ |
| 300 | $(1.4 \pm 0.1) \times 10^{-8}$ | - | - |

Fig. 1. Graphs: a) $\ln(d\epsilon_s/dt)$ as function T^{-1} ; b) $\log(d\epsilon_s/dt)$ versus $\log \sigma$.

Results evaluation at 1350°C ($n = 2.27 \pm 0.23$) and 150 MPa ($Q_c = 101 \pm 5$ kJ/mol), shows that activation energy can be influenced mainly by oxidation. Previous research performed by Liu [17] reported values of activation energies between 92 to 128 kJ/mol, on α -SiC with alumina and yttria additions, evaluated at temperatures from 1200 to 1350°C. Above these values, the activation energy can also be correlated to others mechanisms. Literature review in this field indicates that n between 1 and 2 are related to creep mechanism controlled by grain boundary sliding [10,18-20] accommodated diffusion [1,14,21] and $n = 2.4$ or 4.5 related to climb, dislocation and grain boundary sliding.[5]

Table 2 - Values of activation energy (Q_c) as function of applied stress (σ).

| σ (MPa) | Q_c (kJ/mol) |
|----------------|----------------|
| 150 | 101 ± 5 |
| 200 | 223 ± 12 |
| 250 | 390 ± 100 |

Based on n values (Table 3) predominant mechanism at 1300°C ($n = 1.22 \pm 0.12$) is diffusion and at 1350°C ($n = 2.27 \pm 0.23$) is grain boundary sliding accommodated by diffusion. At 1400°C ($n = 4.12 \pm 0.40$), cavitation.

Table 3 - Values stress exponent as function of creep temperature.

| $T_{\text{creep}} [^{\circ}\text{C}]$ | Stress exponent [n] |
|---------------------------------------|---------------------|
| 1300 | 1.22 ± 0.12 |
| 1350 | 2.27 ± 0.23 |
| 1400 | 4.12 ± 0.40 |

XDR analysis on sample surfaces, after creep, indicated the existence of mullite and $\text{Y}_2\text{Si}_2\text{O}_7$. Both phases are originated from oxidation reactions, considering that all samples are tested in air. SEM micrograph (Fig. 2) on the same surface microcracks, spherical cavities and other cavities with different anti-symmetrical forms can be observed. The anti-symmetrical cavities were observed on samples tested at 1350 and 1400°C (creep temperature). The microcracks observed in this work, after creep, seems to be originated from triple points junctions of grain boundary. This kind of wedge microcrack probably starts during cavities coalescence [22].

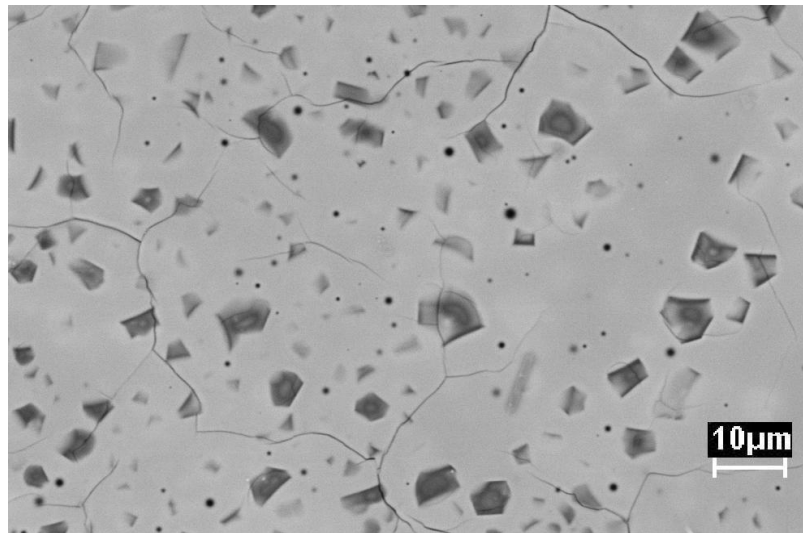


Fig. 4 - Micrographs obtained by SEM (backscattered electrons), after creep tests under 200 MPa and 1400°C.

The spherical cavities are observed on sample surfaces, after creep tests at three temperatures (1300, 1350 e 1400°C) and under different stresses. Under the same stress (200MPa) at three different temperatures, the cavities have decreasing diameter with increasing temperature. For the same temperature (1400°C), under higher tension of 250MPa, cavities diameters increase. This can be resulted from secondary phase evaporation, or higher amount of grain boundary sliding for higher tension test. According to Riedel, the grain boundary sliding seems to be the dominant factor in the cavitation, and the preferential orientation of the cavities observed on the surface generally is normal to the applied stress.[22]

Dislocations on the samples examined by SEM had not been observed. However, a more refined microscopic analysis (high resolution transmission electron microscopy) is necessary in future work, to assure the inexistence of correlated mechanisms of creep to these linear defects.

Conclusions

In all samples, there was an strong contribution of oxidation for the mullite and yttrium silicate formation. At 1300°C ($n = 1.22 \pm 0.12$) and 1350°C ($n = 2.27 \pm 0.23$) with 150MPa ($Q_c = 101 \pm 5$ kJ/mol), the system activation energy values are related to oxidation. At 1300°C, the controller creep mechanism is diffusion. At 1350°C, grain boundary sliding will prevail, still accommodated by diffusion. At 1400°C, grain boundary sliding is much higher, and can not be accommodated anymore by diffusion, and for this case, cavitation becomes operative. Dislocations in the examined samples had not been observed, but a more refined analysis must be performed in future work to eliminate the possible correlation of existing creep mechanism with these linear defects. Therefore, the possible operative creep mechanisms in this system, for the selected processing and tests conditions of this work are diffusion, grain boundary sliding and cavitation.

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