J Mater Sci (2006) 41:6497–6500
DOI 10.1007/s10853-006-0689-0

LETTER

Low temperature degradation of zirconia under a high strength electric field

Cheng Liu · Zhenbo Zhao

Received: 11 April 2006 / Accepted: 19 July 2006 / Published online: 24 August 2006

Since the fabrication of tetragonal zirconia ceramics was first reported by Reith et al. [1], yttria-stabilized zirconia polycrystal materials (Y-TZP) have always held great promise as high strength, moderate toughness engineering ceramics. However, the obvious loss of strength and toughness and instability of Y-TZP when exposed to low temperature (100–400 °C) environments limits its wide application. This is called low temperature degradation (LTD) phenomenon of Y-TZP [2–10]. All preventive methods can be grouped as either "bulk", or "surface" methods. Recently, more and more "surface" methods with different cation-stabilizers were developed due to its advantages in effective preventing LTD and maintaining its mechanical properties at the same time [3–6]. However, not too much attention has been paid to anion stabilizers. One possible reason is that the role of anion stabilizers has not been fully understood. However, ZrO_2 can be stabilized equally effectively for the prevention of degradation in Y-TZP by anions as well as cations. An example of an anion stabilizer for ZrO_2 is nitrogen, in which the nitrogen ions replace the oxygen ions to produce oxygen vacancies [11, 12]. Since carbon is the nearest element to nitrogen in both atom size and electron configuration, using carbon as an anion stabilizer, or using both carbon and nitrogen, to prevent the degradation of 3Y-TZP seemed to have potential. Also, although the effects of oxygen vacancies on LTD of Y-TZP have been known for many years [2, 4], there is no or few experimental evidence to support the involvement of vacancy migration. Kim et al. [10] showed that Y-TZP can degrade at anode side under an applied electric field. However, no clear defect diffusion model was proposed as to why the degradation can occur. Therefore, in the present work, the stability of among 3Y-TZP, a surface-carbon-doped 3Y-TZP (C-Y-TZP) and a surface-carbon and nitrogen-doped 3Y-TZP {(C + N)-Y-TZP} was studied under an applied electric field to elucidate the relationship of oxygen vacancy diffusion with LTD of Y-TZP.

Commercial raw zirconia powders containing 3 mol% Y_2O_3 were used and were uniaxially pressed at 150 MPa into pellets, 25 mm in diameter and 3 mm thick. The samples were then sintered at 1600 °C for 3 h in air and then ground and polished for the phase stability tests. A high sintering temperature of 1600 °C was intentionally used to obtain t-ZrO_2 with a relatively large grain size, which is prone to phase transformation and, thus low-temperature degradation. Some sintered samples with a mirror surface were further heat treated by a surface carburizing and a carbonitriding processes in which the sintered samples of 3Y-TZP were buried in a pure graphite or a mixed powder of ZrN and graphite powder at 1500 °C for 4 h to form C-stabilized or (C + N)-stabilized surface layers. Specimens were placed under an applied high

---

C. Liu (✉)
Department of Mechanical and Industrial Engineering,
Ryerson University, 350 Victoria StM5B 2K3, M5B 2K3
Toronto, Ontario, Canada
e-mail: bessiechengliu@yahoo.ca

C. Liu
School of Material Science and Engineering, Changchun
University of Technology, Changchun 130012, P.R. China

Z. Zhao
Unimotion-Gear, Magna Powertrain Inc, L4G 3M7 Aurora,
Ontario, Canada

strength electric field of 0.2~3.2 kV/mm in a silicon-oil bath and heated from 50 °C to 400 °C for 20 h. Phase analysis near the two surfaces of the specimens was carried out by X-ray diffraction techniques for all samples. The fraction of monoclinic phase on the surface was determined by Garvie's method [13] as follows:

$$X_m = [I_m(111) + I_m(11\bar{1})]/[I_m(111) + I_m(11\bar{1}) + I_c(111)], \quad (1)$$

where, $I_m(111)$ and $I_m(11\bar{1})$ are the intensity of the monoclinic (111) and $(11\bar{1})$ line, $I_c(111)$ is the intensity of cubic (111) line in the X-ray diffraction pattern. The average grain size was determined by scanning electron microscopy (SEM) and the line intercept method [14]. For the SEM observations, the grain boundaries were etched in air at 1450 °C for 0.5 h.

SEM showed that as-cast 3Y-TZP has a relatively narrow grain size distribution. An average value of 0.8 μm was obtained by the line intercept method [14]. The degradation of 3Y-TZP, surface-carbon-doped 3Y-TZP and surface-carbon-nitrogen-doped 3Y-TZP at 180 °C under 1 kV/mm electric field for different aging times was compared with 3Y-TZP at 180 °C without applied electric field and is shown in Fig. 1. The volume fraction of monoclinic phase for 3Y-TZP from both anode and cathode sides produced by the electric field increased in a parabolic rate law manner which shows that the transformation is controlled by a diffusion process. Although the isothermal tetragonal to monoclinic phase transformation can take place with or without an applied electric field in 3Y-YZP, the electric field significantly influences the transformation. Under an applied electric field, the m-phase content of 3Y-TZP near the anode surface is much higher than that near the cathode surface, and even higher than that of 3Y-TZP without an applied electric field. It is thus suggested that the low temperature degradation of Y-TZP results from the diffusion and migration of oxygen vacancies since only the oxygen vacancies have an effective positive charge which can migrate under an applied electric field. However, it is found that the stability of both a surface-carbon-doped Y-TZP and a surface-carbon-nitrogen-doped 3Y-TZP was not decreased significantly when a high strength electric field was applied. The stronger stability of carburized Y-TZP may be attributed to the nature of carbon in the Y-TZP lattice, where it exists in interstitial sites as an atom, rather than an ion with positive or negative charges [9]. The most stability of surface carbonitrided Y-TZP further proves the influence of oxygen vacancies on LTD since nitrogen ions will replace the oxygen ions to produce more oxygen vacancies [11, 12].

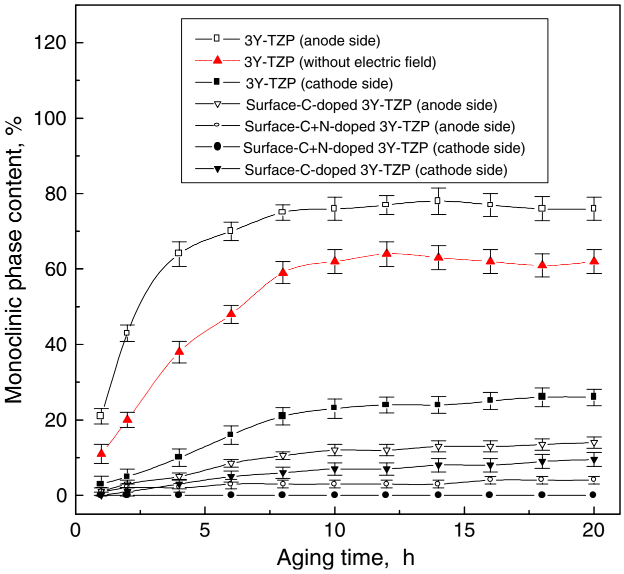

Fig. 1 Comparison of the m-phase content for 3Y-TZP, surface-carbon-doped 3Y-TZP and surface-carbon-nitrogen-doped 3Y-TZP at 180 °C under a 1 kV/mm electric field for different aging times

The influence of temperature on the degradation of 3Y-TZP and surface-carbon-doped 3Y-TZP and surface-carbon-nitrogen-doped 3Y-TZP at a constant electric field of 1 kV/mm for 8 h (the difference in m-phase between the two sides) is compared with 3Y-TZP without applied electric field in Fig. 2. It is found that the transformation can be promoted only in a specific temperature range. This might be related to the different behavior of oxygen vacancies at different temperatures since the diffusion rate of the oxygen vacancies will be typically increased as the temperature increases. However, a further increase in temperature will decrease the degradation because of the uniform distribution (no oxygen vacancy gradient anymore) of oxygen vacancies resulting from easy migration at high temperatures. The bigger difference, smaller difference, and no difference, in m-phase between the two sides for 3Y-TZP, and surface-carbon-doped 3Y-TZP and surface-carbon-nitrogen-doped 3Y-TZP under an electric field, and for 3Y-TZP without applied electric field provide further evidence for the role of an oxygen vacancy gradient on the t-phase stability.

The influence of different electric fields on the degradation of 3Y-TZP, surface-carbon-doped 3Y-TZP and surface-carbon-nitrogen-doped 3Y-TZP, at a constant temperature of 180 °C for 4 h (the difference in m-phase between the two sides) is shown in Fig. 3. As for the influence of temperature on degradation, it is found that the degradation has a maximum value

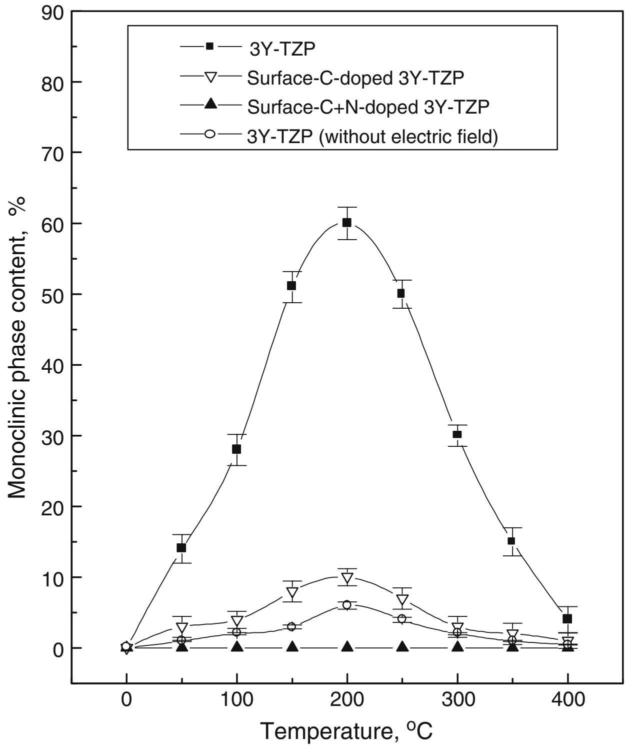

Fig. 2 Influence of temperature on degradation of Y-TZP at a constant electric field of 1 kV/mm for 8 h

at specific electric field strength for each category of samples. When the electric field is low, any increase of electric field increases the potential gradient and thereby increases the migration rate of the vacancies.

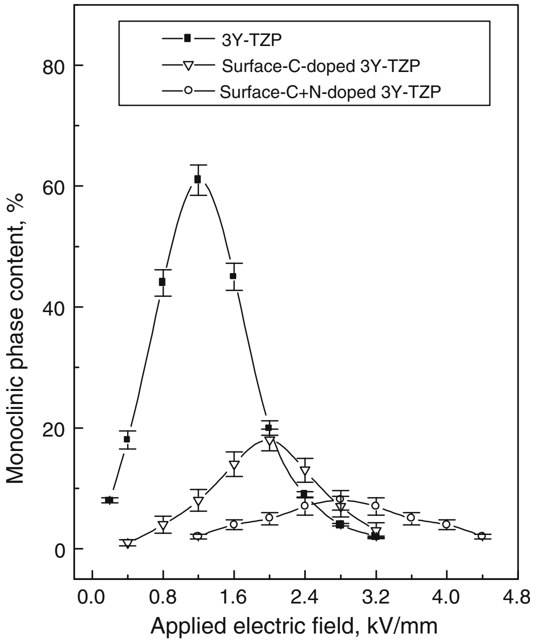

Fig. 3 Influence of electric field on degradation of Y-TZP at constant temperature of 180 °C for 4 h

As the electric field is further beyond that producing maximum degradation, the sample temperature will increase because of the ionic currents, which generate heat in insulators. When heat is produced faster than it is dissipated, because of the low thermal conductivity of 3Y-TZP, electric current can flow between the electrodes by electrical breakdown. The different peak (degradation) positions for the three samples can be attributed to the effects of carbon and nitrogen on the lattice and any associated stress distribution changes on the surface of samples since all studies show that a residual stress accumulation on the specimen surface is the key point for the stability of Y-TZP under LTD [15–17].

According to the Zr–ZrO_2 phase diagram [18], the oxygen vacancies in zirconia can lower the phase transition temperature and enlarge the cubic and tetragonal phase areas. Any decrease in the oxygen vacancy concentration, will increase the instability of the high-temperature phases at a given temperature. Kountouros and Petzow [19] showed that a homogeneous distribution of oxygen vacancies plays a very important role in the nature of stabilized ZrO_2. For example, regions with low vacancy concentration favour the m-phase, or a high vacancy concentration tends to form the c-phase with large grains. It is believed that each oxygen vacancy has an area of responsibility, or affected area, in the crystal lattice. Both the phase stability and the grain size of ZrO_2 are dependent on critical vacancy concentration. Figure 4B shows a 3Y-TZP grain and Fig. 4C shows 3 mol% ytrria created oxygen vacancies in a 3Y-TZP grain at constant grain size. The affected/responsible area of each vacancy is represented by a shaded circle around the vacancy. Continuous increase of the vacancy concentration with constant grain size could be possible up to a certain concentration (maximum vacancy solubility). After exceeding the maximum concentration responsible for the t-phase, the phase as well as the grain size has to change because the small grain size can not afford such high vacancy concentration. Therefore, the t-phase has to transform to the c-phase. An alternative explanation is that, the non-transformable t'-phase is a t-phase grain with a high oxygen vacancy concentration which normally occurs in the c-phase. Under a high strength applied electric field, the oxygen vacancy will migrate from the anode side to the cathode side. The depletion of oxygen vacancies from the anode side forces the grain to change from the t-phase to the m-phase because the affected/responsible area of the vacancies can not cover the extended area and a nucleus is formed (dark shaded triangle region in Fig. 4A). The nucleus could

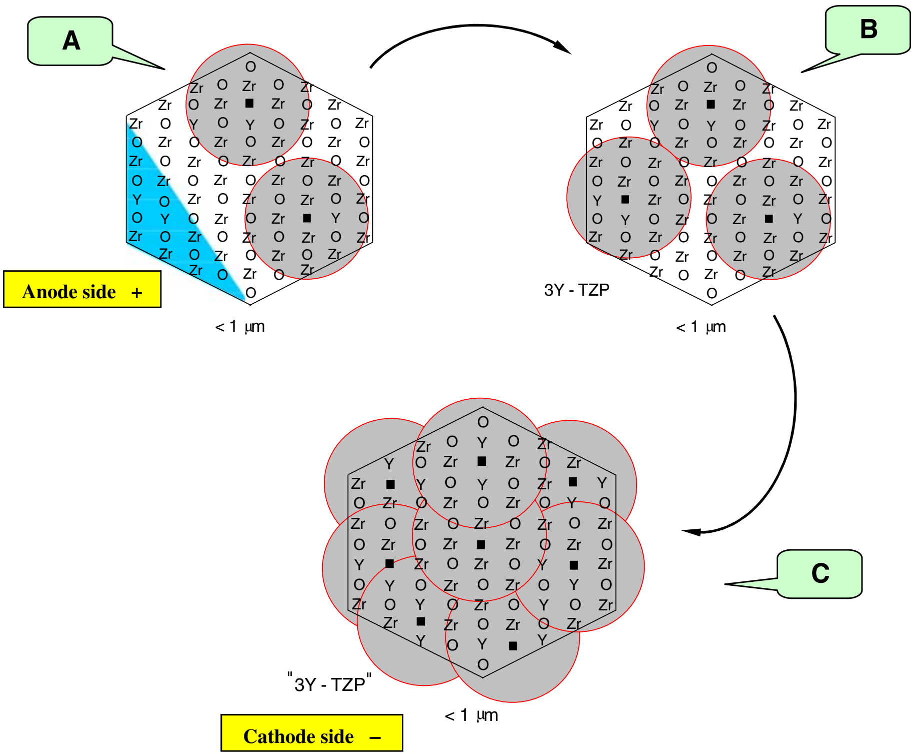

Fig. 4 The influence of an applied electric field on the oxygen vacancy migration and phase stability of a 3Y-TZP

be an area of the crystal lattice in which the vacancy concentration is not high enough (lower than the critical minimum) in order to keep the phase metastable. Therefore, the nucleation (free energy) barrier is surmounted and the grain transforms into the m-phase.

In conclusion, the influence of the high strength electric field on the degradation of 3Y-TZP shows that oxygen vacancies play an important role. The volume fraction of monoclinic phase produced by the electric field increased in a parabolic rate law manner, which shows that the transformation is controlled by a diffusion process. The effect of temperature at a constant electric field on the degradation shows that the transformation can be promoted only in a specific temperature range.

References

1. Reith PH, Reed JS, Nauman AW (1976) Bull Amer Ceram Soc 55:717
2. Lepisto TT, Mantyla TA (1989) Ceram Eng Sci Proc 10:658
3. Zhao Z, Liu C, Yu X, Ni G (1997) Rare Metal Mater Eng 26:50
4. Zhao Z, Northwood DO (1999) Ceram Eng Sci Proc, Amer Ceram Soc 20:95
5. Zhao Z, Liu C, Northwood DO (1999) Mater Design 20:297
6. Zhao Z, Liu C, Northwood DO (2000) Ceram Eng Sci Proc, Amer Ceram Soc 21:619
7. Zhao Z, Liu C, Northwood DO (2000) J Aust Ceram Soc 36:135
8. Zhao Z, Liu C, Northwood DO (2001) Ceram Eng Sci Proc, Amer Ceram Soc, 22:59
9. Zhao Z, Liu C, Northwood DO (2003) Key Eng Mater 233–236:655
10. Kim D, Jung H, Jang J, Lee H (1998) J Am Ceram Soc 81:2309
11. Cheng Y, Thompson DP (1993) J Amer Ceram Soc 76:683
12. Chung T, Song H, Kim G, Kim D (1997) J Amer Ceram Soc 80:2607
13. Garvie RC, Nicholson PS (1972) J Am Ceram Soc 55:303
14. Fullman RL (1953) J Metal Trans, AIME 197:447
15. Schmauder S, Schubert H (1986) J Amer Ceram Soc 69:534
16. Li P, Chen I-W, Penner-Hahn JE (1994) J Amer Ceram Soc 77:1289
17. Li P, Chen I-W, Penner-Hahn JE (1994) J Amer Ceram Soc 77:118
18. Rauh EG, Garg SP (1980) J Am Ceram Soc 63:239
19. Kountouros P, Petzow G (1993) In: Badwal SPS, Bannister MJ, Hannink RHJ (eds) Science and Technology of Zirconia V. Technomic Publishing, USA, pp 30–43