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Effects of $Sr_2Nb_2O_7$ additive on microstructure and mechanical properties of 3Y–TZP/Al_2O_3 ceramics

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Abstract

The effects of $Sr_2Nb_2O_7$ additive on microstructure and mechanical properties of 3Y–TZP/Al_2O_3 ceramics were investigated. $Sr_2Nb_2O_7$ reacted with Al_2O_3 to form $SrAl_{12}O_{19}$ platelets, which could contribute to the fracture toughness due to the elongated grains. The fraction of transformable tetragonal zirconia phase increased firstly with the $Sr_2Nb_2O_7$ content and then decreased when the additive content is beyond a critical value. Also, the fracture toughness increased firstly to a maximum value (10.2 MPa.m$^{1/2}$) with the additive content and then decreased for composites sintered at 1600 °C for 6 h, while it increased linearly with additive content for composites sintered at 1575 °C for 6 h. However, the Vickers hardness decreased linearly with the $Sr_2Nb_2O_7$ content for composites sintered under any condition investigated here. The fracture toughness was affected by the fraction of transformable tetragonal zirconia phase and $Sr_2Nb_2O_7$ content, and the toughening effects should be the integrated result of stress-induced transformation toughening and elongated grain toughening. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Microstructure; C. Mechanical properties; 3Y–TZP/Al_2O_3 ceramics; $Sr_2Nb_2O_7$ additive

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1. Introduction

Zirconia toughened alumina (ZTA) ceramics had been well documented in the past two decades [1–8]. According to previous works, the major toughening mechanisms were stress-induced transformation toughening and microcracking toughening. And improvement of fracture toughness depended on many factors, including particle size, nature of polymorph, content of zirconia and ZrO_2 particle distribution [4,7–8].

On the other hand, Chen et al. [9] proposed a novel toughening approach, in which a piezoelectric and/or ferroelectric secondary phase was introduced into the ceramic matrix as a toughening agent and the energy dissipation and/or conversion due to domain wall motion and piezoelectric effect were considered as a new toughening mechanism. The so-called piezoelectric secondary phase toughening approach was successfully applied in the systems: $BaTiO_3/Al_2O_3$ [9], $Nd_2Ti_2O_7/Al_2O_3$ [10] and $Sr_2Nb_2O_7$/3Y–TZP [11,12].

In the present work, $Sr_2Nb_2O_7$ ferroelectric secondary phase was introduced into the 3Y–TZP/Al_2O_3 ceramic matrix, and the effects of the secondary phase on microstructure and mechanical properties were investigated.

2. Experimental procedure

High-purity alumina (α-Al_2O_3, purity >99.9%), 3Y–TZP (3 mol% yttria-doped tetragonal zirconia polycrystal, purity >99.9%), and synthesized $Sr_2Nb_2O_7$ were used as starting materials. The synthesis route of $Sr_2Nb_2O_7$ powder had reported before in detail [11,12]. First, ZTA powder was prepared according the form of $45ZrO_2{\cdot}55Al_2O_3$ (vol.%). Then, $xSr_2Nb_2O_7/(1-x)$ ZTA composite powders ($x=0.0$, 0.005, 0.01, 0.015, 0.02) were mixed by ball milling with zirconia media in ethanol for 24 h. After drying, such mixed powders were pressed into disc compacts of 12 mm in diameter and 1 to 4 mm in height, and these compacts were sintered in the range 1550 °C to 1600 °C in air for 6 h.

The microstructures were evaluated by scanning electron microscopy (SEM, HITACHI S-570), and the phase constitution of the composite ceramics was characterized

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by X-ray powder diffraction (XRD) analysis using CuK_α radiation. The tetragonal fraction of ZrO_2 in the composites was calculated with the relation of Garvie and Nicholson [13], and the fraction of transformable tetragonal phase was the difference of the tetragonal zirconia fraction of as-sintered surface and crush powder.

The fracture toughness was evaluated by the modified indentation method [14,15] at room temperature using a diamond Vickers indenter with a loading time of 15 s at a constant load of 100 N. The results were averaged over six indentations per specimen and the following formula was used for the calculation:

$$(K_{1C}\phi/Ha^{1/2})(H/E\phi)^{2/5} = 0.035(l/a)^{-1/2} \qquad (1)$$

where K_{1C} was the toughness of the composite ceramic, H the Vickers hardness, E the effective elastic modulus, ϕ the constraint factor (≈ 3), l the length of the crack, and a the half diagonal length of an indentation.

3. Results and discussion

Dense $x\mathrm{Sr_2Nb_2O_7}/(1-x)\mathrm{ZTA}$ composites can easily be obtained when the sintering temperature is higher than 1575 °C and $x < 1.5$ mol%, and their relative densities are shown in Table 2, where the theoretical density is calculated using a mixture rule. The SEM micrographs of $x\mathrm{Sr_2Nb_2O_7}/(1\text{-}x)\mathrm{ZTA}$ composites (Figs. 1 and 2) show that some elongated grains appear when $Sr_2Nb_2O_7$ secondary phase is incorporated into the ZTA ceramic matrix. XRD patterns of these composites confirm that $SrAl_{12}O_{19}$ secondary phase is formed in situ during sintering (Figs. 3 and 4). According to Cutler et al. [16], the following reaction occurs during sintering

$$\mathrm{Sr_2Nb_2O_7} + 12\mathrm{Al_2O_3} \rightarrow 2\mathrm{SrAl_{12}O_{19}} + \mathrm{Nb_2O_5} \qquad (2)$$

Also, the authors find that it is difficult to form strontium aluminate platelets in situ in Y–TZP ceramics, while the present work is just based on the 3Y–TZP/Al_2O_3 ceramic matrix. On the other hand, the fraction of tetragonal zirconia phase decreases with the introduction of $Sr_2Nb_2O_7$ (see Table 1). However, the fraction of transformable tetragonal zirconia phase increases to a critical value firstly and then decreases to very low level. This is consistent with our previous work [11,12], and the reason is that there exists a critical grain size for stabilizing the tetragonal zirconia phase at the room temperature.

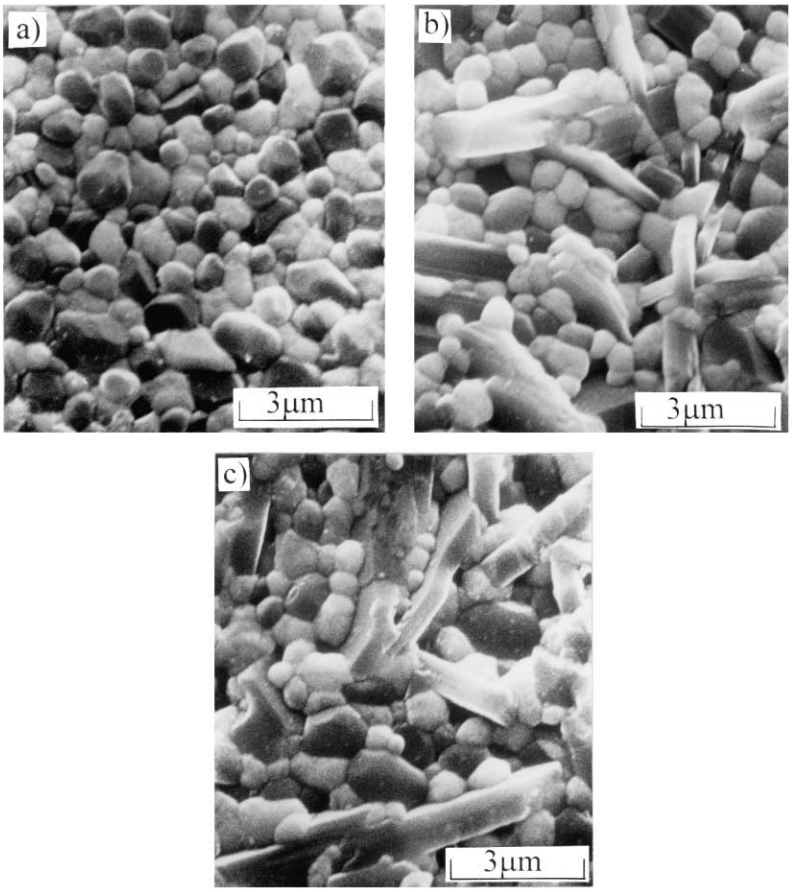

Fig. 1. Scanning electron microscopy images of polished surfaces of $x\mathrm{Sr_2Nb_2O_7}/(1-x)\mathrm{ZTA}$ sintered at 1575 °C for 6 h: (a) $x = 0$ mol%, (b) $x = 0.5$ mol%, (c) $x = 1$ mol%.

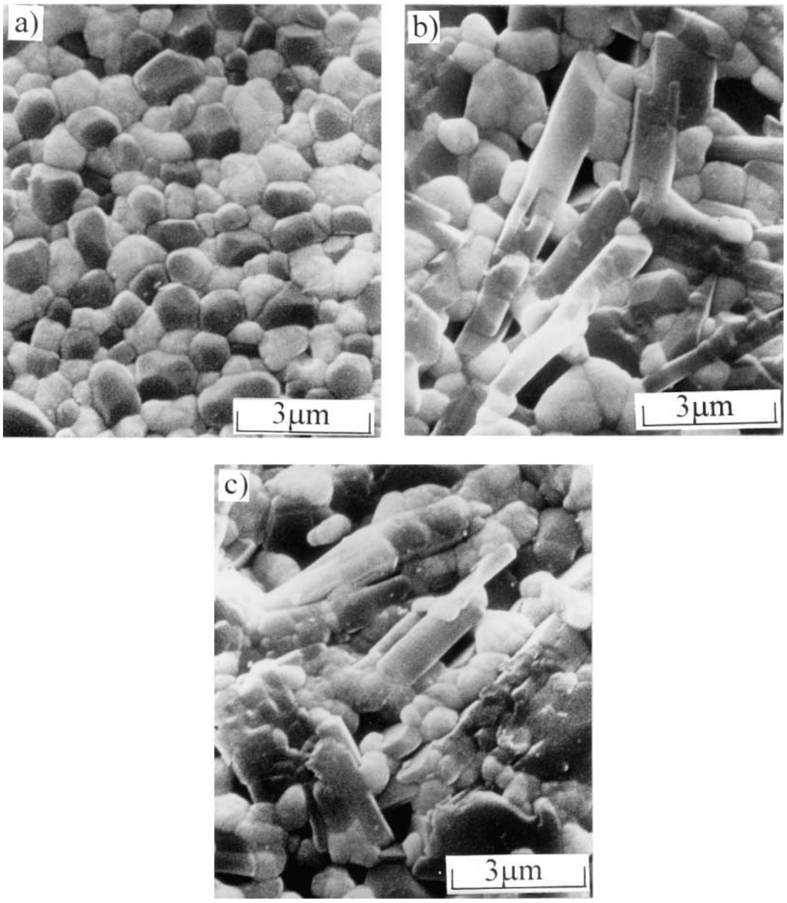

Fig. 2. Scanning electron microscopy images of polished surfaces of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$ZTA sintered at 1600 °C for 6 h: (a) $x=0$ mol%, (b) $x=0.5$ mol%, (c) $x=1$ mol%.

Table 1
Relative density, phase constitution and transformable tetragonal fractions of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$ZTA ceramics sintered under different conditions

Sintering condition	x	Phase constitution[a]	Volume fraction of tetragonal phase[b]	Transformable tetragonal fraction
1575 °C/6 h	0.000	A + T	100%	24.8%
	0.005	A + T + M + SA	89.3%	50.5%
	0.010	A + T + M + SA	48.8%	33.6%
1600 °C/6 h	0.000	A + T	100%	28.1%
	0.005	A + T + M + SA	59.5%	28.1%
	0.010	A + M + T + SA	17.4%	8.7%

[a] A—α-Alumina, T—tetragonal zirconia, M—monoclinic zirconia, SA—strontium aluminate

[b] On as-sintering surface.

The introduction of $\mathrm{Sr_2Nb_2O_7}$ secondary phase significantly enhances the fracture toughness of ZTA ceramics, and the maximum toughness value reaches 10.2 MPa.m$^{1/2}$ for the composites $x=0.5$ mol% sintered at 1600 °C for 6 h, while that of the matrix is 6.9 MPa.m$^{1/2}$. For composites sintered at 1600 °C for 6 h, the fracture toughness increases with $\mathrm{Sr_2Nb_2O_7}$ content to a maximum value firstly and then decreases when the additive content is beyond a critical value, while for composites sintered at 1575 °C for 6 h, the toughness straightly increases with additive content. However, the Vickers hardness decreases straightly with the $\mathrm{Sr_2Nb_2O_7}$ content under any condition investigated here, and the effect of sintering temperature is not obvious (see Table 2).

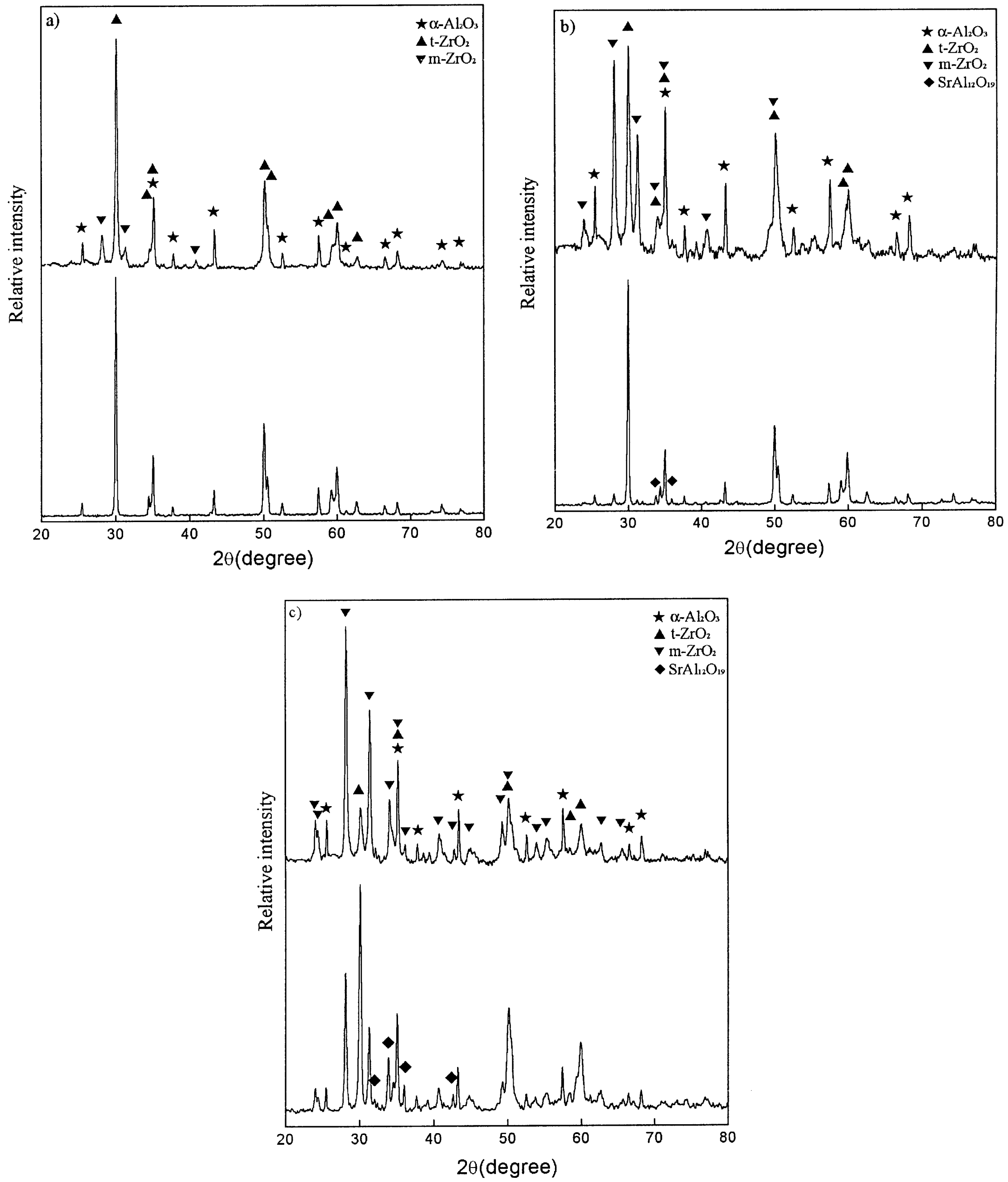

Fig. 3. XRD patterns of as-sintered (lower) and crushed powders (upper) for $x\mathrm{Sr_2Nb_2O_7}/(1-x)$ZTA ceramics sintered at 1575 °C for 6 h: (a) $x = 0$mol%, (b) $x = 0.5$ mol%, (c) $x = 1.0$ mol%.

Table 2
Relative density, Vickers hardness and fracture toughness of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$ZTA ceramics sintered under different conditions

Sintering condition	X	Relative density	Hv (GPa)	K_{IC} (MPa.m$^{1/2}$)
1575 °C/6 h	0.000	98.2%	15.2	6.9
	0.005	100%	14.0	7.6
	0.010	97.6%	11.6	8.0
1600 °C/6 h	0.000	98.7%	15.1	6.9
	0.005	100%	14.0	10.1
	0.010	98.8%	11.5	8.7

According to previous works [17,18], aluminate platelets ($\mathrm{LaAl_{11}O_{18}}$, $\mathrm{LaMgAl_{11}O_{19}}$, $\mathrm{SrAl_{12}O_{19}}$ and $\mathrm{Mg_2NaAl_{15}O_{25}}$) can improve the fracture toughness due to the elongated grains. Note that the piezoelectric effect is absent for $\mathrm{SrAl_{12}O_{19}}$ crystals which belong to central symmetric point groups (P6/mmm) and the piezoelectric secondary phase toughening can not be expected. Therefore, the toughening effects in the present composite ceramics are primarily attributed to stress-induced transformation toughening and elongated grain toughening. The fracture toughness linearly increases with $\mathrm{Sr_2Nb_2O_7}$ content for composites sintered at 1575 °C

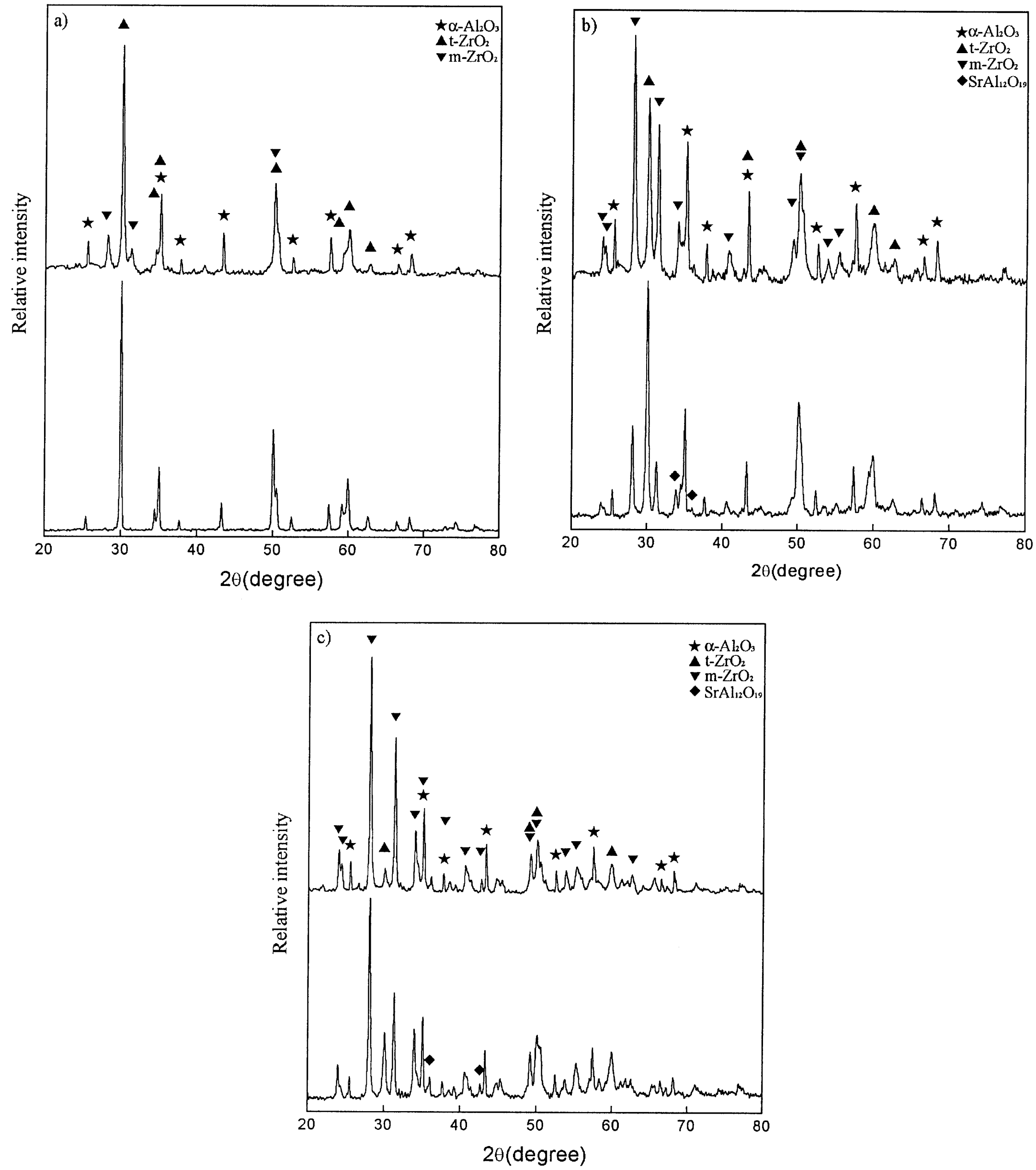

Fig. 4. XRD patterns of as-sintered (lower) and crushed powders (upper) for xSr$_2$Nb$_2$O$_7$/(1$-x$)ZTA ceramics sintered at 1600 °C for 6 h: (a) $x=0$ mol%, (b) $x=0.5$ mol%, (c) $x=1.0$ mol%.

for 6 h, while that of transformable tetragonal zirconia fraction firstly increases to a maximum value and then decreases when additive content is beyond a critical value (Figs. 5 and 6). On the other hand, the contribution of elongated grain toughening should be proportional to the $Sr_2Nb_2O_7$ content as well as that of $SrAl_{12}O_{19}$ for the Sr element in $SrAl_{12}O_{19}$ coming from $Sr_2Nb_2O_7$, and this is why the fracture toughness for composite $x=1.0$ mol% is larger than that for $x=0.5$ mol%. While the fracture toughness firstly increases to a maximum value (10.2 MPa.m$^{1/2}$, and that of the matrix is 6.9 MPa.m$^{1/2}$) and then decreases with $Sr_2Nb_2O_7$ content for composites sintered at 1600 °C for 6 h where the fraction of transformable tetragonal zirconia phase decreases with $Sr_2Nb_2O_7$ content. In this case, the fracture toughness for the composite with $x=1.0$ mol% is less than that for $x=0.5$ mol% due to the contribution of elongated grain toughening which can not compensate the loss of fracture toughness originated by the reduced fraction of transformable tetragonal zirconia phase.

4. Conclusions

The $Sr_2Nb_2O_7$ additive reacted with the Al_2O_3 ceramic matrix to form $SrAl_{12}O_{19}$ platelets, which could contribute to the fracture toughness of composites due

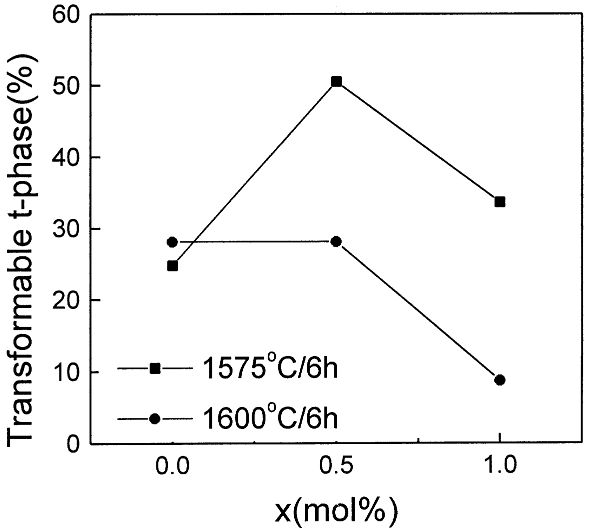

Fig. 5. Effect of $Sr_2Nb_2O_7$ content and sintering temperature on the fraction of transformable tetragonal zirconia phase of $xSr_2Nb_2O_7/(1-x)$ZTA ceramics.

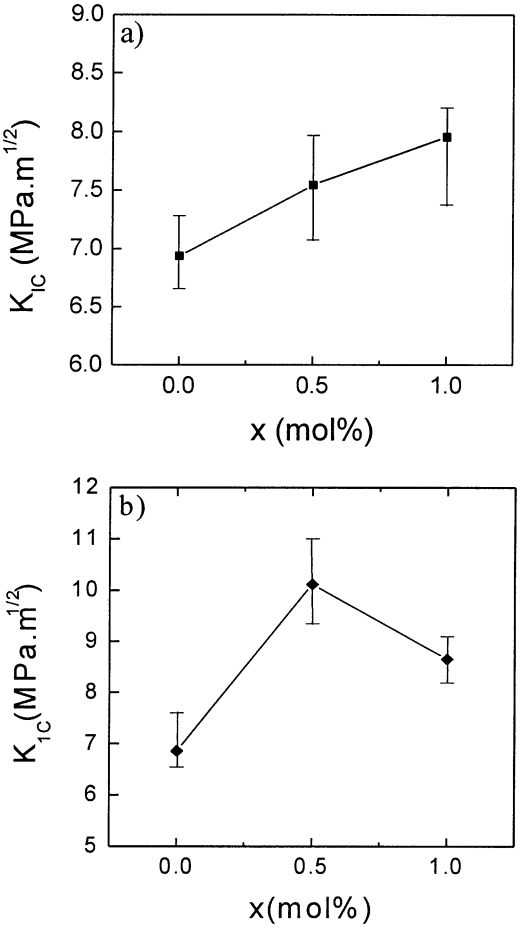

Fig. 6. Effect of $Sr_2Nb_2O_7$ content on fracture toughness of $xSr_2Nb_2O_7/(1-x)$ZTA ceramics sintered under different conditions: (a) 1575 °C/6 h, (b) 1600 °C/6 h.

to the elongated grains. The fraction of tetragonal zirconia phase decreased with increasing $Sr_2Nb_2O_7$ addition, the variation tendency of transformable tetragonal zirconia with the composition was affected by the sintering conditions. For composites sintered at 1575 °C for 6 h, it increased firstly and then decreased when the $Sr_2Nb_2O_7$ content is beyond a critical value, while for composites sintered at 1600 °C for 6 h it decreased with additive content. The Vickers hardness decreased straightly with $Sr_2Nb_2O_7$ additive for all composites sintered under any condition investigated here. However, the fracture toughness increased to a maximum value of 10.2 MPa.m$^{1/2}$ (6.9 MPa.m$^{1/2}$ for matrix) firstly and then decreased with $Sr_2Nb_2O_7$ additive for composites sintered at 1600 °C for 6 h, while it increased straightly with additive for composites sintered at 1575 °C for 6 h. The fracture toughness of the present composites were primarily affected by the fraction of the transformable tetragonal zirconia phase and $Sr_2Nb_2O_7$ content, and the toughening effects should be primarily the integrated result of stress-induced transformation toughening and elongated grain toughening.

Acknowledgements

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References

[1] F.F. Lange, Transformation toughening. Part 4, fabrication, fracture toughness and strength of Al_2O_3–ZrO_2 composites, J. Mater. Sci. 17 (1982) 247–254.

[2] Y.S. Shin, Y.W. Rhee, S.J.L. Kang, Experimental evaluation of toughening mechanisms in alumina-zirconia composites, J. Am. Ceram. Soc. 82 (5) (1999) 1229–1232.

[3] G. Orange, G. Fantozzi, P. Homerin, F. Thevenot, A. Leriche, F. Cambier, Preparation and characterization of a dispersion toughened ceramic for thermomechanical uses (ZTA), Part II: thermomechanical characterization. Effect of microstructure and temperature on toughening mechanisms, J. Eur. Ceram. Soc. 9 (1992) 177–185.

[4] T. Kosmaè, M. Swain, N. Claussen, The role of tetragonal and monoclinic ZrO_2 particles in the fracture toughness of Al_2O_3–ZrO_2 composites, Mater. Sci. Eng. 71 (1985) 57–64.

[5] M. Rühle, N. Claussen, A.H. Heuer, Transformation and microcrack toughening as complimentary processes in ZrO_2-toughened Al_2O_3, J. Am. Ceram. Soc. 69 (3) (1986) 195–197.

[6] M. Rühle, Microcrack and transformation toughening of zirconia-containing alumina, Mater. Sci. Eng. A105/ 106 (1988) 77–82.

[7] P.F. Becher, K.B. Alexander, A. Bleier, S.B. Waters, W.H. Warwick, Influence of ZrO_2 grain size and content on the transformation response in Al_2O_3–ZrO_2 (12 mol% CeO_2) system, J. Am. Ceram. Soc. 76 (3) (1993) 657–663.

[8] K. Ranjbar, B.T. Rao, T.R.R. Mohan, C.S. Harendranath, Effect of chemically added zirconia and yttria on the mechanical prop-

erties of zirconia-dispersed alumina, Am. Ceram. Soc. Bull. 73 (2) (1994) 63–66.

[9] X.M. Chen, B. Yang, A new approach for toughening of ceramics, Mater. Lett. 33 (1997) 237–240.

[10] B. Yang, X.M. Chen, Alumina ceramics toughened by piezoelectric secondary phase, J. Eur. Ceram. Soc. 20 (11) (2000) 1687–1690.

[11] X.M. Chen, X.Q. Liu, F. Liu, X.B. Zhang, 3Y–TZP ceramics toughened by $Sr_2Nb_2O_7$ secondary phase, J. Eur. Ceram. Soc. 21 (2001) 477–481.

[12] X.Q. Liu, X.M. Chen, Effects of composition and sintering conditions upon microstructures and fracture toughness of $Sr_2Nb_2O_7$-toughened 3Y–TZP ceramics, Mater. Sci. Eng. (in press).

[13] R.C. Garvie, P.S. Nicholson, Phase analysis in zirconia systems, J. Am. Ceram. Soc. 55 (1972) 303–305.

[14] A.G. Evans, E.A. Charles, Fracture toughness determinations by indentation, J. Am. Ceram. Soc. 59 (7-8) (1976) 371–372.

[15] K. Niihara, R. Morena, D.P.H. Hasselman, Evaluation of K_{IC} of brittle solids by the indentation method with low crack-to-indent ratios, J. Mater. Sci. Lett. 1 (1982) 13–16.

[16] R.A. Cutler, R.J. Mayhew, K.M. Prettyman, A.V. Virkar, High-toughness Ce-TZP/Al_2O_3 ceramics with improved hardness and strength, J. Am. Ceram. Soc. 74 (1) (1991) 179–186.

[17] P.L. Chen, I.W. Chen, In-situ alumina/aluminate platelet composites, J. Am. Ceram. Soc. 75 (9) (1992) 2610–2612.

[18] M. Yasuoka, K. Hirao, M.E. Brito, S. Kanzaki, High-strength and high-fracture-toughness ceramics in the $Al_2O_3/LaAl_{11}O_{18}$ systems, J. Am. Ceram. Soc. 78 (7) (1995) 1853–1856.