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High Hardness Nanocrystalline Yttria-Stabilized Zirconia and Alumina-Zirconia Composites

Oleg Vasylkiv* **, Yoshio Sakka*, Hanna Borodians'ka**, and Valeriy V. Skorokhod**
*National Institute for Materials Science
1-2-1, Sengen, Tsukuba, Ibaraki, 305-0047, Japan
Fax: 81-298-592415, e-mail: Oleg.VASYLKIV@nims.go.jp
**Institute for Materials Science, NASU
3, Krzhizhanivs'kogo Str., Kiev, 03680, Ukraine

Abstract
Nanocrystalline tetragonal zirconia and γ-alumina – zirconia (3Y-TZP) nano-composite ceramics with (1 to 5 wt% of alumina) were produced by low-temperature sintering. The Vickers indentation tests were performed in order to obtain the hardness values of the ceramic. The influence of the ceramic processing conditions (i.e. resulting density and microstructure) as far as the influence of γ-alumina amount on the hardness and toughness were determined. Nanostructured yttria-stabilized zirconia ceramic with average grain size of 110 nm was shown to reach hardness of 11.1–12.5 GPa. Addition of alumina allowed the sintering process to be intensified. Nano-grained microstructure with average grain size of 95 nm was obtained and hardness increased to 14.9–16.2 GPa.

Keywords: Nanostructured ceramic, Zirconia -Alumina Nano-Composites, Hardness, Toughness

1. INTRODUCTION

The producing of materials and devices with new properties by means of the controlled manipulation of their microstructure on the nano-level has become an emerging interdisciplinary field based on solid-state physics, chemistry, and materials science.[1]

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramic attracts the major attention because of the possibility of obtaining the nano-grained bulk ceramic with controllable microstructure and improved mechanical properties.[1-13, 29-34]

For structural applications, improved mechanical properties are the usual objective. At low temperatures, the important properties include hardness and fracture toughness (K_{1c}). These measurable properties are usually giving an indication of a materials performance under operation conditions. Indentation techniques are commonly used for studying the hardness and toughness of a wide range of ceramics. Hardness indentation method is particularly useful for brittle materials with low fracture toughness since it is both simple, rapid and permits small sample sizes. The fracture toughness is an important parameter required for the prediction of the mechanical performance of structural ceramic.[9-34]

The addition of one ceramic to another often produces a composite with more desirable properties than the individual components. The addition of alumina (Al_2O_3) to yttria-stabilized tetragonal zirconia polycristals has produced ceramics with improved toughness. An examples of the effect of small alumina addition are shown by Kihara *et al.*[34] K_{1c} increased by 17% and 15% with an addition of 1 and 4 vol% Al_2O_3 respectively. Many other investigations of Y-TZP ceramic have shown improved K_{1c} with various alumina additions.[15-29]

However, results have not always been consistent. For example, Y-TZP ceramics with slightly different yttria contents (2 – 3 mol%) showed opposite K_{1c} values after alumina addition.[16] Also, K_{1c} values of alumina-zirconia composites showed a dependence on testing and evaluation techniques. Fukuhara showed that alumina addition to Y-TZP increased hardness, but decreased K_{1c}.[29] Bhaduri *et al.* showed the nanocrystalline Al_2O_3 – ZrO_2 composite full dense ceramic with average hardness and toughness values of 4.45 GPa, and 8.38 MPa·m$^{1/2}$, respectively. F. F. Lange reported a hardness of 15 GPa for a conventionally processed ceramic.[35] The main discrepancies in the results should be attributed to different starting materials and fabrication routes.

Room temperature deformation of nanocrystalline ceramics has been sporadically reported in the literature. However, the results from the indentation tests performed to date are all questionable due to the existence of sample porosity. Porosity can allow materials to appear to deform plastically underneath an indenter, when in fact the material is merely densifying by the fracture and sliding of grains into pores.[13, 31-34]

In the current study the influences of the γ-alumina content in 1 to 5 wt% alumina-doped zirconia as far as sintering conditions of zirconia and alumina-zirconia composites on the microstructure and mechanical properties were considered.

2. EXPERIMENTAL PROCEDURE

3 mol% yttria-stabilized zirconia, and alumina doped (1 to 5 wt% γ-alumina) samples were sintered pressurelessly in air at the temperature of 1150 °C and times ranging from 2 to 50 h, in order to produce ceramic with a range of densities and grain sizes. The samples were heated at 5 °C/min to the desired temperatures, held for the prescribed times, and furnace-cooled. The densities of the sintered bodies were measured by the Archimedes method. Relative density of zirconia ceramic was based on a 6.06 g/cm^3, relative densities of zirconia – alumina composites were calculated according to the wt% of Al_2O_3 in each composite, assuming the α form (d=3.98 g/cm^3). Preparation technique of composite ceramic was described in previous paper.[4]

The samples for Vickers indentation (Hardness Testing Machine (MVK-H2), Akashi Co. Japan) tests were square shape with approximately 4mm height and 12 mm side. The surface on which indentations were performed was previously polished with diamond paste in an ordinary metallographic polisher. The quality of finishing was checked by optical microscopy in order to avoid the presence of scratches on the surfaces prior to testing. Grain sizes were determined by linear analysis of SEM micrographs of polished and etched (1100 °C for 1 h) surfaces. Hardness indentations were obtained by applying the force of both 4.9 N and 9.81 N (0.5 kg and 1 kg masses, respectively) for a dwell time of 15 s. For each sample 10 indentations were used to obtain the average hardness and standard deviation. In addition, the high load (98 N+15 s hold) indentation tests were performed on each sample to generate cracks and from them the values of the fracture toughness were obtained. From the two diagonal crack lengths, two fracture toughness values were obtained for each indentation. An average fracture toughness and standard deviation for each sample were computed from the total number of fracture toughness values per sample (10 values).

Because zirconia cracks in a Palmqvist mode the fracture toughness (K_{1c}) was obtained from the expression given by Niihara et al.[14] for Palmqvist cracks in brittle materials:

$$\left(\frac{K_{1c}\cdot\varphi}{H\cdot a^{1/2}}\right)\cdot\left(\frac{H}{E\cdot\varphi}\right)^{2/5}=0.035\cdot\left(\frac{l}{a}\right)^{-1/2} \quad (1)$$

Where H is the Vickers hardness, E the Young's modulus, $2a=d$ is the diagonal of the indentation, φ is the constrain factor, l is the crack length. So-called Palmqvist cracks (l) begin only at the end of the diagonals of the indentation, and criteria for such cracks are as follows: $0.25 \leq l/a \leq 2.5$.[14] Expression for the fracture toughness (Eq. 2) was obtained from the above relation (Eq. 1):

$$K_{1c}=9.052\cdot10^{-3}\cdot H^{3/5}\cdot E^{2/5}\cdot d\cdot l^{-1/2} \quad (2)$$

A value of $E = 210$ GPa has been assumed for all the ceramic samples, irrespective of their composition. In addition, the crack lengths were measured immediately after the indentation was carried out in order to avoid slow crack growth after removing the load.[13, 14]

3. RESULTS AND DISCUSSION

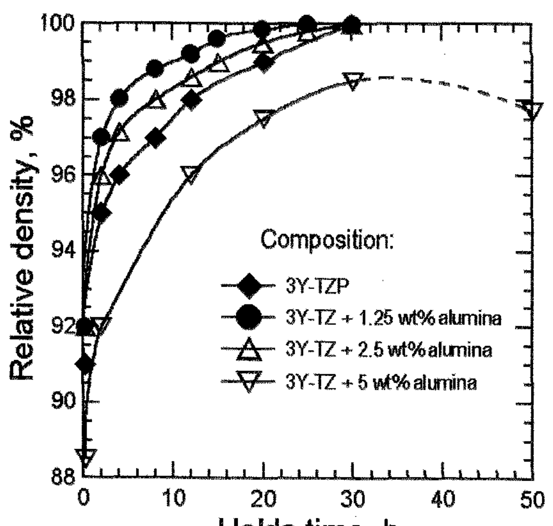

Fig. 1. Presureless sintering at constant temperature of 1150 °C.

The isothermal sintering results for the 3Y-TZP and alumina-doped 3Y-TZP samples are shown in Fig. 1, where relative densities are plotted as a function of the sintering times. Densification of 3Y-TZP ceramic, D = 97% was demonstrated by sintering at 1150 °C for 12 h. 30 h hold allowed to produce ceramic 99.5% dense. Addition of γ-alumina allowed the ceramic densification to be intensified in comparison with alumina-free samples. 1.25wt% Al_2O_3-doped zirconia ceramic demonstrated 99% densification after only 12 hours holds. Full-dense 1.25wt% alumina – zirconia composite, and nearly full-dense (D = 99.5%) 2.5 wt% alumina – zirconia ceramic were obtained after 20 h holds at 1150 °C.

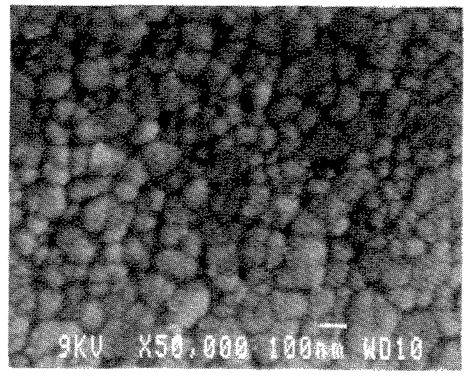

Fig. 2. SEM micrograph of 3Y-TZP + 2.5 wt% γ-alumina ceramic sintered at 1150 °C for 20 h.

Figure 2 shows the SEM microstructure of the 2.5 wt% Al_2O_3 – 3Y-TZP composite sintered at a temperature of 1150 °C for 20 h. This figure coupled with Fig. 1 indicate, that the addition of γ-alumina powder increased reactivity and reduced densification time. The average grain size of 1.25 and 2.5 wt% alumina-doped zirconia ceramic was 94 nm and 87 nm respectively.

Once sintered, the ceramic samples had varied densities (92 to 100% relative density) and grain sizes (60 to 160 nm) depending of the sintering parameters and composition.

Figure 3 shows the sample optical micrograph with Vickers hardness analysis data for 2.5 wt% alumina – zirconia nano-ceramic sintered at a temperature of 1150 °C for 15h.

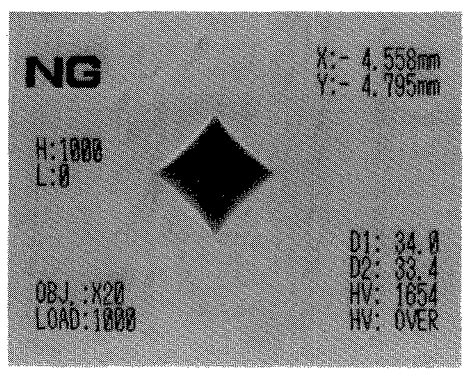

Fig. 3. Optical micrograph of indented surface of 2.5 wt% alumina – zirconia nano-composite (load 9.8N).

As can be seen from Fig. 4, the average hardness increases with increasing of the holds time. Hardness of 1.25 wt% alumina – zirconia composites reaches the maximum value at 24 h hold. Hardness of 2.5 wt% alumina – zirconia composites reaches the maximum value at 15 h hold. Subsequent holds at the temperature allowed to increase the relative density, actually reach the full density (Fig.1), however, the average hardness of such ceramics gradually decreased (Fig. 4, 5). The highest average hardness of 16.2 GPa was demonstrated

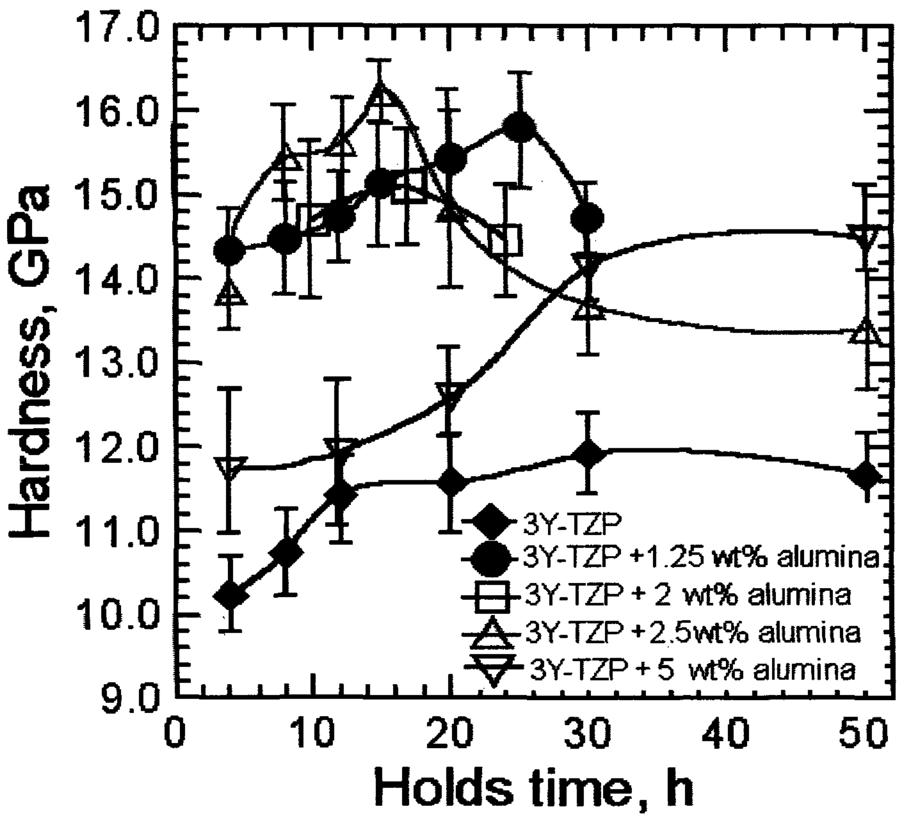

Fig.4. Dependence of Vickers hardness on the holds time during sintering at 1150 °C.

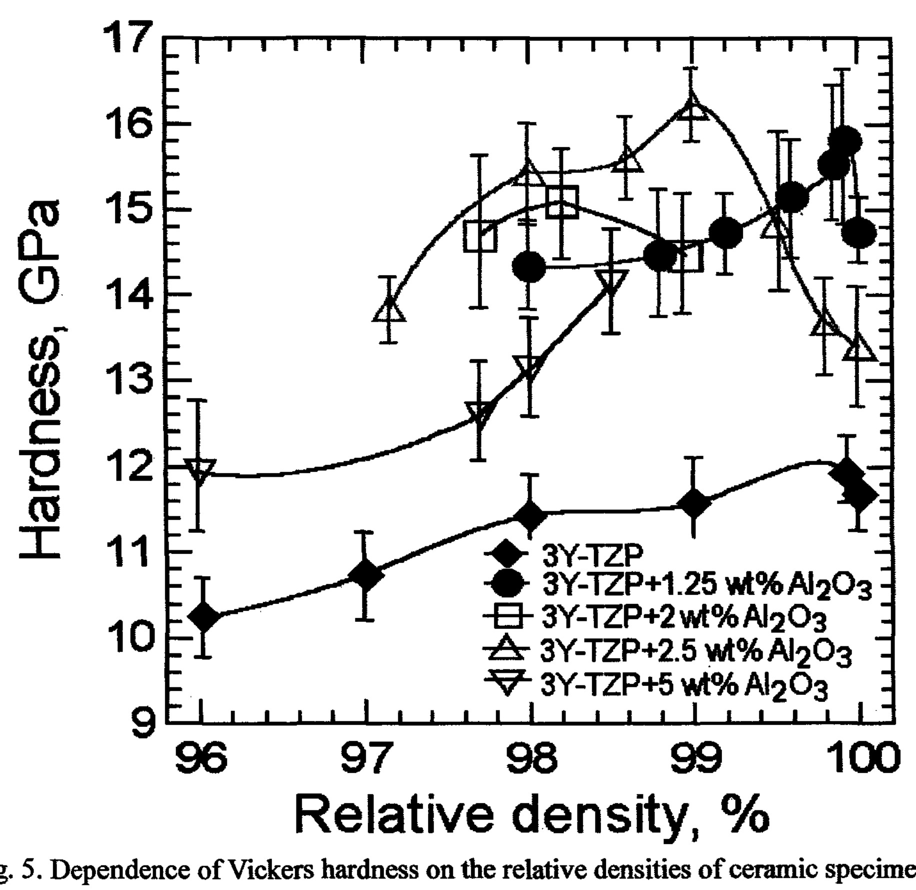

Fig. 5. Dependence of Vickers hardness on the relative densities of ceramic specimens.

density of 99%. We attributed such phenomena to the gradual decreasing of the average grain size because of the shortening of the hold time necessary for densification.

There is a controversy regarding the values of fracture toughness in the literature. Recently, Cottom and Mayo showed that without phase transformation toughening, the fracture toughness is in the range of 2.25 to 4.25 MPa·m$^{1/2}$, a value comparable to brittle ceramics.[13] However, there was a problem with their data analysis. The crack geometry was Palmqvist type at the loads they used, however, instead of using an equation related to the Palmqvist geometry, they used an equation for the median crack geometry. This should result in an error even though the trend in toughness should be valid. F. F. Lange[35] reported a toughness value of 6.73 MPa·m$^{1/2}$. It should be noted that this value was based on a transformation-toughened composite, i.e. occurred during the crack propagation.

Table 1. Fracture Toughness of Zirconia and Alumina-Zirconia Nano-Composites.

Chemical composition	Relative density, %	Hold time, h	VH, GPa	K_{Ic}, MPa·m$^{1/2}$
3Y-TZP	97.5	12	11.43	7.31
	98.8	20	11.58	8.62
3Y-TZP + 1.25 wt% Al_2O_3	99.2	12	14.73	6.31
	99.8	20	15.42	6.73
3Y-TZP + 2.5 wt% Al_2O_3	98.6	12	15.62	7.49
	99.1	15	16.23	7.86
	99.5	20	14.84	5.66
3Y-TZP + 5 wt% Al_2O_3	98.5	30	14.12	5.36
ZrO2, pure monoclinic	100	-	-	2.6

The lower hardness values of alumina-free 3Y-TZP ceramics increased the average fracture toughness values in comparison with alumina-doped ceramics (Table 1). The average value of 8.62 MPa·m$^{1/2}$ was measured using 10 kg (98 N) of load. The load smaller than that did not reveal any significant cracks. This means that such ceramic resistant to cracking. Compared to this result 2.5 wt% alumina – zirconia composite ceramic showed the maximum average fracture toughness value of 7.86 MPa·m$^{1/2}$ (for a comparable ceramic density (Table 1)). However, with subsequent densification ceramic became more brittle and, as a result fracture toughness gradually lowered.

4. CONCLUSION

We showed that dense alumina-doped zirconia nano-ceramic was obtained by low-temperature sintering at 1150 °C. We can conclude from this research that addition of γ-alumina intensified the sintering process and allowed to produce the nanoceramic with high hardness and toughness. The average hardness and toughness of 2.5 wt% alumina-doped 3Y-TZP ceramic were 16.23 GPa and 7.86 MPa·m$^{1/2}$ respectively. The higher hardness of 3Y-TZP ceramics was found to be 12.5 GPa. The higher fracture toughness of 8.62 MPa·m$^{1/2}$ of 3Y-TZP alumina-free ceramics was obtained at the hardness value of 11.58 GPa..

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