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Nb_2O_5 and Ta_2O_5 Codoped Zirconia

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Abstract

Orthorhombic zirconia codoped with 5 mol-% Nb_2O_5 and 5, 7, 10, 12 and 15 mol-% Ta_2O_5 as well as samples with 5 mol-% Ta_2O_5 and 7, 10, 12 and 15 mol-% Nb_2O_5, respectively, were made from precursors prepared by hydrolysis of the metalalkoxide solutions in 1-propanol with water. The amorphous, coprecipitated hydroxides were converted to the oxides at 900°C. The powders were characterized by the specific surface areas, the particle size distributions and by electron microscopy. The codoped zirconia powders were attributed, isostatically compacted and sintered at temperatures ranging from 1500 to 1650°C. Three-point bend-strengths, Weibull moduli, fracture toughnesses, Vickers hardnesses, densities and phase compositions were measured for the sintered specimens. Average three-point bend-strengths ranged between 85 and 257 MPa. No phase transformations occurred during fracture. Fractography showed that the fracture origins were either surface flaws or pores near the tensile surface. Depending on the composition and the sintering conditions, fracture toughnesses between 2·1 and 3·6 MPa $m^{1/2}$, Vickers hardnesses between 6·8 and 9·9 GPa and theoretical densities between 96·8 and 99·0% were observed. Increasing dopant concentrations resulted in increases in the b- *and* c-*axes and in a decrease in the* a-*axis of the orthorhombic cell.*

1 Introduction

Single doping of zirconia with either Nb_2O_5 or Ta_2O_5 above 12 mol-% of the dopant stabilized the orthorhombic phase at room temperature.[1] In a previous publication we reviewed the literature on orthorhombic zirconia and reported the preparation and mechanical properties of zirconia doped with varying concentrations of either Nb_2O_5 or Ta_2O_5. These studies are now extended to investigations on the preparation of zirconia powders codoped with Nb_2O_5 and Ta_2O_5, on the sintering conditions, the mechanical properties and the fractography of Nb_2O_5–Ta_2O_5 codoped orthorhombic zirconia ceramics, for which such data have not been reported before.

2 Experimental

2.1 Powder preparation and sintering

The preparation of the precursor materials niobium penta-l-propoxide and tantalum penta-l-propoxide from niobium pentachloride and tantalum pentachloride respectively, has been reported.[1] Zirconium-l-propoxide was commercially available (Johnson Matthey, USA). Solutions of the alkoxides of zirconium, niobium and tantalum in l-propanol were prepared in a glove-box under the exclusion of moisture to prevent decomposition. The solutions of the metal alkoxides were then sprayed into water. The precipitated hydroxides were filtered, first washed with water and then with ethanol. The powders were dried at 70°C and 670 Pa followed by a calcination at 900°C (heating rate 5 K min^{-1}). Thermogravimetric measurements showed that conversion of the hydroxides to the oxides was completed around 700°C.[1] The calcined oxides were attrition milled in portions of 30 g with 1200 g of yttria stabilized zirconia balls (2 mm diameter, 600 min^{-1}) in 160 ml of l-propanol for 4 h in an attritor lined with polyethylene. Upon filtering off the balls through a 1 mm sieve, the solvent was evaporated under vacuum. The powders were dried at 100°C at 670 Pa and then heated to 600°C to burn out the polyethylene. The powders were isostatically compressed at 800 bar into blocks of 20 mm × 15 mm × 48 mm. These blocks were presintered at 1000°C. Specimens of 5 mm × 4 mm × 40 mm were cut from the blocks and polished. These samples were then sintered at a rate of 1 K min^{-1} up to 400°C and kept there for 1 h. The temperature was then increased at

Table 1. Properties of Nb_2O_5–Ta_2O_5 codoped zirconia

Mol.% Nb_2O_5	*Ta_2O_5*	*Specific surface area[a] ($m^2\,g^{-1}$)*	*Crystallite size[a] (nm)*	*Green bulk densities ($g\,cm^{-3}$)*	*Bulk densities after sintering* 1500°C	1550°C	1600°C	1650°C
5	5	25·9 (2)	36	2·899 (4)	4·181 (3)	4·806 (2)	5·923 (2)	6·319 (10)
5	7	27·2 (2)	33	3·043 (4)	4·410 (2)	5·257 (3)	6·239 (4)	6·492 (10)
5	10	23·0 (1)	38	3·173 (8)	5·835 (6)	6·730 (9)	6·817 (2)	6·715 (10)
5	12	22·8 (1)	37	3·205 (10)	6·965 (8)	6·996 (4)	6·927 (8)	6·331 (8)
5	15	22·5 (1)	37	3·247 (2)	7·094 (4)	6·992 (6)	6·914 (2)	6·713 (8)
7	5	25·9 (1)	35	2·962 (5)	5·554 (9)	6·268 (8)	6·464 (1)	6·420 (8)
10	5	24·1 (1)	38	3·020 (9)	6·390 (10)	6·456 (5)	6·440 (1)	6·219 (9)
12	5	25·9 (3)	35	2·967 (10)	4·965 (8)	6·125 (2)	6·452 (1)	6·335 (15)
15	5	20·9 (3)	44	3·072 (2)	6·417 (4)	6·209 (2)	6·082 (2)	5·413 (2)

[a] Attrited powders.

5 K min^{-1} to 1000°C and at 3 K min^{-1} to the final sintering temperature. The final sintering temperature was maintained for 2 h. The samples were cooled at 20 K min^{-1}. The powders for the analysis of the lattice parameters were heated to 1000°C at a rate of 5 K min^{-1}, then to 1400°C at 3 K min^{-1}. The cooling rate was 20 K min^{-1}.

2.2 Apparatus and procedures

BET-surface area measurements were carried out on a Quantasorb (Quantachrome, USA) and crystallite sizes were calculated from the specific surface areas from the equation: $d = 6/\rho A_s$ where d is the crystallite diameter, ρ the density and A_s the specific surface area. The particle size distribution was analysed by means of a laser particle sizer (Coulter LS 130, USA).

X-Ray diffraction spectra were measured on a Geigerflex D/max II with Ni-filtered Cu K_α radiation (Rigaku, Japan) between 25° and 80° (40 kV, 20 mA) with Si (99·999% Balzers, Liechtenstein) as internal standard. X-Ray fluorescence analysis was performed on a Geigerflex M 3064 spectrometer with a Rh anode (Rigaku, Japan) with 35 kV and 15 mA. Electron micrographs were obtained on JSM-6400 scanning microscope (Jeol, Japan). Thermogravimetric measurements were carried out on a TG-770 (Stanton Redcraft, UK). A HT 64/17 (Naber, Germany) oven with a maximum temperature of 1750°C served for sintering. Three-point bend-strength measurements were carried out on a dead weight loaded system (Tonitech, Germany).

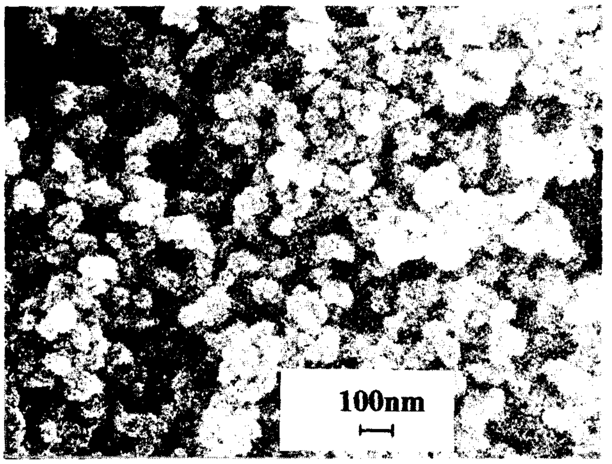

Fig. 1. SEM micrograph of zirconia powders codoped with 5 mol.% Nb_2O_5 and 10 ml.% Ta_2O_5, 50 000×.

2.3 Mechanical properties and microstructure

Three-point bend-strength tests were carried out on 4 mm × 3 mm × 40 mm samples employing a 20 mm span. The tensile surfaces of the samples were diamond-polished to a 1 μm finish and the edges chamfered prior to the bending tests. The load during the testing was increased at a rate of 12 N s^{-1}. Vickers hardnesses were measured with the load of 49 N. Fracture toughness values were obtained from the indentation fracture technique[2] with an indentation load of 49 N. The mean diagonals of the indentation sites and the indentation crack lengths were measured by optical microscopy. The fracture toughness values were calculated using the equation $K_{Ic} = 0{\cdot}0824\ P/c^{1{\cdot}5}$ (K_{Ic}: in MPa $m^{1/2}$, P: indentation load in MN, c: half of the half-penny crack diameter in m). The microstructure of the samples was analysed by optical and scanning electron microscopy. Specimens were either chemically etched in 60 wt% NaOH for

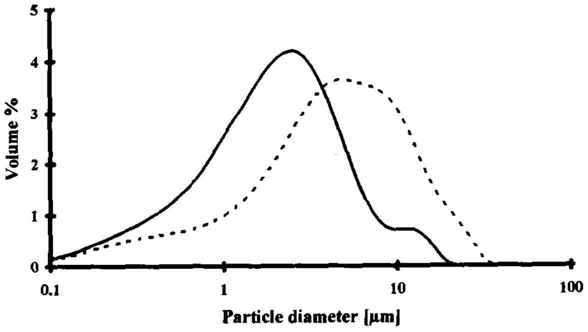

Fig. 2. Particle size distribution of calcined zirconia powders codoped with 10 mol.% Nb_2O_5 and 5 mol.% Ta_2O_5; – – – before attrition, —— after attrition.

Table 2. Mechanical properties of sintered Nb_2O_5-Ta_2O_5 codoped zirconia

Mol.% Nb_2O_5	Ta_2O_5	Sintering temp.	$\sigma_{3P}{}^{a}$ (MPa) aver.	max	m^b	HV^c (GPa)	K_{Ic} (MPa $m^{1/2}$)	ρ^d (g cm^{-3})	Relative density (%)	Orthorh. phase (%)	Grain width^e (μm)
5	5	1650	85 ± 34	134	2·7	6·8	3·6 ± 0·1	6·319	96·8	100	—
5	7	1650	188 ± 58	235	3·5	7·7	2·5 ± 0·6	6·492	97·1	100	0·9/2·5
5	10	1600	242 ± 39	278	6·5	8·5	3·0 ± 0·2	6·817	98·5	100	1·0/2·4
5	12	1550	241 ± 42	296	5·9	9·8	2·1 ± 0·1	6·996	99·0	100	0·8/2·0
5	15	1500	193 ± 33	241	6·4	9·9	2·5 ± 0·1	7·094	97·5	100	1·0/2·2
7	5	1600	230 ± 30	266	8·6	8·6	2·5 ± 0·2	6·464	99·0	100	0·8/2·5
10	5	1600	257 ± 58	350	4·8	9·0	2·6 ± 0·1	6·456	98·7	100	0·4/2·0
12	5	1600	240 ± 47	280	5·3	8·7	2·8 ± 0·5	6·452	98·6	100	0·7/2·5
15	5	1500	215 ± 29	227	8·5	8·7	3·4 ± 0·5	6·417	98·0	100	0·7/2·4

[a] Three-point bend-strength; [b] Weibull modulus; [c] Vickers hardness; [d] Bulk density; [e] Two types of elongated grains with average aspect ratios ranging from 3 to 4.

2 h at 180°C or thermally etched for 2 h at 1450°C. During etching experiments we found that the Nb_2O_5–Ta_2O_5 codoped zirconia were quite corrosion resistant in both acid and basic media. Fractographic studies were carried out to learn about the fracture origins (strength degrading defects) and fracture mechanisms by means of scanning electron microscopy.

3 Results and Discussion

3.1 Powder characteristics and mechanical properties

The hydroxides obtained after hydrolysis were amorphous. The specific surface areas and the densities of the calcined, attributed powders are summarized in Table 1. The specific surface areas of the attrited Nb_2O_5–Ta_2O_5 codoped zirconia powders were very similar and ranged from 21 to 27 m^2 g^{-1}. Crystallites sizes between 33 and 44 nm were calculated from the specific surface areas, in close agreement with observations made by scanning electron microscopy (Fig. 1). The particle size distribution analysis of the calcined powders showed that the prime crystallites had formed larger particles with mean diameters between 6 and 10 μm. No particles larger than 40 μm were found. Attrition milling improved the particle size distributions, yielding particles with mean diameters around 2–3 μm (Fig. 2). The largest particles observed in the attrited powders were around 20 μm.

Fig. 3. SEM micrograph of zirconia codoped with 5 mol.% Nb_2O_5 and 12 mol.% Ta_2O_5 (thermally etched).

For total concentrations of the doping oxides up to 12 mol.% an increase in the densities with increasing sintering temperatures up to 1650°C was noted. Ceramics doped with higher concentration of the doping oxides showed a slight decrease in the densities with the sintering temperatures for the temperature range studied. The temperatures for the sintering of the specimen for mechanical testing were selected according to the highest values for the densities.

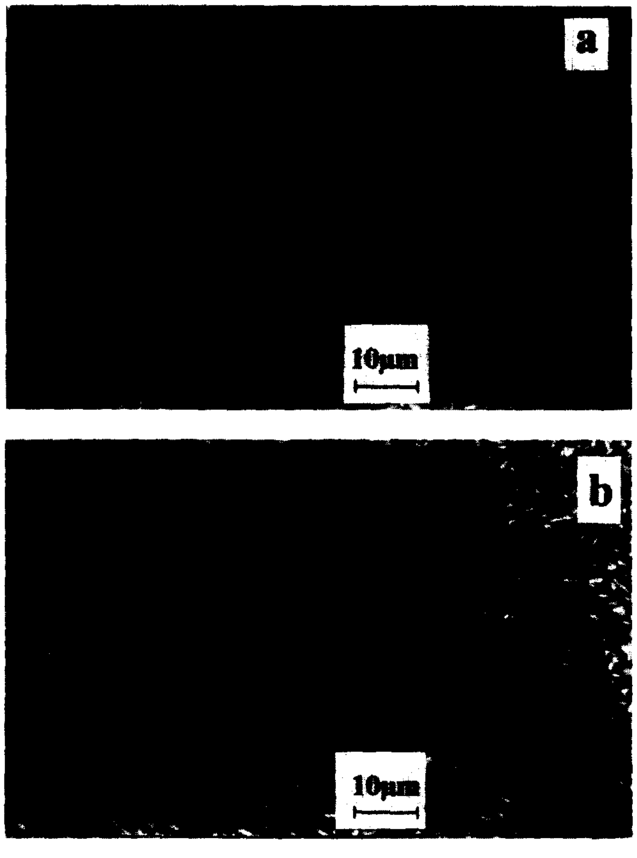

Fig. 4. Comparison of the microstructure of codoped zirconia: (a) 5 mol.% Nb_2O_5 and 10 mol.% Ta_2O_5. (b) 10 mol.% Nb_2O_5 and 5 mol.% Ta_2O_5.

Table 3. Lattice parameters and theoretical densities for Nb_2O_5–Ta_2O_5 codoped zirconia

Nb_2O_5 mol.%	Ta_2O_5 mol.%	*a* (nm)	*b* (nm)	*c* (nm)	Theor. density (g cm^{-3})
0[a]	0	0·5042	0·5092	0·5257	6·062
5	5	0·5003	0·5123	0·5289	6·525
5	7	0·4991	0·5130	0·5301	6·689
5	10	0·4967	0·5143	0·5300	6·920
5	12	0·4957	0·5159	0·5309	7·068
5	15	0·4948	0·5151	0·5304	7·280
7	5	0·4986	0·5128	0·5297	6·531
10	5	0·4964	0·5146	0·5304	6·539
12	5	0·4981	0·5137	0·5304	6·551
15	5	0·4948	0·5156	0·5308	6·544

[a] Ref. 4.

The mechanical properties of the sintered bodies are summarized in Table 2. The bending strengths and fracture toughnesses of the studied ceramics were rather low and showed considerable scatter. Due to the involved procedures in preparing the powders only 8 to 12 sintered specimens were available for the three-point bend-strength measurements. Table 2 therefore contains both the standard deviations and the Weibull moduli, although we realize that the number of specimens is small for reliable Weibull statistics. The maximum strength values were achieved for samples having a total dopant concentration between 15 and 17 mol.%. Maximum values from 280 to 350 MPa could be obtained for these dopant concentrations. The hardness of the samples increased with increasing Ta_2O_5-concentration in codoped samples with 5 mol.% Nb_2O_5. The fracture toughnesses varied modestly between 2·1 and 3·6 MPa $m^{1/2}$.

A comparison of the mechanical properties of the Nb_2O_5–Ta_2O_5 codoped zirconia ceramics with the Nb_2O_5 or Ta_2O_5 singly doped ceramics showed that the values for the three-point bend-strengths were higher by about 100 MPa for the codoped samples than for either the Ta_2O_5 or the Nb_2O_5 singly doped ceramic.[1] We attribute this increase in bend-strength to the improved microstructure of the codoped ceramics. The K_{Ic} values and Vickers hardness values are comparable.

The microstructures of the Nb_2O_5 and Ta_2O_5 codoped ceramics were very similar. They consisted of fine grain sized matrix with mean grain widths of 0·5–1·0 μm. The average aspect ratio was 3. The matrix formed about 70% of the material. Larger elongated grains (average width 2–2·5 μm, average aspect ratio 4) were imbedded in this matrix (Fig. 4). Pores usually ranged from 1·0 to 10·0 μm. Larger pores with pore diameters up to 150 μm were rare.

Fractographic analysis of the fracture surfaces of the samples after the bend-strength tests revealed that the main strength degrading defects were either half-penny shaped surface flaws approximately 25 μm in depth and 60 μm wide (Fig. 5) or machining damages.

Fractures occasionally also originated from

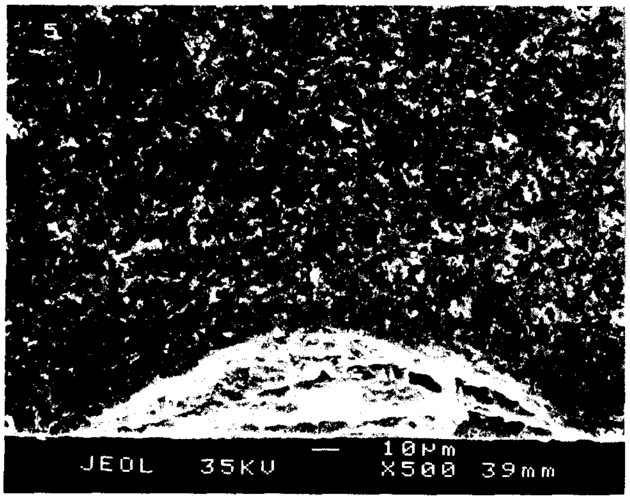

Fig. 5. Fracture origin of zirconia codoped with 12 mol.% Nb_2O_5 and 5 mol.% Ta_2O_5 (defect located at the tensile surface).

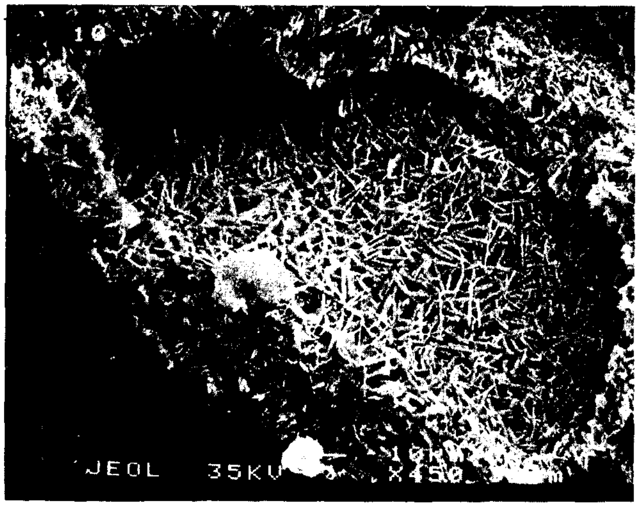

Fig. 6. Volume defect of zirconia codoped with 5 mol.% Nb_2O_5 and 15 mol.% Ta_2O_5 as fracture origin.

Table 4. Coefficients for the calculation of lattice parameters of Nb_2O_5 and Ta_2O_5 codoped zirconia from the equation: $a(b, c) = a_0(b_0, c_0) + k_a k_b, k_c)$ (X_2O_5/mol.%)

Oxide	a_0 (*nm*)	k_a $\times 10^4$	r^a	b_0 (*nm*)	k_b $\times 10^4$	r^a	c_0 (*nm*)	k_c $\times 10^4$	r^a
5 mol.% Nb_2O_5 5–15 mol.% Ta_2O_5	0.503 (7)	−6.460	0.99	0.509 (8)	4.278	0.95	0.526 (8)	3.127	0.88
5 mol.% Ta_2O_5 5–15 mol.% Nb_2O_5	0.503 (5)	−5.813	0.95	0.509 (8)	3.981	0.96	0.526 (6)	3.268	0.92

[a] Correlation coefficient.

volume defects, usually from large pores (100–150 μm) or pores filled with agglomerates of grains (Fig. 6). No marks around the fracture origins (mist, mirror, hackle) were identified. The fractures of the very brittle ceramics were transgranular in all cases without any reinforcing mechanisms such as crack deflection or crack bridging as shown in Fig. 3, on a crack initiated by Vickers indentations.

3.2 Lattice parameters

All codoped samples studied were composed of the orthorhombic phase (Fig. 7). Generally a slight decrease in the *a*-axis and an increase in the *b*- and *c*-axes were observed with increasing dopant concentrations (Table 3). The changes in the lattice parameters for codoped samples, with either 5 mol.% Nb_2O_5 and varying concentrations of Ta_2O_5 or with 5 mol.% Ta_2O_5, and varying concentrations of Nb_2O_5 can be presented by the following equation: $a(b,c) = a_0(b_0,c_0) + k_a(k_b,k_c)$ (X_2O_5/mol.%). X_2O_5 represents the oxide, the concentration of which has varied. The respective values for a, b, c, a_o, b_o, c_o, k_a, k_b and k_c together with the theoretical densities for Nb_2O_5 and Ta_2O_5 codoped zirconia—obtained from the lattice parameters—are summarized in Table 4. The Miller indices for the crystal planes of orthorhombic zirconia were assigned as published for $8ZrO_2 \cdot Nb_2O_5$.[3]

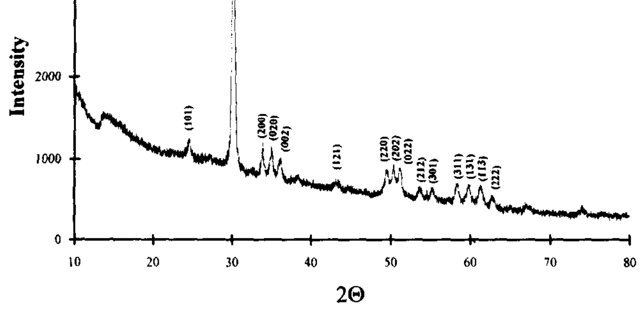

Fig. 7. X-ray diffraction of zirconia codoped with 5 mol.% Nb_2O_5 and 10 mol.% Ta_2O_5.

4 Conclusions

Zirconia ceramics codoped with Nb_2O_5–Ta_2O_5 yielded orthorhombic sintered bodies with three-point bend-strengths ranging from 140 to 260 MPa. This brittle, corrosion resistant material showed transgranular fractures originating generally from surface flaws or pores near the tensile surface. No transformation toughening, crack deflection or crack bridging occurred upon fracture. Bend-strengths for the codoped material were generally higher by 100 MPa than for Nb_2O_5 or Ta_2O_5 monodoped zirconia due to the improved microstructure in the codoped samples.

Vickers hardness values ranged between 6·8 and 9·9 GPa, relative densities between 96·8 and 99·0%, and K_{Ic}-values varied between 2·1 and 3·6 MPa $m^{1/2}$. The best values for the mechanical properties were found for a total content of doping oxides of about 15–17 mol.%.

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