Journal of the European Ceramic Society 18 (1998) 1779–1785

PII: S0955-2219(98)00104-6
0955-2219/98/$—see front matter

Effect of $LaNbO_4$ Addition on the Mechanical Properties of Ceria-Tetragonal Zirconia Polycrystal Matrices

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(Received 22 October 1997; accepted 20 March 1998)

Abstract

The formation of needle-like grains of $LaNbO_4$ *in* CeO_2*-stabilized tetragonal zirconia (Ce-TZP) matrices was studied using powders produced by different methods. The amount as well as the aspect ratio of the elongated grains is a function of the sintering temperature and the way the powders have been produced. The formation of these needles is triggered by the presence of silica in the starting powders and, therefore, by the occurrence of a liquid phase. During sintering, also diffusion of Ce in* $LaNbO_4$ *occurs. The matrices are therefore depleted in stabiliser's content affecting their transformability. Because of the elongated nature of the grains enhanced crack wake bridging occur, this bridging should be also accounted for the observed increase of strength and toughness. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Ceramics materials, such as Si_3N_4, SiC, Al_2O_3, are potential candidates for structural applications at high temperatures.[1,2] However, these materials, like the majority of monolithic ceramics, are brittle and their use, in various systems, is limited.

The usual approach to improve the mechanical properties of ceramics is to reduce the critical flaw size or to produce materials in which energy dissipative mechanisms make a 'flaw tolerant' behaviour possible. In the latter case, the material fall into the 'ceramics composite' group, and generally consist of two or more phases with a controlled heterogeneous microstructure where either particles, whiskers or fibres are used to reinforce ceramic matrices. Among ceramic composites, those containing whiskers seemed to be promising since they can be processed following classical routes leading to improved mechanical properties. Unfortunately, concerns about these materials include availability and price of the reinforcing phase, as well as toxicological problems in handling whiskers.[3,4] Although these reinforced ceramics exhibit higher mechanical performances compared to monolithic ceramics, the aforementioned problems have led to a search for alternative ceramics composites.

It seems therefore interesting to explore the possibility of growing *in situ* an elongated second phase and therefore producing a whisker-like reinforced ceramic. There are already several examples of this kind of *self-reinforced* materials, silicon nitride and silicon carbide with elongated grains are well known,[5,6] but recently alumina was also reinforced with the *in-situ* formation of needle-like aluminum niobate.[7,8]

Concerning this latter compound, in a recent work,[9] $LaNbO_4$ powders using either coprecipitation or mechanical alloying have been produced. It was found that powders prepared by coprecipitation are amorphous and become tetragonal when heated up to 400°C. They maintain this crystal structure upon further heating, and transform to monoclinic upon cooling below 400°C. Therefore at room temperature the monoclinic form is the only detectable phase. The $LaNbO_4$ powders derived from mechanical alloying are instead cryptocrystalline at room temperature, assume the tetragonal structure when heated above 400°C, and remain tetragonal on further heating and subsequent cooling even at room temperature. It

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has also been demonstrated[9] that during the tetragonal–monoclinic transformation these powders have a volume change of 1%. This behaviour is similar to that of zirconia[10–13] although in the latter case the volume change is 3–5%, the precise value being a function of both, type and amount of oxide stabiliser. As known this transformation gives rise to excellent mechanical behaviour of the zirconia based materials.[14–18]

The previously mentioned lanthanum niobate has an insufficient volume change to cause a transformation toughening effect which enables to considerably enhance the mechanical properties of pure $LaNbO_4$ materials, but it is worthwhile to consider it as an additive for another matrix in order to improve the mechanical properties of the composite. Moreover, Garcia *et al.*[19] have shown that the introduction of niobia in zirconia-toughened-alumina (ZTA) based materials induces the production of elongated crystals. They suggested that such crystals are due to the reaction between zirconia and niobia and that their growth is promoted by the presence of a liquid phase. On this ground, we have introduced $LaNbO_4$ powders produced by either mechanical alloying or coprecipitation in some ceria-tetragonal zirconia (Ce-TZP) matrices up to a maximum of 15% vol%, which is close to the percolation limit for the second phase. Four Ce-TZP compos i ns were chosen, starting from the lower limit of the tetragonal solid solution up to the field of the fully stabilized zirconia.

The aim of this work is to produce a composite material where lanthanum niobate acts as a promoter for the nucleation of elongated grains due to the reaction with zirconia; in this way the mechanical properties of the material should increase due to the presence of another phase that undergoes the tetragonal to monoclinic transformation and at the same time elongated grains might increase toughness and strength also through a crack bridging effect.[20]

2 Experimental methods

Preparation and characterisation of $LaNbO_4$ by coprecipitation and mechanical alloying are reported elsewhere.[9] Two commercially available TZP powders supplied by UNITEC CERAMICS (Stafford, UK) containing 14 and 25 wt% CeO_2 (corresponding to 10 and 20% mol), respectively, and 0·15 wt% of SiO_2 were used as starting matrix powders; the former having a stoichiometry close to the tower limit of the tetragonal solid solution, the latter being in the field of fully stabilized zirconia. Two other powders of intermediate composition, 12 and 14 mol% CeO_2 were prepared by coprecipitation in concentrated ammonia (28 wt%) a 0·5 molar solution of required amounts of cerium nitrate hexahydrate (Aldrich Chem., 99·0%) and Zirconium oxychloride octahydrate (Aldrich Chem., 98%). After coprecipitation, the pcducts were washed several times with distilled water and then with aceton–toluene–aceton (ATA procedure[21]). After drying a TG/DTA analysis was performed in order to assess the crystallization temperature. The two powders were then calcinated for 1 h at 650°C and air cooled at room temperature. After calcination the powders were wet milled for 2 h in isopropyl alcohol.

The four matrices 10, 12, 14 and 20% mol CeO_2, (from now on called CZ10, CZ12, CZ14 and CZ20) were added with the desired amount of lanthanum niobate produced by mechanical alloying and wet milled for 2 h in water, using polyethylene containers, with Y-TZP balls as milling media together with binder (Resicel V2-Fratelli Lamberti, Faenza, Italy) and lubricant (Mobilcer A-Mobil, Milano, Italy), then the slurries were dried in oven at 80°C and sieved through a 100 μm screen.

For the addition of the chemically prepared $LaNbO_4$ a different method was followed in order to improve the homogenity of the mixture. Matrix powders were dispersed in diluted ammonia under constant stirring alcoholic solutions (0·5 molar) of lanthanum chloride and niobium chloride were added dropwise to the stirred suspensions. After coprecipitation the stirring was discontinued and the segregated phase was separated by the clear supernatant. The product was washed several times with water and ATA, dried and calcinated 2 h at 800°C based upon previous studies.[9] Finally the powders were milled again as reported above, dried and sieved.

Green samples were obtained using an uniaxial pressing at 35 MPa followed by cold isostatic pressing at 200 MPa. Thermoanalysis and dilatometric tests were performed on a Netzsch 410 STA the latter up to 1500°C using in both cases a heating rate of 10°C min^{-1}.

Phases compositions were examined by X-ray diffraction (XRD) using an INELXRG 300 (Les Ulis Cedex, France) instrument and the Co radiation. Microstructural development was characterised on polished samples, with a scanning electron microscopy coupled with a microprobe analyser.

Modulus of rupture was assessed using a four point bending test (spans 40 and 20 mm) on 4×3×50 mm samples, ground and polished on the tensile surface (5–7 samples were tested for each composition). Samples with the same geometry were also used for measuring toughness with the indentation strength in bending method.

3 Results and discussion

3.1 Relation between processing and microstructure

3.1.1 Materials from commercial powders (CZ10 and CZ20)

The addition of $LaNbO_4$ to any matrix resulted in the production of elongated grains. Due to the different processes (coprecipitation or mechanical alloying), the two $LaNbO_4$ powders are initially crystallographically different but, after sintering, the XRD patterns are the same (i.e. for the $LaNbO_4$ the XRD shows only the monoclinic phase). After sintering for short periods (< 30 min) at 1450°C, CZ10 and CZ20 with different amounts of $LaNbO_4$, develop a dense, fine grained microstructure. However after prolonged isothermal sintering (3 h) a microstructure containing elongated grains can be observed. Figure 1 shows the microstructure of a CZ10 composite containing a 15 vol% of $LaNbO_4$ produced by coprecipitation and sintered for 3 h at 1450°C. The presence of elongated crystals emerging from the matrix is coupled with a significant quantity of cracks (arrows). The diffractometric analysis of the surface confirmed a large amount of monoclinic zirconia. Samples containing the same amount of $LaNbO_4$ produced by mechanical alloying gave the same phases, but a larger amount of elongated crystals. A dilatometric analysis provides explanations for this phenomenon. The dilatometric behaviour of pure $LaNbO_4$ green compacts, produced by coprecipitation (curve a) and by mechanical alloying (curve b), are reported in Fig. 2. It can be seen that sample (b) melts at 1350°C while such an event did not occur in sample (a). The same behavior can be highlighted by the DTA analysis on green as well as on fired samples. In fact, the La_2O_3/Nb_2O_5 phase diagram[22] shows that $LaNbO_4$ has a melting temperature higher than that of adjacent compounds such as $LaNb_3O_4$ and La_3NbO_7. During mechanical alloying, a mixture of products are formed. Although $LaNb_3O_4$ and La_3NbO_7 are present in such small quantities that they can not be detected by X-ray diffraction, their presence is sufficient to promote a liquid phase through the formation of two eutectics at 1350 and 1545°C, respectively. The former acts as a melting aid and gives rise to a liquid phase at a temperature lower than that expected for the pure $LaNbO_4$. Powders prepared by coprecipitation, however, are more homogeneous and the temperature required for the appearance of the liquid phase is very close to that reported in literature.[22] A similar event could be also expected in the mixture $ZrO_2/CeO_2/LaNbO_4$ where the higher number of components could form liquid eutectics even at lower temperatures. Therefore the presence of a liquid during the sintering process partially explains both the higher amounts of elongated crystals and the prevalence of the monoclinic with respect to the tetragonal phase on the matrix in all samples produced by mechanical alloying. Furthermore, the liquid phase promotes a fast growth of the matrix grains so that it is easier to exceed the critical dimension of zirconia grains which transform to monoclinic on cooling. After sintering at 1450°C regardless of the holding time, it is very difficult to avoid a wide spontaneous transformation within the composite on cooling so therefore the properties of such materials are poor. In samples containing $LaNbO_4$ produced by coprecipitation, the presence of the liquid phase has not been detected, but it cannot be excluded *a priori.*

Fig. 1. SEM microstructure of a CZ10 sample containing 15 vol% $LaNbO_4$ introduced by coprecipitation. Arrows indicate cracks.

It is known that sintered CZ10 materials maintain the tetragonal structure at room temperature if grains do not exceed the dimension of $2{\cdot}5\,\mu m$.[18,23–25] after which they spontaneously transform upon cooling. In our CZ10 composites containing both types of $LaNbO_4$ this limit has never been exceeded and therefore, spontaneous transformation should not occur.

In addition (see Table 1), it has been found that increasing quantities of $LaNbO_4$ to the CZ10 matrix results in a proportional increase of elongated grains but, at the same time, there is a concomitant reduction in the tetragonal phase despite constant density ($> 98\%$). Microprobe analysis revealed an enrichment in ceria in most of $LaNbO_4$ grains of all the samples. Therefore a migration of ceria from zirconia to the lanthanum niobate lattice seems reasonable. As a consequence, many tetragonal particles directly transform to monoclinic on cooling. On the other hand, matrices with higher CeO_2 content due to the aforementioned Ce diffusion, become more transformable and their mechanical properties are enhanced. By reducing

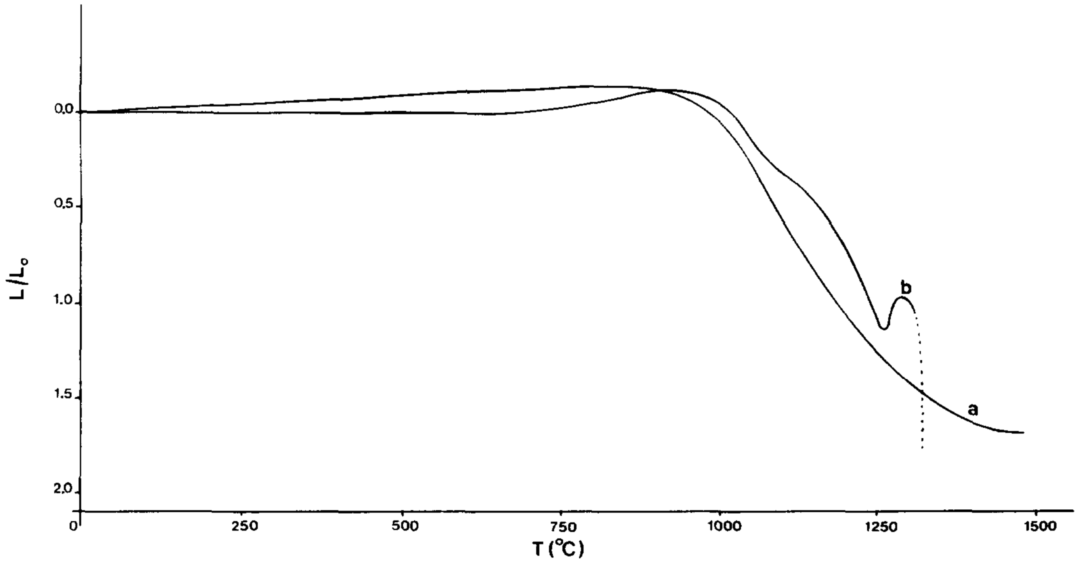

Fig. 2. Dilatometric curves of $LaNbO_4$ produced: (a) by coprecipitation and (b) by mechanical alloying.

Table 1. Density, phases and mechanical properties for the composites tested, with the $LaNbO_4$ amount added, are presented

Material	*$LaNbO_4$ (vol%)*	*Relative density (%)*	*Zirconia crystal phases*	*Elongated crystals*	*Crystal size (μm)*	*Flexural strength (MPa)*	*Relative flexural strength**	*K_{IC} (MPa√m)*
CZ10	0	99·7	TZ°	no	—	500	—	12
CZ10	2·5	99·4	TZ° + m m = 20	yes (very few)	long (> 10)	310	0·9	
CZ10	5	99·1	TZ° + m m = 40%	yes (few)	long (> 10)	100	0·6	
CZ10	10	99·1	TZ° + m m = 50%	yes	long (> 10)	100	0·2	
CZ10	15	99·1	TZ° + m m = 80%	yes	long (> 10)	80	0·16	3
CZ12	15	98·7	TZ°C	yes	short (< 5)	590	1·15	10
CZ14	15	98·5	TZ°	yes	short (< 5)	560	1·4	9·1
CZ20	15	99·2	TZ° + TZ′	yes	long (> 10)	480	1·6	6·5

*Relative flexural strength is the ratio between the matrix and composite strength. For the pure matrices we measured the following values: CZ10, $\sigma_0 = 500$ MPa, $K_{Ic} = 12$ MPa$\sqrt{m}$; CZ12, $\sigma_0 = 510$ MPa, $K_{Ic} = 9$ MPa$\sqrt{m}$; CZ14, $\sigma_0 = 400$ MPa, $K_{Ic} = 7$ MPa$\sqrt{m}$; CZ20, $\sigma_0 = 300$ MPa, $K_{Ic} = 3.5$ MPa$\sqrt{m}$.

the amount of added $LaNbO_4$ from 15 to 10, 5, 2·5 vol%, it is indeed possible to reduce the amount of monoclinic with respect to the tetragonal phase as reported in Fig. 3 and in this way, the mechanical properties of the materials are progressively improved, although they remain lower than those of the matrices (Table 1). However, the composites show a progressive reduction of the *in situ* whisker-like structure that was the aim of the present research.

If sintering is carried out at 1350°C for 1 h, the length of elongated crystals is shorter, their quantity is lower and the density of the composite is reduced.

Regarding the CZ20 the starting powder consists of fully stabilized zirconia and particles of the sintered materials do not spontaneously transform into monoclinic even if large amount of $LaNbO_4$ are added, therefore cracks were not observed in the composite. The microstructure of a sample sintered 3 h at 1450°C is reported in Fig. 4. As shown, a monosized particle distribution of the matrix is coupled with some $LaNbO_4$ large dispersed grains and randomly oriented elongated crystals are also visible with a length/thickness ratio > 10.

3.1.2 Materials from coprecipitated powders (CZ12 and CZ14)

Powders containing 12 and 14 mol% CeO_2 and up to 15 vol% $LaNbO_4$ sintered 3 h at 1450°C have almost full density (> 98% T.D.). The zirconia matrix remains tetragonal and the microstructure shows several elongated crystals, with aspect ratio < 10 (see Fig. 5).

Silica melts at the sintering conditions leading to the presence of liquid phase at the grain boundaries of the composites. The liquid phase promotes the growth of elongated $LaNbO_4$ crystals. Since coprecipitated CZ12 and CZ14 contain less silica than commercial CZ10 and CZ20 powders, it is assumed that less or no liquid phase is present. Therefore it can be concluded that the amount of liquid phase controls the aspect ratio.

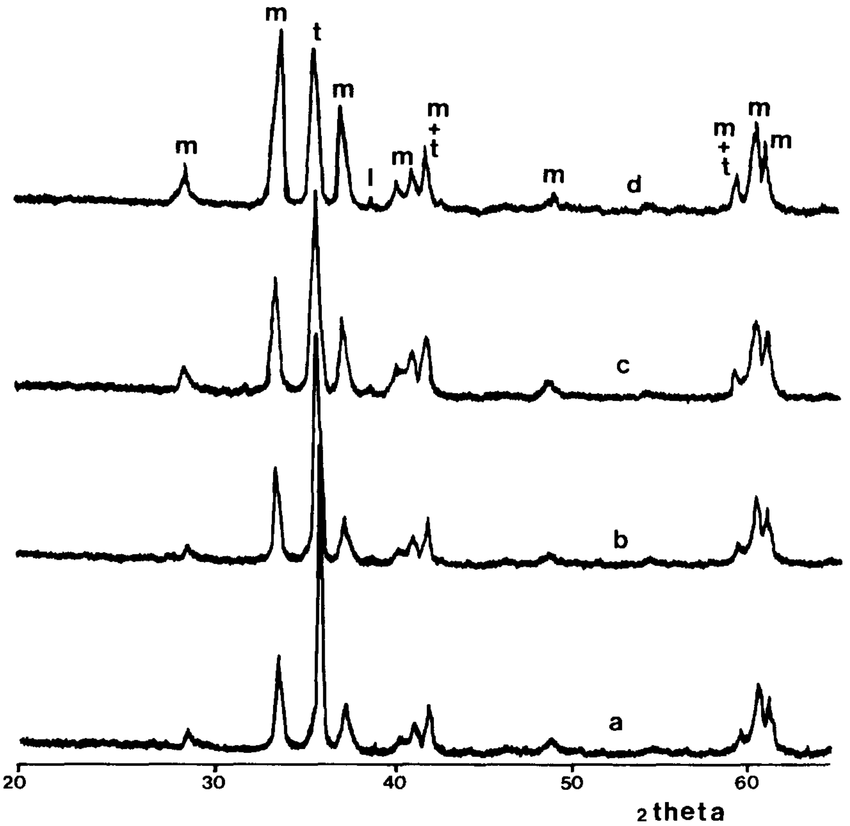

Fig. 3. X-ray diffraction patterns of CZ10 samples containing, respectively, (a) 2·5%, (b) 5%, (c) 10% and (d) 15%, respectively, of $LaNbO_4$ produced by coprecipitation and sintered for 3 h at 1450°C (m = monoclinic, t = tetragonal, l = monoclinic $LaNbO_4$).

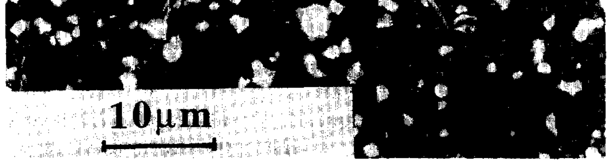

Fig. 4. SEM microstructure (back scattering mode) of polished and thermally etched CZ20 sample containing 15 vol% produced by coprecipitated and sintered for 3 h at 1450°C.

3.2 Mechanical properties

As stated in the previous paragraphs, the materials produced using powders obtained from coprecipitation showed better microstructures and the same crystallographic phases than those produced using powders from mechanical alloying; therefore the mechanical properties have evaluated only for the former materials.

Also in Table 1 are the list of the relative flexural strength ($\sigma_{composite}/\sigma_{matrix}$) for the different materials tested.

As mentioned before the addition of even small quantities of $LaNbO_4$ to the CZ10 matrices results in the presence of the monoclinic phase in the matrix. The spontaneous transformation takes place with a volume change and therefore can cause cracks. The mechanical properties of the CZ10 composites are therefore poor and even the addition of only 5% of $LaNbO_4$ reduces the strength to 60% of that of the matrix. Due to the higher amount of stabiliser (CeO_2), the CZ12 and CZ14 matrices remain tetragonal despite concentration as high as 15 vol% $LaNbO_4$. The CZ12 strength's with 15 vol% of $LaNbO_4$ is higher than

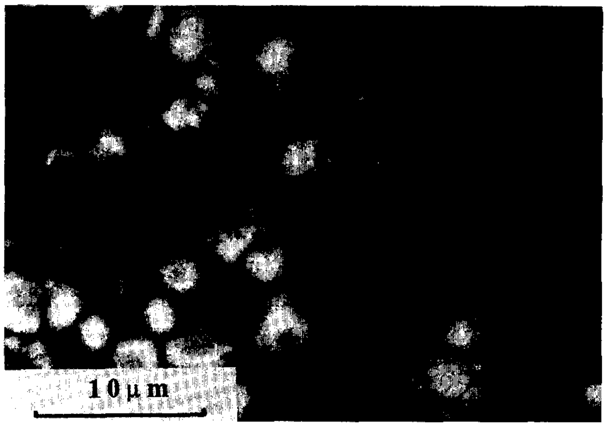

Fig. 5. SEM microstructure (back scattering mode) of a CZ14 sample containing 15 vol% vol. $LaNbO_4$ produced by coprecipitation and sintered for 3 h at 1450°C.

that of the pure matrix (1:15 times) even though the $LaNbO_4$ is present in the monoclinic form and the aspect ratio of the elongated grains is not very high (~5). CZ14 is less prone to transformation and in fact the addition of $LaNbO_4$ leaves the matrix completely tetragonal, and besides the elongated grains have a higher aspect ratio (~10) therefore the material strength increases and reaches a maximum of 1:4 times the strength of the pure matrix.

In the CZ20 matrix, two tetragonal phases (i.e. called TZ° and TZ′) □coexist, the TZ° is the one stable for CeO_2 compositions ranging from 7·5 to 16 mol%, the other exists for compositions from 16 to 50 mol%. The former can transform under an applied stress raising the material toughness, whereas the TZ′ is stable and it does not transform neither on cooling nor during the application of external load as it derives from the high temperature cubic form.[26] When $LaNbO_4$ is added the ratio of the two TZ phases changes with an increase for the TZ°. Being the TZ° the only phase that can transform during loading, the contemporary effect of the higher content of TZ° as well as the presence of elongated grains increases the strength of the composite compared with the value of the matrix.

A flexural strength of 480 MPa was measured and should be compared with the value of 300 MPa of the pure CZ20.

Even if the strength cannot be considered low, it is far enough from values obtained on other Ce-TZP based ceramics,[16] because in CZ20 materials, as mentioned before, the transformation involves only a fraction of the bulk particles. Most of them do not transform at all and remain tetragonal even under an applied stress field.

4 Conclusions

$LaNbO_4$ produced via coprecipitation or mechanical alloying has been introduced in different Ce-TZP matrices up to 15 vol%. In both cases the resulting microstructure contained elongated grains. The morphology of the final microstructure is determined principally by maximum processing temperature and composition of the starting powders, in fact the liquid phase promotes the growth of elongated $LaNbO_4$ crystals. Due to the high purity of the reagents used, Ce-TZP prepared by coprecipitation contains a very small amount of silica that melts at the sintering conditions and this can explain the smaller length/diameter ratio of the elongated grains found in these materials. This study has also shown that in every sample, the $LaNbO_4$ grains are enriched in ceria. As a consequence, zirconia matrices result more transformable and many tetragonal particles directly transform to monoclinic on cooling. For several compositions the $LaNbO_4$ additon results in a strength increase which can be ascribed to a larger fraction of transformable matrices.

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