Bi-modal distribution of stabilizers to regulate the dual-phase microstructure and transformability in Nd₂O₃/Y₂O₃-doped zirconia ceramics

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Abstract

The phase relationship and microstructural characteristics were systematically studied for co-stabilized ZrO₂ ceramics with Nd₂O₃–Y₂O₃ additives coated onto starting powder. Polishing induced surface morphological changes by tetragonal-to-monoclinic transformation were observed by SEM. EDS analysis revealed a bi-modal distribution of the stabilizers correspondingly to smaller transformable tetragonal grains and larger non-transformable cubic grains. The correlation of co-stabilizer concentrations with the dual-phase microstructures leads to a probable two-stage sintering enabled by transient liquid-phase started from coating. Small *t*-ZrO₂ grains inherited the starting nanopowder to take less stabilizers via diffusion, and larger *c*-ZrO₂ grains incorporate directly stabilizers during growth from liquid-phase accumulated more stabilizers. The transformability of *t*-ZrO₂ grains is influenced by neighboring *c*-ZrO₂ grains when a compressive stress on the former is sufficiently large from the latter in larger size and high modulus, which could be regulated by the two-stage process to optimize the dual-

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phase microstructure.

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1. Introduction

Zirconia ceramics with tetragonal phase (TZP) have excellent flexural strength and fracture toughness owing to a stress-induced tetragonal-to-monoclinic ($t \rightarrow m$) transformation upon fracture, hence they are used widely from body implants and dental applications to thermal-barrier-coatings (TBC) for several decades [1, 2]. The transformable t -ZrO₂ phase is stabilized by rare-earth dopants in Ce-TZP and especially Y-TZP, and the grain size is directly correlated with the t -phase transformability and the ceramic toughness [3, 4], which is also true in nano-crystalline Y-TZP [5]. Furthermore, an inhomogeneous distribution of the stabilizer doped via the powder coating route could effectively enhance the toughness [6]. Indeed, the stabilizer level was found to increase inversely with the grain size in Ce-TZP, which indicates that the sintering process could control not only the grain size but also the distribution of the stabilizer [7].

Most Y-TZP ceramics suffer from low-temperature degradation (LTD) when exposed to ambient humidity, which severely limits its application as biomaterial [8, 9]. Addition of Ce as co-stabilizer could effectively eliminate the LTD effect in Ce/Y-TZP, and the powder coating approach retained superior mechanical properties [10, 11]. In comparison, better mechanical properties and phase stability were demonstrated for Nd/Y-TZP ceramics pressureless sintered at 1400-1450°C from stabilizer-coated starting powder at relatively low stabilizer levels [12-14]. The effect of the co-stabilizer distribution in the microstructure on the t -phase transformability and hence the fracture toughness and hydrothermal stability however is still unknown. In this work, we will study the phase relations in Nd/Y-TZP ceramics, especially focusing on the stabilizer

distribution by micro-chemical analysis in a scanning (SEM) and transmission electron microscope (TEM). Dual-phase (*t/c*) microstructure is found to dominate the co-stabilized TZP ceramics, which is similar to recent observation in Y-TZP but will be rationalized with rather different mechanism [15].

2. Experimental

ZrO₂ powder was coated with 0.1 molar Nd(NO₃)₃·6H₂O (99.9%, Aldrich) and Y(NO₃)₃·6H₂O (99.9%, Aldrich) solutions. The appropriate amount of solution was mixed on a multidirectional mixer (Turbula type) with pure *m*-ZrO₂ powder (Tosoh grade TZ-0, 27 nm, Japan) in ethanol in a polyethylene container for 24 h with 3Y-TZP milling balls to break the agglomerates. After calcination at 800°C for 1 hour, another mixing was performed in ethanol to break agglomerates of stabilizer-coated ZrO₂ nanopowder. After cold isostatic pressing at 300 MPa, the green bodies were sintered into fully densified ceramics in a tube furnace (TGA-171, Cahn, USA) for 2 h at 1450°C under an air flow of 100 ml/min. Two Nd/Y-TZP ceramics were investigated in this study, both with 2 mol. % Nd₂O₃ but with a different Y₂O₃ amount of 1.5 and 2.5 mol.%, referred to as 4302 and 4502 according to the corresponding NdO_{1.5} and YO_{1.5} mole contents and holding time of 2 hours at the sintering temperature. Further details about the material processing and physical properties are reported elsewhere [14].

Although the microstructures of various Nd/Y-TZP ceramics were briefly compared 15 years ago, we re-examined detailed microstructural features of these two samples by a combination of SEM (model G300, Carl Zeiss, Germany) and TEM (model JEM-2100F, JEOL, Japan) imaging and analytical capabilities. Besides secondary electron (SE) and backscattered electron (BSE) imaging modes, this SEM is also equipped with an energy dispersive X-ray spectrometer (model AZtec, Oxford Instrument, UK) and electron backscatter diffraction (EBSD, Oxford, UK) systems to

analyze the local chemistry and crystal structures. EDS point analysis in SEM was performed with an accelerating voltage of electron probe under 10 kV to include all cations into the quantitative analysis using standards from the commercial system. Elemental mapping was performed under 5 kV to achieve better lateral resolution. EBSD mapping was performed under 20 kV and a step size of 30 nm to guarantee sufficient signal intensity.

Bulk phase identification on mechanical polished surface was carried out using X-ray diffraction (model D2, Bruker, Germany) with a scan-step of 0.02°, enabling to identify and quantify the different ZrO₂ phases. The phase contents were calculated from the relative intensities of corresponding reflections by commercial software (JADE). The TEM was operated under an accelerating voltage of 200 kV, and equipped with an X-ray spectrometer (model EDAX, Edax Instrument, USA) for EDS analysis. Quantification of cation ratio in TEM was processed in a standard-less mode using the thin-specimen approach. TEM specimens were prepared by ion milling (model EM RES101, Leica, Germany) after cutting, polishing and dimpling. For better imaging and analysis, all samples were coated with a ~3 nm thin carbon coating (model EM ACE600, Leica, Germany).

Most studies on TZP microstructures use thermal etching to highlight the grain morphology after mechanical polishing. In this study, the triple ion-beam cutting technology (model EM TIC 3X, Leica, Germany) was used to expose the native surface for imaging and EDS analysis to minimize the effect from mechanical polishing instead. This implies an ion slope cutting (ISC) performed under 6.5 kV at 0° tilt for 3.5 h for each sample surface. Vibration polishing (VP, model VibroMet 2, USA) was applied on the sample surface for EBSD analysis. In addition to the conventional TEM specimen preparation for both ceramic samples, a TEM cross-sectional specimen was thinned by focused ion-beam equipment (FIB, model Helios G4 UX, Thermo Fisher Scientific, China) from a vibration polished 4302 surface.

3. Results

3.1 *Phase identification by SEM imaging*

The highest fracture toughness among a series of co-stabilizer contents and sintering times was measured for the 4302 ceramic, and the absence of m -ZrO₂ phase implies that there was only transformable t -ZrO₂ phase co-existing with c -ZrO₂ phase [14]. As shown in Fig. 1 for both 4302 and 4502, ion cutting reveals the grain morphology of the ZrO₂ ceramics in both SE and BSE mode images, even though the SE mode images clearly indicate that the ISC surfaces are not as flat as other surfaces. Furthermore and especially in the BSE images, not only the grains could be further distinguished by a bright and dark contrast, but there are also gray contrast grains, especially in 4302. These gray grains often exhibit a twinned structure either below or above the surface, and the latter appears as a striped pattern as marked by the red circles. This twin-structure can only be attributed to the presence of m -phase in the Nd/Y-TZP ceramics. The fact that some of these nanometric m -phase grains are protruding out of the surface is due to the volume expansion upon transformation from the initial t -phase grains.

Fig. 1 SE/BSE (upper/lower panels) images of ion slope cut 4302 and 4502 Nd/Y-TZP ceramics revealing bright (large), dark (smaller) and gray contrast ZrO_2 grains. The gray contrast grains in 4302 have a twinned appearance, as marked by the red circles, which is much less pronounced in 4502.

EBSD analysis of a flat polished 4302 surface revealed that the bright and dark contrast phases correspond to *c*- and *m*-phase respectively as shown in Fig. 2, while almost no *t*-phase was detected. The large grains correspond mainly to *c*-phase, and a small number of points inside these grains are recognized mistakenly as *t*-phase. Analysis of small grains fails at the majority of black points to manifest as zero resolution, and all the non-zero points corresponds to *m*-phase, regardless of small grain size and even smaller twin features that are hard to resolve by EBSD. The dark grains in 4502 are smaller hence even harder to know whether they are transformed or not, while the bright grains are all in *c*-phase.

Fig. 2 BSE image (upper) and corresponding EBSD mapping (lower) for phase identification of the individual ZrO_2 grains in the 4302 ceramic.

To assess whether some or all t -phase grains transformed into m -phase grains during 15 years staying in ambient condition in a desiccator to prevent excessive humidity, high-resolution XRD analysis on mechanically polished surfaces was performed on both ceramics. The t - and c - ZrO_2 remained as primary phases as shown in Fig. 3, even though weak m - ZrO_2 peaks were also detected. Both Nd/Y-TZP ceramics are largely untransformed to signify a mild LTD effect, as compared to the XRD analysis of the as-sintered samples where no m -phase was detected [16-18]. Therefore, t -phase grains have mostly transformed on the surface of the 4302 ceramic, as induced by the mild ion-cutting, revealed as the twin-structures, while it is not the case for the majority of the t -phase grains in the 4502 ceramic (Fig. 1).

Fig. 3 XRD patterns of the 4302 and 4502 Nd/Y-TZP ceramics obtained from the mechanical polished surface, revealing cubic (c), tetragonal (t) and monoclinic (m) ZrO_2 phases.

method	sample	<i>monoclinic</i>		<i>tetragonal</i>	<i>cubic</i>	
XRD	4302	12.8%		52.9%	34.3%	-
	4502	18.6%		37.7%	43.7%	-
		<i>dark</i>	<i>transformed</i>	<i>gray</i>	<i>bright</i>	<i>hole</i>
SEM	4302	13.5%	54.7%	4.1%	26.5%	1.2%
	4502	16.5%	7.0%	33.5%	41.0%	2.0%

Table 1 Phase fractions of *m*-, *t*- and *c*- ZrO_2 phases calculated from XRD patterns (Fig. 3) in comparison with quantitative analysis of ZrO_2 grain contrast in SEM (such as Fig. 1) for the 4302 and 4502 Nd/Y-TZP ceramics, averaged over total imaging areas of 180 and 192 μm^2 respectively.

As summarized in Table 1, it is more revealing for the Nd/Y-TZP ceramics to compare the phase fractions obtained from high-resolution XRD patterns with the relative areas of ZrO_2 grains in different contrasts from SEM images. The fraction of bright contrast corresponds to the *c*-phase in this comparison, which is also consistent with the EBSD analysis (Fig. 2). The area of gray contrast in 4502 fits rather well to *t*-

phase measured by XRD, while it is only the twin-structures in 4302 to match the amount of t -phase detected by XRD. Such twin-structures are giving a mixed gray contrast, which are similar to the “twinned features” from the stress-induced $t \rightarrow m$ transformation in Ce- and Y-TZP ceramics [16-18]. Furthermore, the phase transformation in 4302 also uplifts the surface as shown in Fig. 1. A similar phenomenon was observed in an AFM study of Ce-TZP ceramics [19]. Therefore, the grains in both the gray contrast and twin-structures correspond to the t -ZrO₂ phase, while they transformed largely into m -phase in 4302 but untransformed in 4502.

Dark grains may or may not correspond to the m -phase grains, although their fractions match rather well with the XRD results. The contrast in SEM images is not associated only to the crystal structures of ZrO₂ phases, since the differences in the grain orientation and conductivity could also contribute to this contrast, which make the distinctions between t and m phases more complicated. Furthermore, the stabilizer elements, especially the heavier Nd, could also contribute to the BSE contrast, hence the stabilizer concentration in different contrast grains should be measured to better understand these phase structures.

3.2 Co-stabilizer distribution in the dual-phase microstructures

EDS analysis were performed in various modes to reveal the distribution of Y and Nd stabilizers within the dual-phase ZrO₂ microstructures. Elemental mappings of 4302 are given in Fig. 4 together with the corresponding BSE image, taken at a beam voltage of 5 kV for better resolution. It reveals a higher level of both co-stabilizers in solid solution in the bright c -phase grains and a lower level of both solutes in the dark homogeneous and gray spackled grains. The distributions of both Y and Nd are rather uniform within the bright or dark/gray grains, respectively, and even an embedded dark grain could be identified from the surrounding bright grain as marked by the arrow, which is similar to the grains marked in Fig. 2. Two levels of co-stabilizers suggest that there is a bi-modal distribution of co-stabilizers in the largely dual-phase

microstructures of Nd/Y-TZP ceramics, which is consistent with the predominant *t*- and *c*-phases detected by XRD. The distinction between *t*- and *m*-phases from SEM images is less important, since the *m*-phase originates all from the *t*-phase, earlier or later. Thereafter we refer them all as *t*-phase and dark grains for simplicity.

Fig. 4 Elemental EDS mapping of 4302 revealing two levels of stabilizers distributed within the dual-phase microstructure of Nd/Y-TZP.

To know more about the Y and Nd co-stabilizer content of the bright and dark grains, their solution levels were measured by EDS analysis in individual grains. This was performed at a beam voltage of 10 kV, since the Nd lines could not be quantified at 5 kV [20]. Data from about 200 grains are plotted in Fig. 5 for both ceramics, and the bright and dark grains are distinguished by open and filled symbols, respectively. The grain size was determined by measuring the area of each grain and then converting into an equivalent diameter. The correlations between the stabilizer level and the grain size are significantly different for the bright and dark grains of both ceramics. The Y and Nd content of the bright grains slowly increased over a wide range of grain sizes. Despite the same overall Nd content, the Nd content in the bright grains of 4302 is higher than that in 4502, whereas the Y content in these grains is substantially lower in 4302 than in 4502 to follow their doping. For the dark grains, the data are more scattered in 4302

than in 4502, and the Nd content is higher than the Y content in one ceramics whereas it is the opposite in the other.

Fig. 5 Y and Nd stabilizer levels in individual ZrO_2 grains against the grain sizes, splitting for dark and bright grains, measured as cat.% by EDS analysis in SEM. EDS results in TEM are also given for comparison without distinguishing the grain contrasts.

Since the effect of the electron beam penetration and broadening is more pronounced in the smaller dark grains when analyzed by SEM-EDS, EDS analysis were also done in the TEM mode, although this did not allow to differentiate the ZrO_2 grains based on their contrast as in the SEM imaging. The TEM data are also plotted against the grain size in Fig. 5, which confirms and reinforced the bi-modal distribution of Nd/Y stabilizers. The range of grain sizes analyzed in the TEM mode is much narrower and contains more small grains, which allow them to associate unmistakably with the lower level of stabilizers of the dark grains observed in SEM. The stabilizer contents are much less scattered in the TEM analysis and significantly lower than the SEM data, especially for the dark grains, hence in clear contrast to the probe effect in the SEM analysis.

This probe effect is much less pronounced for the bright grains observed in SEM, hence the higher levels of dissolved Nd measured by TEM match rather well with those by SEM in both ceramics. The higher level of Nd in *c*-phase grains in the 4302 ceramic than in the 4502 ceramic, which is consistent with its higher fraction in the latter as measured by both XRD and SEM. The Y levels measured by TEM are significantly lower than those obtained by SEM, which might originate from a systematic difference in separating the overlapping Y and Zr signals in the EDS spectra by TEM and SEM,

or in Y reference between the different EDS systems. Nevertheless, the data for the bright grains in SEM extend to a much wider grain size than the grains measured by TEM, especially for 4502. Indeed, the Y solubility increases steady with grain size at a similar rate in both ceramics, whereas the Nd solubility saturates relative fast against grain size. Therefore, although the bi-modal co-stabilizer distribution has been observed in both SEM and TEM, it is more reliable to use the TEM data for the lower levels of stabilizers, while it is more suitable to use the SEM data for the high levels in larger grains.

4. Discussion

4.1 ZrO₂ phase evolution by a two-stage sintering mode

This systematic study of stabilizers in correlation with the phase relation and microstructure could bring us new insights into the sintering behavior for TZP ceramics. In a recent review on microstructure study of Y-TZP ceramics, the formation of *c*-phase was explained by a grain boundary segregation-induced phase transformation (GBSIPT) mechanism, which based on an inhomogeneous distribution of Y stabilizer within *c*-phase grains of size similar to *t*-phase grains [15]. In other words, *c*-phase was formed from *t*-phase via diffusion, after the grain growth has completed. In the present dual-phase ZrO₂ ceramics, the bi-modal distribution of co-stabilizers signifies rather uniform Nd and Y solution in each phase, and even more so within each grain. Such a local uniformity is hard to achieve via the grain boundary for *c*-phase with much higher levels of stabilizers. The dissolution of Nd/Y into the ZrO₂ grains of *t*- and *c*-phases should occur under separate diffusional mode, or in separate stages of the sintering process. This is because two uniform distributions could not be realized at a same rate or time of diffusion. It is most likely that stabilizers in the *c*-phase grains were not incorporated via diffusion, but instead via grain growth. Indeed, diffusion of so high stabilizers into

c-phase grains requires an equal amount of Zr to diffuse out of the grains, prior to the diffusion-in by the stabilizers, which is improbable at the sintering temperature. We propose an alternative two-stage sintering picture with the presence of a transient liquid-phase during sintering, which enables the large *c*-phase grains to grow directly from such liquid-phase containing both rare-earth cations in high concentrations, and highly uniform. Coating of oxide dopants onto the nanometric *m*-phase powder initiates the liquid-phase, promoted by surface structure and nanometer size of ZrO₂ powder to lower the melting point by hundreds of degrees. This is effectively solution–reprecipitation process similar to SiAlON and SiC ceramics, which incorporate also additives into uniform solid-solution by liquid-phase sintering [21-23].

The transient liquid-phase can rationalize the bi-modal distribution of co-stabilizers in the dual-phase microstructures of Nd/Y-TZP in similar way. First, not only both dopants could melt to form the initial liquid, but the nanometric *m*-ZrO₂ powder could also dissolve partially from the surface to form a liquid-phase of Zr–Nd–Y–O. Second, this transient liquid could enable the co-stabilizers to diffusion into ZrO₂ grains, in exchange of Zr cations to diffuse from these grains into the liquid-phase. The exchange rate and diffusion time are both limited, permitting only low a level of stabilizers to diffuse into the grains while turning them into the *t*-phase. Third, when the ceramic body was largely densified by the transient liquid-phase and the low-level solubility of stabilizers was reached by the exchange diffusion, remaining liquid-phase carries still rather high concentration of dopants into larger pockets of the *t*-grain microstructures, from which the *c*-phase grains could precipitate directly. As demonstrated in Fig. 1, large *c*-phase grains exhibit generally concave boundaries to reveal their original nature of liquid-phase in accommodating the shapes of *t*-phase grains then already formed. The large *c*-grains develops from the liquid-phase by self-nucleation, or in the reprecipitation mode to grow onto adjacent *t*-phase grains.

In this solution–reprecipitation picture, two ZrO₂ phases are developed separately in separate stages of the liquid-phase process to result in the bi-modal distribution of co-stabilizers. This two-stage sintering process is similar to the liquid-phase sintering of SiAlON and SiC ceramics, which incorporate Al₂O₃ or AlN dopants into the ceramic

phase in two levels of solid-solution. This occurs not only in the liquid-phase sintered SiC ceramics, but also in the solid-state sintered SiC ceramics where the liquid-phase could only formed locally [21-23]. In the latter case, two levels of uniform AlN solution was found even in same SiC grains. This was also often observed in the present case with tiny *t*-phase grains imbedding inside *c*-phase grains, as marked by red arrows in Figs. 2, 4 and 7. Co-existence of dual-phases in such a way confirms further that the *t*-phase was formed before *c*-phase in these ZrO₂ grains. The small *t*-phase grains with less stabilizers serve as seeds for the large *c*-phase grains to grow in epitaxy mode with more stabilizers.

Fig. 6 Correlated distribution of co-stabilizers in the Nd-Y-TZP ceramics. Nominal ratios of the two dopants are plotted in dashed lines as references.

To reveal further information from the dual-phase microstructure developed in such two-stage sintering, we re-plotted Fig. 5 into Fig. 6 to correlate the Y and Nd stabilizer contents for every bright and dark grain in both Nd/Y-TZP ceramics. Two dashed lines represent their nominal ratios from dopants, which can serve as the references for comparison of trends between the two stabilizers. For the 4302 ceramic, stabilizer ratios between grains of both phases or contrasts fall into a common trend, while in a higher

Nd:Y ratio than the nominal value. In contrast, there are two populations of stabilizers for 4502, divided largely between the bright *c*-phase grains and dark *t*-phase grains, while the overall ratio stays with the nominal of two dopants. The bi-modal distribution of co-stabilizers and their ratio could be altered systematically by the EDS-SEM analysis when the neighboring grain is from the other phase, especially for the 4302 with relatively small grains. For 4502 with much larger bright grains, this correlation of co-stabilizers reveals a saturated trend of Nd in *c*-phase against Y level, which increases steadily over a wide range of grain size (Fig. 5). Although the transient liquid-phase might start from a similar composition, the diffusion rate of both stabilizers in the *t*-phase grains should be different, which leaves a variable ratio of stabilizers in the liquid-phase hence similar trends in subsequent *c*-grain growth. Opposite to this Y trend in 4502, a decrease of stabilizer with grain size was reported previously in Ce-TZP, processed also by powder coating [7], which demonstrates further that the diffusional behaviors of rare-earth could correlate the phase relationship with their microstructural development during sintering process. Therefore, the re-distribution of dopants into the bi-modal distribution in the present study exposes not only the two-stage sintering process promoted by the transient liquid-phase, but also the perspective to regulate the dual-phase microstructures by optimized design of doping and sintering schedules in future.

4.2 Constraining $t \rightarrow m$ transformation by *c*-phase grains

Due to the bi-modal distribution of both stabilizers, a dual-phase microstructure dictates the mechanical behavior of Nd/Y-TZP, and especially dominates the $t \rightarrow m$ phase transformation upon fracture. As revealed in a previous study of the Nd/Y-TZP system [14], sintering of 1 or 2 h at 1450°C (4301 and 4302) left no detectable amount of *m*-phase, while *m*-phase to appear after 3 h sintering still at 1450°C (4303). After storing in ambient condition for 15 years, we have detected 12.8 vol.% *m*-phase in 4302, and a higher fraction but still below 20 vol.% in 4502, which should have transformed

from the t -phase by the LTD effect. The original t -ZrO₂ transformability reached ~65 vol.% for 4302, and probably 55% vol.% for 4502 assuming little m -ZrO₂. In contrast to rather mild LTD effect for both Nd/Y-TZP ceramics, significantly different amount of m -phase results from surface polishing, which shed new light into the mechanism of $t \rightarrow m$ transformation in the dual-phase microstructures. As compared in Fig. 1 and Table 1, even the relatively mild ion-cutting for 4302 has induced a majority of twinned-features from the otherwise t -phase grains underneath the surface, while the t -phase in 4502 remains largely untransformed. The extensive transformation enables some grains to lift up from the ion-cut 4302 surface to relieve the constrained strain, which is similar to the case of Ce-TZP as studied by AFM [24]. Porosity of both ceramics are also found in rather similar levels, and the most significant difference between two ceramics is the size of c -phase grains in the dual-phase microstructures.

Fig. 7 Bright-field STEM image of a focused-ion-beam cross-sectioned 4302 surface demonstrating a transformed zone of twinned grains close to the surface (above the red-line) induced by mechanical polishing.

To further compare with the effect of mechanical polishing, a TEM cross-sectional specimen was prepared by focused ion beam (FIB) from the vibrational polished surface of 4302, as shown in Fig. 7. It reveals clearly that twinned grains dominate underneath the polished surface until a depth of ~500 nm, as marked by a red line.

Below this depth, there is no sign of such twinned grain, and a small grain is again found inside a large grain as marked by the arrow, which is common to the cases marked in Fig. 2 and 4. As compared in Table 1, ion-cutting results in a 7 vol.% *t*-phase transformation of a 4502 surface out of a total of 35 vol.%, indicating that the transformability of most *t*-ZrO₂ grains remains mostly constrained in 4502 under the same polishing condition as in 4302.

Fig. 8 Conventional bright-field TEM images of a thick (left) and thin (right) regions in Nd/Y-TZP specimens demonstrating strain fields built into small grains to constrain the transformability.

The *t*-phase grains in 4302 and 4502 are of similar size, but the grain sizes of *c*-ZrO₂ are in twice the range for 4502 than 4302, or approaching an order of difference in their volume of individual *c*-phase grains. The small *t*-phase grains with low level of Y/Nd stabilizers are susceptible to the *t*→*m* transformation when opened up to free space. The more of small *t*-phase grains to agglomerate together, the higher for their transformability, hence it is only the *c*-phase grains in large size that could constrain effectively the transformation of neighboring *t*-phase grains. On the other hand, the stabilizer content in the *t*-phase grains of the 4302 ceramic is also lower than that in the 4502 ceramic, boosting up further their transformability. This effect will compete with the constrain effect from the *c*-phase grains on the transformation to further widen the gap of observed transformability between the two TZP ceramics. Upon cooling the *c*-

ZrO_2 phase shrinks usually slower than the $t\text{-ZrO}_2$ phase, hence a c -phase grain should generate a compressive stress into the matrix of t -phase to constrain the transformability in its neighborhood. In the standard TEM specimens thinned down by mild ion-milling, transformation was not found in both Nd/Y-TZP ceramics as predominant as in FIB sample, as demonstrated in Fig. 8. Instead, strain contrasts are often observed to develop into the small grains especially surrounding a large grain free from such strain (left panel of Fig. 8). The small grains could accommodate the compressional stress by elastic deformation within the thin TEM foils, which is in contrast to the SEM observation opening up to free space especially in 4302. It is the combination of differences in Young's modulus and in grain size between the two phases to dictate the transformability of the t -phase grains in the neighborhood.

Fig. 9 The two-phase relationship of both Nd/Y-TZP ceramics plotted in the ternary $\text{ZrO}_2\text{--Nd}_2\text{O}_3\text{--Y}_2\text{O}_3$ phase diagram, taken averages from EDS results in SEM and TEM modes (see Fig. 5 and Table S1). Data are more reliable for the $t\text{-ZrO}_2$ phase from the low level in TEM, and for $c\text{-ZrO}_2$ phases from bright grains in SEM, respectively; they are represent by filled symbols. The nominal stabilizer compositions are marked by round dots, from which the re-distribution of co-stabilizers separate the ZrO_2 structures into two phases. Two phase boundaries are calculated for 1450°C in Ref. [12].

After revealing the bi-modal distribution of co-stabilizers, we can renew the dual-phase relationship into the ternary $\text{ZrO}_2\text{--Nd}_2\text{O}_3\text{--Y}_2\text{O}_3$ phase diagram, as shown for the ZrO_2 -rich corner in Fig. 9. The nominal composition of 4302 lies almost on the first phase boundary between the *t*- and mixed-phase zones, and 4502 locates rather deep into the predicted dual-phase zone. Although we plotted both sets of stabilizer contents measured by SEM-EDS and TEM-EDS as all averaged in Table S1, the SEM data from bright grains are more representative for *c*- ZrO_2 phase, and the low level TEM data (TEM *L*) for *t*- ZrO_2 phase, as compared in the results section. The nominal compositions in two TZP ceramics from starting powder are both on the tie-lines of two ZrO_2 phases, demonstrating that a clear “phase separation” has occurred for the dual-phase relationship. This phase-separation starts from very close compositions for *t*-phase to diverge towards rather different composition for *c*-phase, manifesting a dictating effect of the transient liquid-phase to guide the stabilizer distribution and the dual-phase relation in the two-stage process. It is the powder coating that enables the transient liquid-phase to form early and in uniform composition, which enables the first stage to start early to leave ample time for diffusion into uniform levels, both in the *t*-phase and in the transient liquid-phase to reach a clear correlation between the co-stabilizers and the dual-phase microstructures. Other processing routes may not homogenize the stabilizers in similar dual-microstructures into clear-cut two-stages. Whether the stabilizer level is sufficient to stabilize or over-stabilize the *t*-phase depends also and more on the *c*-phase developed in the second-stage. Further elaboration of co-stabilizer distributions and phase relations in future will lead to a systematic understanding and optimization of the structure–property relations for TZP ceramics.

5. Conclusions

By quantitative analysis of stabilizer distribution within two Nd/Y-TZP ceramics,

we reveal a bi-modal distribution within the dual-phase microstructures. In comparison of various SEM observation and XRD analysis, different behaviors of $t \rightarrow m$ transformation on polished surface are found to originate from a difference in grain size distribution between the two ceramics of similar dual-phase relations. A transient liquid-phase was proposed to rationalize the formation of t - and c -ZrO₂ phases in a two-stage sintering process, which explains the re-distribution of stabilizers into the bi-modal distribution to develop the common dual-phase microstructures. This study further demonstrates that the transformability of t -phase grains could be constrained from the neighboring c -phase grains especially in much large size. Such inherent association of the dual-phase relationship and their microstructures opens new perspectives to tailor the dual-phase microstructures of TZP ceramics for better performance.

Fig. S1 Typical EDS spectra of bright and dark grains in 4502, data presented in Fig. 5 are processed from similar spectra.

Samples	stabilizers	bright	dark	TEM <i>H</i>	TEM <i>L</i>
4302	Y ₂ O ₃	1.88±0.5	0.99±0.4	1.38±0.2	0.37±0.1
	Nd ₂ O ₃	3.90±0.9	1.80±0.8	3.83±0.8	0.31±0.1
4502	Y ₂ O ₃	3.45±0.9	1.49±0.4	2.07±0.1	0.48±0.1
	Nd ₂ O ₃	3.02±0.8	1.08±0.4	3.39±0.4	0.09±0.07

Table S1 High and low levels of stabilizers in the two-phase Nd/Y-TZP ceramics, measured by EDS analysis in TEM or averaged from bright/dark grains in SEM. They are all plotted in Fig. 9 for comparison and further discussion.

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