Effect of NiO dissolution on the microstructural development of t'-ZrO$_2$ with 5 mol% Y$_2$O$_3$

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The ageing (1300 °C for 1–300 h) dependence of the microstructure of the metastable tetragonal (t'-) ZrO$_2$ (plasma-sprayed Y-PSZ with 5 mol% Y$_2$O$_3$) in the sintered (1300 °C, 5 h) t'-ZrO$_2$/NiO (10 mol%) composite was studied by transmission electron microscopy. Short-term (10 h) ageing caused incomplete decomposition of t'-ZrO$_2$ into tweed assemblages containing t'-ZrO$_2$ relics and tetragonal (t-) ZrO$_2$ precipitates in the cubic (c-) ZrO$_2$ matrix. The t'-ZrO$_2$ relics retained anti-phase domain boundary (APB) and primary deformation twins, but no secondary deformation twins. Further ageing (e.g. up to 100 or 300 h) caused growth of the twin variants of t-ZrO$_2$ with {1 0 1} habit plane. The large t-ZrO$_2$ variants transformed directly into m-ZrO$_2$ twins, but not into t-ZrO$_2$ colonies. In addition to the relics in the aged samples, t'-ZrO$_2$ with APB may also form locally from a solute-redistributed c-ZrO$_2$ by slow cooling.

1. Introduction

Zirconia-based material has been used for surface modification of metal alloys. For example, plasma-sprayed zirconia for thermal barrier coating (TBC) on nickel- or cobalt-based superalloys with MCrAlY-type (M = Co, Ni, Fe) bond coat, are commonly used with approximately 2–7 mol% Y$_2$O$_3$ which transforms on rapid cooling primarily into a metastable tetragonal (t'-) ZrO$_2$ whose solute content is nearly the same as the original cubic (c-) ZrO$_2$ [1]. The t'-ZrO$_2$ has characteristic anti-phase domain boundaries (APBs) and secondary deformation twins and is suggested to form via a displacive c–t' transformation [2] which occurs below a critical temperature, T_0, determined by the curvature of the free energy versus composition curves [3,4]. In principle, this t' phase is crystallographically identical with the regular tetragonal material, except that the t' phase is highly resistant to stress-induced, i.e. martensitic, transformation to the mono-clinic (m) phase despite a large grain size, hence referred to as nontransformable t' phase. This behaviour is presumably due to the stress dependence of the twin variants of t' phase ([5] and literature cited therein). The t' phase also exhibits excellent resistance to martensitic transformation after low-temperature ageing (e.g. at 275 °C for up to 1000 h in air) [5]. On the other hand, high-temperature exposure of t'-ZrO$_2$ caused its decomposition to the equilibrium high-solute c- and low-solute t-ZrO$_2$ [6], named yttria–partially stabilized zirconia (Y-PSZ). The t-ZrO$_2$ has a {1 0 1} habit plane (indexed as a slightly distorted version of the c-fluorite unit cell) in the early stage of precipitation in the c matrix, but it commonly develops "colonies" of twin-related variants which do not readily transform to m-ZrO$_2$ even when they become quite large [7].

Recently, the interdiffusion dependence of the phase equilibria of TBC were evaluated by X-ray diffraction in a simplified composite system NiO/t'-ZrO$_2$ (Y-PSZ) [8,9]. Above 1400 °C the dissolution of NiO in t' phase stabilizes the c phase but not the (c + t)-ZrO$_2$ assemblages [9]. At lower temperatures, e.g. 1200 and 1300 °C, the dissolution of NiO in t' phase facilitated its decomposition to (c + t)-ZrO$_2$ assemblages, but suppressed the subsequent t-ZrO$_2$ to monoclinic (m-) ZrO$_2$ transformation [8]. Annealing of this composite material also caused defect clustering at the grain boundary of the nonstoichiometric Ni$_{1-x}$O phase [10]; however, the effect of NiO dissolution in Y–PSZ on the morphology of t-ZrO$_2$ was not studied.

It has been suggested from observations of the slowly cooled samples that t'-ZrO$_2$ did not necessarily form by rapid quenching of c-ZrO$_2$ in Y–PSZ. Examples include (1) a single crystal of two-phase alloy (8 wt % Y$_2$O$_3$) having been heated at 1600 °C for 50 h [11], and (2) sintered (1400 °C, 2 h) and solute-redistributed Y–PSZ [12]. The t'-ZrO$_2$ formed by slow cooling has APBs but no deformation accommodation twins [11, 12]. It has also been noted that inter-diffusion prevented the formation of t'-ZrO$_2$ phase in a Y–PSZ/Ni$_2$AlTi cermet [13] which was sintered and slowly cooled under the same conditions as for Y–PSZ [12]. It is, therefore, of interest to study if the inter-diffusion of NiO/Y–PSZ composite also suppresses the formation of t' phase. The effect of NiO dissolution on the features of APBs or deformation twins in the decomposing t'-ZrO$_2$ also remains to be studied.

In this work, transmission electron microscopy (TEM) was used to study the microstructures of the NiO/t'-ZrO$_2$ composite with regard to (1) the

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morphology of t phase in the ternary (Ni, Y)–PSZ composition system, and (2) the effect of NiO-dissolution on the decomposition behaviour of t'-ZrO_2.

2. Experimental procedure

Detailed procedures to prepare plasma-sprayed powder of Y–PSZ (5 mol% Y_2O_3) were given previously [8]. This powder contains 85 mol% t'-ZrO_2, 11.5 mol% c-ZrO_2 and 3.5 mol% m-ZrO_2, estimated by X-ray (CuK_α) diffraction, and designated YZ specimen [8]. Powders of ternary composition were prepared by mixing YZ powder with 10 mol% NiO-source precursor (nickel acetate tetrahydrate) [8] and were designated NYZ specimens. The NYZ powders were die-pressed at 50 MPa into disc and sintered at 1300 °C for 5 h followed by annealing at 1300 °C for 1, 10, 50, 100, 200 and 300 h, respectively, and cooled in an open-air furnace. The sintered pellets are dark green in colour and with negligible weight loss.

Methods for the phase identification (e.g. t-versus t'-ZrO_2 using tetragonality criterion), the phase-content estimation of ZrO_2 and the d-spacing measurements using X-ray diffraction (CuK_α, 35 kV, 25 mA) were given previously [8]. As commonly adopted, a slightly distorted version of the c-fluorite unit cell was used to index the diffracting planes of zirconias. The NYZ samples fired at 1300 °C for 10, 100 and 300 h were selected for transmission electron microscopy (TEM, Jeol 200CX, at 200 kV) observations. TEM foils were prepared by ion-milling the thin sections (about 10–20 μm thick) to electron transparency.

3. Results

As reported previously [8], the t'-ZrO_2 in the plasma-sprayed and then slightly sintered YZ specimen is ~ 1 μm in size and has characteristic deformation twins and APBs (Fig. 1). There are also minor amounts of m- and c-ZrO_2 grains which are several hundreds of nanometres in size according to TEM observation [8]. Ageing of the NiO-added specimens (i.e. NYZ) caused variation of the phase content (Table I) and the morphology of zirconias as described below.

3.1. Decomposition of t'-ZrO_2

For NYZ samples annealed at 1300 °C for more than 10 h, the t'-ZrO_2 phase could not be easily detected by X-ray diffraction; however, a minor amount of t'-ZrO_2 was still observed by TEM. Short-period (10 h) firing caused the decomposition of t'-ZrO_2 into a complex feature in the bright-field image (BFI) (Fig. 2a). A dark-field image (DFI) illuminated with the {1 1 2} spot (Fig. 2b) revealed the twin variants of t'-ZrO_2 (ca. 0.2–0.3 μm long) which survived in a matrix consisting of finely tweed t-ZrO_2 precipitates (about tens of nanometres in size) in the c-ZrO_2. Compared with the microstructure of the as-sprayed t'-ZrO_2 (Fig. 1) the t'-relic in the annealed NYZ specimens shows primary deformation twins, but not secondary deformation twins (Fig. 2b). A finely tweed array of anti-phase
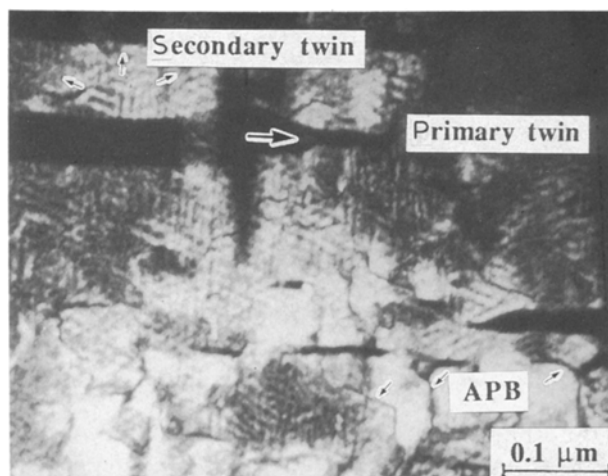

Figure 1 Transmission electron micrograph of a slightly sintered (1400 °C, 0.5 h) t'-ZrO_2 which has been prepared by plasma spraying of Y–PSZ powders. Note primary and secondary deformation twins in addition to the anti-phase domain boundary (APB) which appeared when imaged with the {1 1 2} spot of t'-ZrO_2 (after [8]).

TABLE I Firing conditions, phases and c-ZrO_2 content of NYZ specimens determined by X-ray (CuK_α) diffraction

Ageing Conditions		Phases[a]	c-phase in ZrO_2 (mol%)
°C	h		
1300	1	t', c, m, NiO	48
1300	10	c, t, m, NiO	85
1300	50	c, t, m, NiO	85
1300	100	c, t, m, NiO	85
1300	200	c, t, m, NiO	85
1300	300[b]	c, t, m, NiO	85
As-sprayed Y-PSZ		t', c, m	12

[a] Phases listed in order of decreasing abundance.
[b] Present work, other data [8].

domains (about tens of nanometres in size), which are similar to those observed in Y-PSZ by Lanteri *et al.* [11], also survived occasionally in t'-ZrO_2 (Fig. 2b).

3.2. Formation of c + t assemblages upon ageing

Ageing up to 100 h caused coarsening of t-ZrO_2 to form the plate-like variants (~ 0.1 μm long) which adjoined the c-ZrO_2 matrix with {1 0 1} habit plane (Fig. 3a). It is noteworthy that the c-ZrO_2 matrix showed diffuse scattered intensity (DSI) in the selected-area diffraction (SAD) pattern (Fig. 3b). Within the c + t assemblages, tweed arrays consisting of domains (approximately tens of nanometres in size), which resemble the APBs of t'-phase, were still observed in specimens aged for 100 h (Fig. 3c). These domain-like features were probably newly formed from the c phase rather than being a relic surviving prolonged ageing (> 100 h), as discussed in Section 4.2.
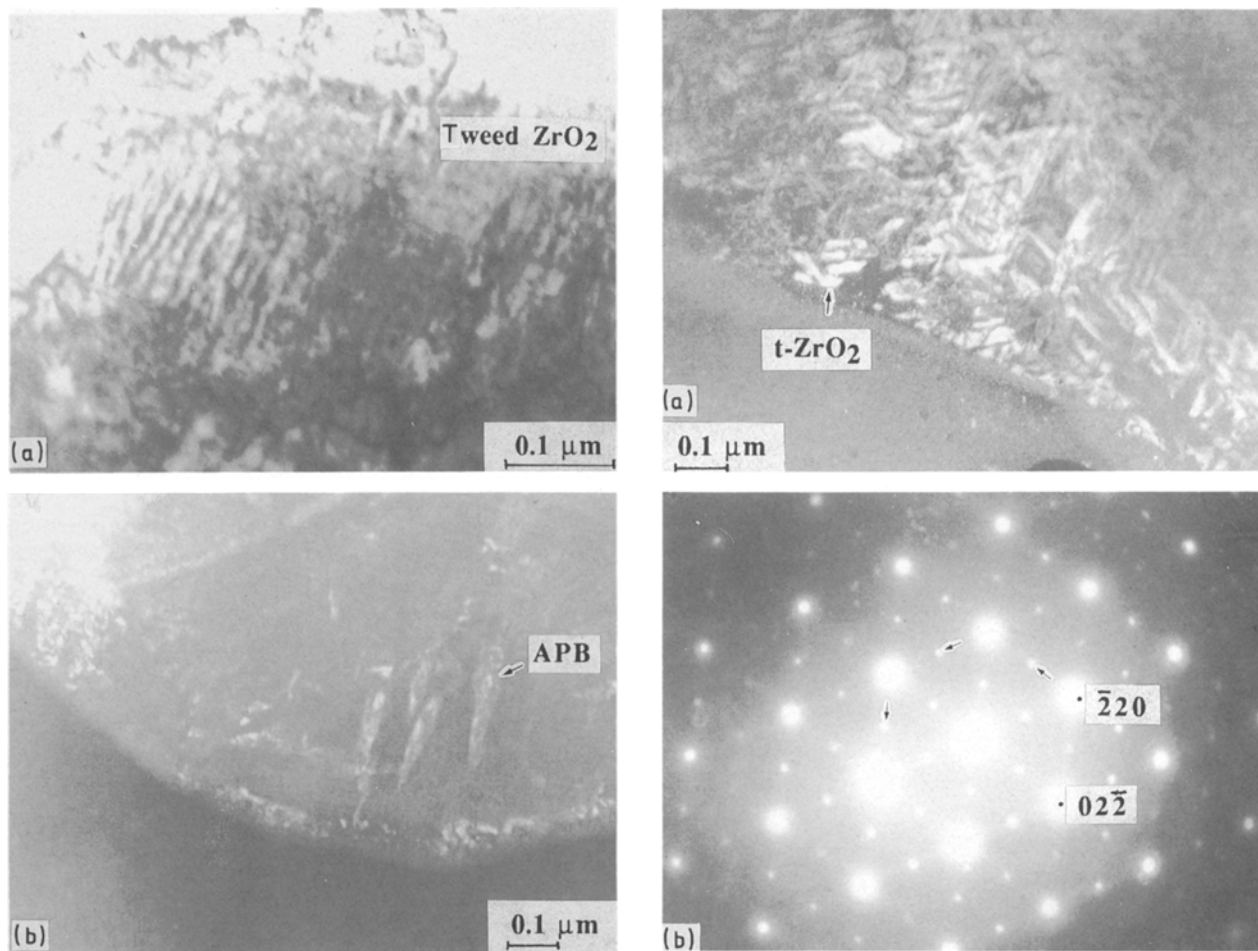
Figure 2 Transmission electron micrograph of short-term (1300° C, 10 h) fired NYZ sample, (a) BFI showing tweed contrast caused by t'-ZrO_2 relics and the (c + t) ZrO_2 assemblages, (b) CDFI (g = 1 1 2) showing APB-like features in t'-ZrO_2.

3.3. t-ZrO_2 precipitates in overaged samples

The morphology of t-ZrO_2 precipitates in the NYZ specimen subjected to prolonged ageing (300 h) is shown in Fig. 4. Instead of forming colony structures, as in the Y–PSZ system [7], the t-ZrO_2 precipitates developed individually ranging from 100 to several hundreds of nanometres in size (Fig. 4a). It is noted that the t-ZrO_2 precipitates transformed into a mosaic-like pattern of m-ZrO_2 twin variants (Fig. 4b) when they become quite large.

3.4. Confined ZrO_2 particles

Confined m-ZrO_2 particles which occurred intergranularly and caused residual strain to the surrounding PSZ grains were found in the aged (300 h) samples (Fig. 4c). These m-ZrO_2 particles were likely due to chemical inhomogeneity of the plasma-sprayed Y–PSZ powders [8]. Intergranular t-ZrO_2 particles with a high density of dislocations also appeared in the aged (10 h) samples (Fig. 5). These t-ZrO_2 particles were possibly derived from the plasma-sprayed m-ZrO_2 or c-ZrO_2 grain by solute redistribution which stabilized the t phase. The retention of large t-ZrO_2 particles (~ 0.5 μm in size) supported the previous experimental results [8] which indicated that NiO dissolution suppressed $t \rightarrow m$ transformation. The dislocations in t-ZrO_2 were likely caused by
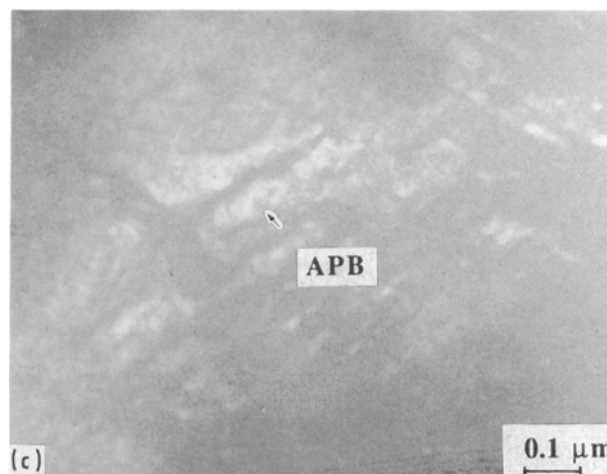

Figure 3 Transmission electron micrograph of further aged (1300 °C, 100 h) NYZ sample showing (a) coarsened variants of lenticular t-ZrO_2 with {1 0 1} habit plane, (b) DSI diffracted from c-ZrO_2 matrix, (c) newly formed t'-ZrO_2 with APB (see text).

thermal mismatch and/or phase transformation. Incoherent $Ni_{1-x}O$ particles, either intra- or intergranular, were also confined in the zirconia matrix of the aged NYZ samples. Defect clusters which developed at grain boundaries of these $Ni_{1-x}O$ particles when aged beyond 100 h at 1300 °C, will be reported elsewhere [10].

4. Discussion

4.1. Effect of NiO dissolution on twins of t'-ZrO_2
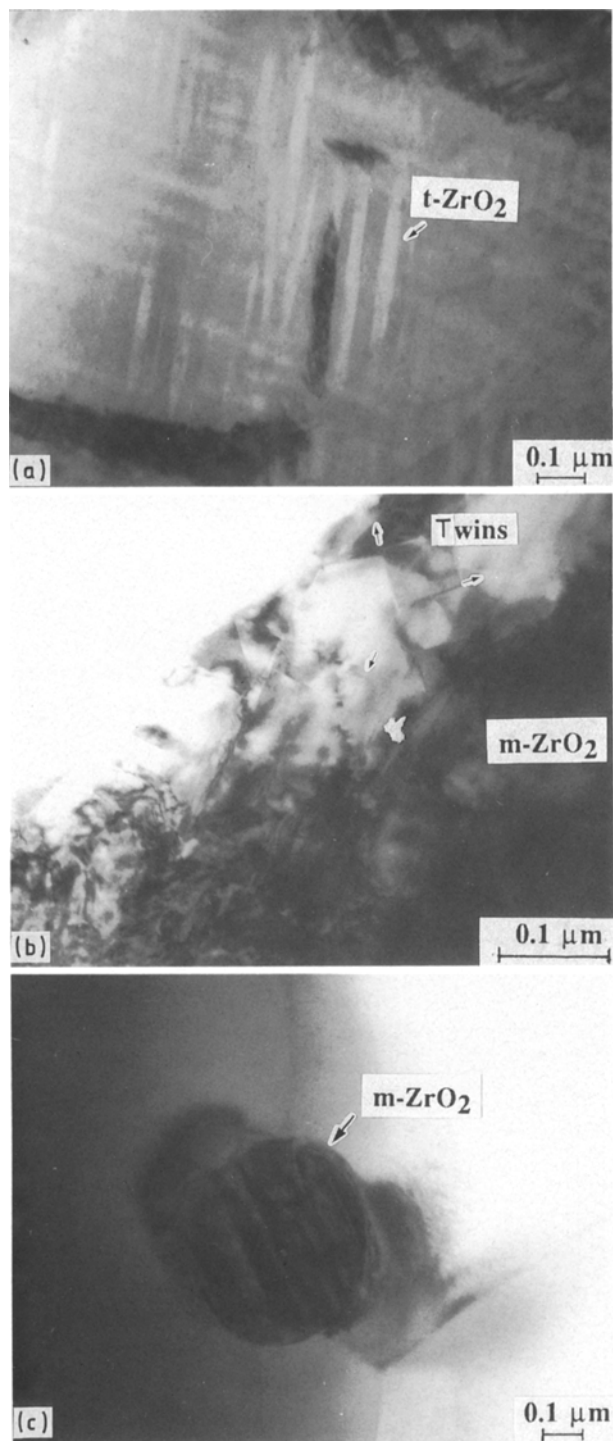
Primary deformation twins were retained, whereas

secondary deformation twins hardly survived during the incipient decomposition of t'-ZrO$_2$ in NYZ specimens. Survival of primary deformation twins was also observed for the polymorphic decomposition (above $\sim$ 1450 °C) of t'-ZrO$_2$ into a metastable c'-ZrO$_2$ in the Y–PSZ system [14], although the decomposition products (c'-ZrO$_2$ for Y–PSZ, but (c + t)- ZrO$_2$ for NYZ specimen) were different. Because a higher density of lattice strain energy was probably associated with the finely spaced twins, the restoration of ions across
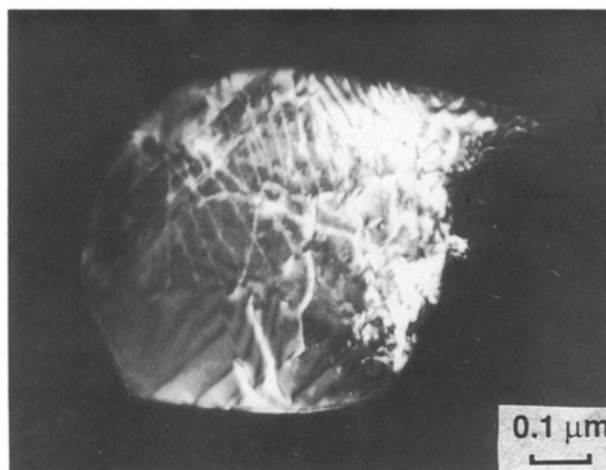
secondary deformation twins could be readily thermally induced compared with primary twins.

Twin variants also appeared when t'-ZrO$_2$ transformed finally into c + t assemblages in both the Y–PSZ [14] and NYZ specimens. Because the solute content differed for t' and equilibrium t phase, the twin variants of t-ZrO$_2$ could not be the relics of the primary and/or secondary twins of t'-ZrO$_2$ in these systems. One should note that t'-ZrO$_2$ almost transformed completely to c + t-ZrO$_2$ assemblages within 10 h at 1300 °C in NYZ specimens, whereas incubation time as long as 16 h was required for the c' → c + t transformation which occurred after the t' → c' transformation at 1600 °C in the Y–PSZ system [9]. This indicated that NiO addition facilitated diffusion and hence affected the transformation kinetics. Alternatively, the driving force for t'-ZrO$_2$ decomposition varied with both the reaction routes and the free energy curves which were NiO component dependent.

4.2. t'-ZrO$_2$ formed by slow cooling of solute-redistributed c-ZrO$_2$

For NYZ samples subjected to prolonged annealing (e.g. beyond 100 h), the finely tweed arrays in some zirconia grains could also be t'-ZrO$_2$, but they were probably newly formed rather than relics. The microstructures and possible formation mechanism of this newly formed t'-ZrO$_2$ are discussed in this section by analogy with that observed in Y–PSZ ([12] and literature cited therein).

4.2.1. Microstructural characteristics

The tweed arrays in the long-aged (> 100 h) NYZ specimens were similar to the Y–PSZ single crystal [11] and polycrystals [12], both being slowly cooled after firing. The tweed arrays thus formed in Y–PSZ single crystal were interpreted either as t'-phase or equilibrium c + t phase assemblages [11]. However, the Y–PSZ polycrystals slowly cooled after sintering at 1400 °C showed clear evidence of t'-phase [12]. The

t'-phase formed by slow cooling [11,12] has slightly different morphology compared with that quenched [2], the former being free of secondary deformation twins which were ubiquitous in the latter because of a martensitic-like transformation involved during rapid cooling [2]. Two-step development of t'-phase in arc-melted ZrO_2-Y_2O_3 alloys has been proposed: APBs are formed initially and plate-like or lenticular features later [15]. It is suggested that only the first step occurred for both the Y-PSZ [11,12] and NYZ specimens if slow cooling reduced the transformation strain and/or thermal shock.

4.2.2. Free-energy and domain-size considerations

The free-energy curves of c- and t-ZrO_2 intersect at a critical temperature, T_0, which defines a univariant line in the T-X phase diagram. It has been observed in a sintered (1400 °C) and solute-redistributed Y-PSZ (12Y-PSZ added with TZ3Y) [12], that the domain size (50–60 nm) within each t' plate appeared to be independent of the grain size of zirconia, and the domain size of 50 nm corresponded to the C_0 of 5 mol% Y_2O_3 following the relationship between the domain size and the yttria content in Y-PSZ [15]. This has been used as evidence that the 12Y-PSZ (6.9 mol% Y_2O_3) grain has been modified to a lower solute content during sintering [12]. Accordingly, the solute content of the c-matrix in the original Y-PSZ powder could be lowered during sintering at 1400 °C due to its mixture with solute-poor TZ3Y, and hence enabled its transformation into t'-phase by cooling through T_0 (about 1100–1200 °C, see locus of C_0 versus temperature in Figs 1 and 2 of [2]).

In the present (Ni, Y)-PSZ composition system, the fine tweed arrays of t'-ZrO_2 remained nearly the same size, regardless of the ageing time at 1300 °C, indicating the tweed arrays could be formed during cooling. It is likely that NiO dissolution modified the free-energy curves of c- and t-ZrO_2 (hence the locus of C_0, which determined the appropriate composition and temperature for c $\rightarrow$ t' transformation [3,4]) to favour this displacive transformation. Alternatively, ZrO_2 grains could have modified (at 1300 °C) their solute content to form c-ZrO_2, which then transformed to t'-ZrO_2 upon cooling. The size of the tweed arrays [15] could be a clue to the origin of t'-ZrO_2, i.e. relics or newly formed as in Y-PSZ system [12]; however, the relationship between domain size and the solute content in the ternary system was not known, as this does not permit analogous discussion.

4.3. Morphology of t-ZrO_2

In the present ternary (Ni, Y)-PSZ system, the tweed morphology of t-ZrO_2 in c-ZrO_2 appeared similar to that in binary Y-PSZ, but the coarsened t-ZrO_2 did not form apparent colony structure. Instead, coarsened t-variants developed individually into m-ZrO_2. Morphological features of t-ZrO_2 in ternary systems of (Mg, Ca)-PSZ [16], (Mg, Y)-PSZ [17], (Ca, Ti)-PSZ [18], (Mg, Ti)-PSZ [19] and in

Y-PSZ/Ni_2AlTi cermet [20], have also been reported. Differences in the morphology and the habit plane behaviour of the t-ZrO_2 phase in these systems have been attributed to the misfit in lattice parameters and interfacial energy between the t-ZrO_2 precipitates and the c-ZrO_2 matrix [16–21] following Khachaturyan's theory [22]. NiO dissolution in Y-PSZ increased the lattice strain energy between the t-ZrO_2 precipitates and c-ZrO_2 matrix [8]; however, the habit plane of t-ZrO_2 remained the same for Y-PSZ and NYZ specimens. This indicated that the elastic strain energy was probably less important than other energy terms for the determination of habit plane. The absence of t-ZrO_2 colony structure in the (Ni, Y)-PSZ system suggested that the t/c ZrO_2 interface rather than the twin planes of t-ZrO_2, was energetically favoured. It is noteworthy that t-ZrO_2 precipitates varied in size in the same ZrO_2 grain, indicating nucleation has proceeded with ageing.

5. Conclusions

NiO-addition (10 mol%) caused the following microstructural development of the metastable t'-ZrO_2 (Y-PSZ with 5 mol% Y_2O_3) when sintered at 1300 °C for 5 h followed by ageing at 1300 °C for 1 h up to 300 h.

1. Short-term (10 h) firing caused incomplete decomposition of t'-ZrO_2 into tweed assemblages containing t'-ZrO_2 relics and t-ZrO_2 precipitates in the c-ZrO_2 matrix.

2. The t'-ZrO_2 relic retained anti-phase domain boundary (APB) and primary deformation twins but not secondary deformation twins.

3. t'-ZrO_2 with APB also formed locally from a solute-redistributed c-ZrO_2 upon cooling.

4. The microstructure of t'-ZrO_2, either relics or newly formed in (Ni, Y)-PSZ, was basically the same as in Y-PSZ.

5. Plate-like t-ZrO_2 with {1 0 1} habit plane developed upon ageing, but did not develop colonies as in the Y-PSZ system.

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