

# Effect of 7YSZ on the long-term stability of YTaO<sub>4</sub> doped ZrO<sub>2</sub> system

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## Abstract

The long-term stability of Ta<sub>0.16</sub>Y<sub>0.16</sub>Zr<sub>0.68</sub>O<sub>2</sub> (TaYSZ) has been studied for possible application in thermal barrier coatings. X-ray diffraction was used for the characterization of the phase stability from 1100 to 1500 °C. Long-term stability of TaYSZ in presence of 7YSZ at 1250 °C has also been checked. At 1500 °C, TaYSZ remains as a single tetragonal phase. TaYSZ, however, when treated at 1250 °C for 600 h decomposes to *m*-ZrO<sub>2</sub> and contains a minor YTaO<sub>4</sub> phase and *t*-TaYSZ. In the presence of 7YSZ, decomposition of TaYSZ was suppressed. Decomposition of TaYSZ follows a different mechanism when treated in air and under vacuum. TaYSZ once pretreated at 1500 °C does not show any decomposition when treated at 1250 °C for 600 h, though weak reflections of Y<sub>3</sub>TaO<sub>7</sub> are seen in the X-ray diffraction pattern. The onset of sintering and the coefficient of thermal expansion (CTE) of TaYSZ have been found to be ~1200 °C and 11.24 × 10<sup>-6</sup> K<sup>-1</sup>, respectively.

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## 1. Introduction

Partially stabilized zirconia (7YSZ, 7–8 wt.% Y<sub>2</sub>O<sub>3</sub> in ZrO<sub>2</sub>) is currently broadly used as a thermal barrier coating (TBC) for gas turbine blades. 7YSZ offers the best balance of mechanical and thermal properties required for gas turbine application. However, 7YSZ exists as metastable “non-transformable ‘t’” phase at room temperature (when formed by conventional plasma spray process) and undergoes transformation into transformable yttria-deficient tetragonal ‘t’ and yttria-rich cubic ‘c’ (fluorite) phases when treated for longer time at and above ~1200 °C: t' → t + c.<sup>1–3</sup> The transformable t-phase of 7YSZ undergoes a martensitic transformation to monoclinic phase (t → m) upon cooling accompanied with a catastrophic volume expansion (~4–5%). Hence, there is a strong need for improvement of the stability of 7YSZ. In order to enhance its stability beyond 1200 °C, many researchers have tried further doping of the YSZ system, for example, with bigger or smaller cations of rare-earth elements.<sup>1,3</sup> Ta-doped YSZ, which is stable up to

1500 °C has been reported as one prospective TBC.<sup>4</sup> The peculiarity of the ZrO<sub>2</sub>–YO<sub>1.5</sub>–TaO<sub>2.5</sub> system is in strong interaction of the Y<sup>3+</sup> and Ta<sup>5+</sup> cations in the tetragonal ZrO<sub>2</sub> matrix, leading to a much higher solubility of the resulting YTaO<sub>4</sub> species compared to the individual solubility of YO<sub>1.5</sub> and TaO<sub>2.5</sub> in the ZrO<sub>2</sub> matrix.<sup>4–6</sup>

The transformability of tetragonal ZrO<sub>2</sub> can be correlated with tetragonality (function of *c/a* ratio), often used for the characterization of YSZ and related systems. This correlation was suggested for the classification of oxides into stabilizers (decreasing tetragonality) and destabilizers of *t*-ZrO<sub>2</sub> (increasing tetragonality).<sup>7</sup> It was shown that alloying Ta<sub>2</sub>O<sub>5</sub> with the ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> system decreases the stability of both *t*- and *c*-phases in the binary system.<sup>5,7</sup> This destabilization can be explained by the increase of the lattice distortions due to alloying with Ta<sub>2</sub>O<sub>5</sub> (or with other refractory oxides, for example Nb<sub>2</sub>O<sub>5</sub> or HfO<sub>2</sub>). On the other hand, incorporation of stabilizing oxides such as Y<sub>2</sub>O<sub>3</sub> decreases the tetragonal distortion and increases the stability of the ZrO<sub>2</sub> lattice. One of the explanations of the stability of ZrO<sub>2</sub> with Y<sub>2</sub>O<sub>3</sub> addition is related to the formation of oxygen vacancies.<sup>8</sup> In the TaYSZ system, however, the stability is found to increase with an increase in tetragonality, irrespective of the fact that there was no formation of oxygen

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vacancies. The increased stability in this case was explained by defect association of the smaller Ta<sup>5+</sup> and bigger Y<sup>3+</sup> cations in the ZrO<sub>2</sub> lattice.<sup>5</sup>

It was also shown that 20 mol% YTaO<sub>4</sub>-stabilized ZrO<sub>2</sub> (TaYSZ) has a Young's modulus of 150 GPa compared to 200 GPa for 7YSZ. The low Young's modulus and the possibility of a high coefficient of thermal expansion (CTE) make this system a potential candidate for TBC application.

Along with the remarkable phase stability and mechanical properties, the YTaO<sub>4</sub>-doped ZrO<sub>2</sub> system was also found to be suitable for plasma spraying.<sup>9</sup> Moreover, strong interaction between the Y<sup>3+</sup> and Ta<sup>5+</sup> ions are beneficial for the TBC applications because it (a) leads to remarkably low thermal conductivity even in absence of oxygen vacancies and (b) could reduce individual activities of cations and hence make the Y<sup>3+</sup> cations less susceptible to react with foreign ions such as V<sup>5+</sup>. It has been reported that the TaYSZ system has a higher corrosion resistance against sulfate and vanadate melts as compared to 7YSZ.

It was proposed that 20 mol% YTaO<sub>4</sub>-doped ZrO<sub>2</sub> is the best TBC candidate as it has the same stability as 22 mol% YTaO<sub>4</sub>-doped zirconia along with a sufficiently low thermal conductivity of 2 W/mK and a fracture toughness of 4 MP am<sup>1/2</sup>, which is twice that of 7YSZ. Besides, 20 mol% YTaO<sub>4</sub>-doped ZrO<sub>2</sub> has also shown promising results in the preliminary burner rig test.<sup>9</sup>

Previous works report the presence of a single stable tetragonal solid solution of TaYSZ only at and above 1500 °C. The presence of the YTaO<sub>4</sub> phase below 1500 °C was also reported.<sup>4</sup> Hence, it was assumed that the tetragonal phase is present as the major phase at all temperatures. However, previous works did not report the long-term stability of YTaO<sub>4</sub>-ZrO<sub>2</sub> systems. In this work, we studied both the short-term and long-term stability of the 20 mol% YTaO<sub>4</sub>-ZrO<sub>2</sub> system (Y<sub>0.166</sub>Ta<sub>0.166</sub>Zr<sub>0.668</sub>O<sub>2</sub> or TaYSZ) at 1250 °C in order to investigate the equilibrium phases. Furthermore, the long-term compatibility of YTaO<sub>4</sub>-ZrO<sub>2</sub> with 7YSZ was checked by studying the reactivity in this mixture. A preliminary model for the stabilization of TaYSZ in the presence of 7YSZ is also proposed.

## 2. Experimental

Starting powders corresponding to Y<sub>0.166</sub>Ta<sub>0.166</sub>Zr<sub>0.668</sub>O<sub>2</sub> stoichiometries were prepared by a reverse co-precipitation technique. ZrOCl<sub>2</sub>·8H<sub>2</sub>O (99.9%, Alfa-Aesar GmbH, Karlsruhe, Germany), Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9%, Alfa-Aesar GmbH, Karlsruhe, Germany) and TaCl<sub>5</sub> (99.99%, Sigma-Aldrich GmbH, Steinheim, Germany) were used as precursors for precipitation of corresponding hydroxides of Zr, Y and Ta. Precursors were mixed in an ethanol solution and slowly dropped into an ammonia solution at pH 10. Precipitates were washed thoroughly, dried overnight and calcined at 1000 °C for 4 h. Calcined powders were annealed at temperatures from 1100 °C to 1500 °C for 4 h. Commercial 7YSZ was used (HC Stark GmbH, Germany). Long-term annealing of the powders was done at 1250 °C for 600 h. Two powders were chosen for long term annealing: (1) TaYSZ (preannealed at 1200 °C for 4 h after calcination) and

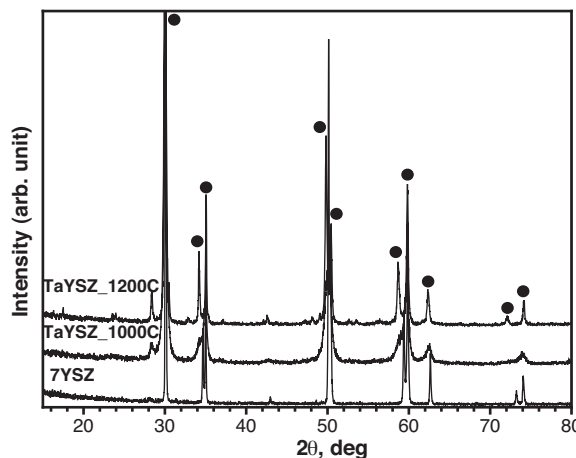


Fig. 1. XRD patterns of TaYSZ treated at 1000 °C, TaYSZ treated at 1200 °C and 7YSZ. ●: t-TaYSZ.

(2) TaYSZ15 (preannealed at 1500 °C for 4 h after calcination). For analysis of the mixtures, powders were mixed in an equal volume proportion, pressed into a pellet and treated at 1250 °C for 600 h. Equal volume of the powders were mixed deliberately to make the relative phase quantification simpler. For all the thermal treatments, the heating and cooling rates were maintained at 10 K/min. Phases formed at different temperatures were analyzed with an X-ray powder diffractometer (Xpert Pro PANalytical, 7600 AA ALMELO, the Netherlands) using Cu K $\alpha$  radiation. The microstructure was analyzed by scanning electron microscopy (SEM, LEO 1530, Carl Zeiss SMT AG, Oberkochen, Germany). CTE and sintering temperature were determined using a dilatometer (DIL 402C, Netzsch GmbH & Co. Holding KG, Selb, Germany).

## 3. Results and discussion

### 3.1. Stability of the TaYSZ system

X-ray diffraction patterns of TaYSZ after pyrolysis at 1000 °C and after annealing at 1200 °C are shown in Fig. 1. The XRD pattern of 7YSZ is inserted for comparison of the tetragonality. The major phase was t-TaYSZ (marked with filled circles). The remaining peaks are that of monoclinic YTaO<sub>4</sub>. After pyrolysis at 1000 °C, the powder was nanocrystalline as shown by the broad diffraction peaks. The particle size increases along with the prominent appearance of YTaO<sub>4</sub> peaks when treated at 1200 °C. It is known that nanosized particles are obtained when synthesized by chemical routes. The tetragonality of TaYSZ treated at 1200 °C ( $c/\sqrt{2a} = 1.0248$ ) is much higher compared to 7YSZ ( $c/\sqrt{2a} = 1.009$ ) as can be seen from the larger peak separation in the {400} region ( $\sim 2\theta = 74^\circ$ ) of the TaYSZ powder compared to 7YSZ. The tetragonality of TaYSZ samples treated for different temperatures has been reported in our previous publication.<sup>10</sup> It was also reported that the YTaO<sub>4</sub> peak completely dissolves in ZrO<sub>2</sub> at 1500 °C resulting in a single highly tetragonal TaYSZ phase ( $c/\sqrt{2a} = 1.0262$ ). This higher tetragonality of TaYSZ has been attributed to the ordering of Y and Ta ions in the ZrO<sub>2</sub> lattice.

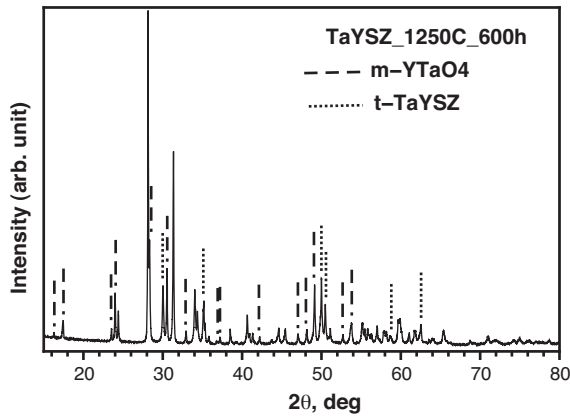


Fig. 2. XRD patterns of a TaYSZ sample treated at 1250 °C for 600 h. YTaO<sub>4</sub> phase and t-TaYSZ phase are marked with dotted lines. The other peaks correspond to m-ZrO<sub>2</sub>.

Upon long-term annealing (1250 °C, 600 h), TaYSZ decomposes completely into m-ZrO<sub>2</sub> solid solution (ss) with some minor YTaO<sub>4</sub> and t-TaYSZ phases. The XRD pattern of the TaYSZ sample treated at 1250 °C for 600 h is shown in Fig. 2. It is known that high-temperature stable phases are present as a metastable phase at room temperature when the particles size is below a critical value. Upon 4 h treatment at 1200 °C, the particles were below this critical value and hence the tetragonal phase was observed. When the same powder was treated at 1250 °C for 600 h, the particle size increases, crosses the critical size and hence a room-temperature stable phase (m-ZrO<sub>2</sub>) was obtained.

However, once treated at 1500 °C, the TaYSZ system turns stable as can be seen in Fig. 3. Some weak reflections were seen after the long-term treatment. These may correspond to an yttria-rich ‘YT’ phase (Y<sub>3</sub>TaO<sub>7</sub> or Y<sub>2.8</sub>Ta<sub>1.17</sub>O<sub>2.8</sub>). The overlapping peaks make its analysis difficult. However, from the lattice constant calculations it is observed that after 600 h treatment, the cell volume decreases (68.8424 to 68.7617 unit) and the tetragonality increases (1.0262 to 1.0271). The decrease in volume could be due to removal of more Y<sup>3+</sup> ion from the lattice, which has bigger ionic radius than the Ta<sup>5+</sup> ion. The precipitation of the yttria-rich component is more prominent from the increase in tetragonality. Equal removal of Y<sup>3+</sup> and Ta<sup>5+</sup> would have

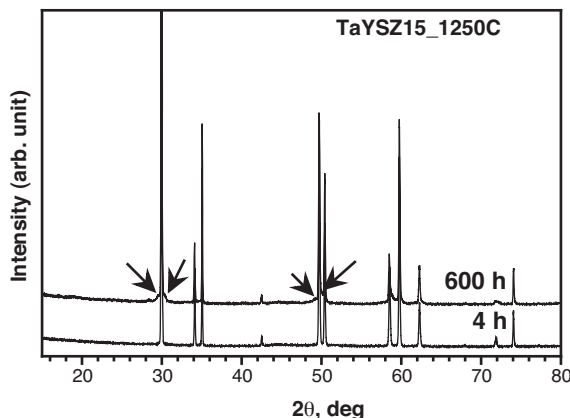


Fig. 3. XRD patterns of TaYSZ15 (TaYSZ preannealed at 1500 °C for 4 h) treated for 4 h and 600 h at 1250 °C. Weak reflections are marked with an arrow.

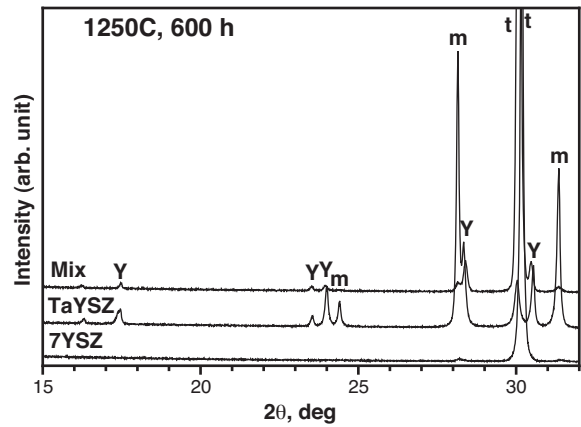


Fig. 4. XRD patterns of individual 7YSZ, TaYSZ and their mixture when treated for 600 h at 1250 °C. Y: YTaO<sub>4</sub>, t: t-TaYSZ, m: m-ZrO<sub>2</sub>.

resulted in a decrease in tetragonality as the higher dissolution of YTaO<sub>4</sub> in ZrO<sub>2</sub> results in a higher tetragonality.

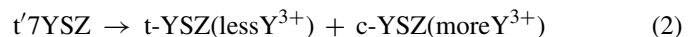
### 3.2. Stabilization of TaYSZ in presence of 7YSZ

In the presence of 7YSZ, the decomposition of TaYSZ was slowed down as can be seen in Fig. 4. The intensity of the diffraction peak of the m-phase decreased in the mixture along with a decrease in the YTaO<sub>4</sub> content.

At 1250 °C, TaYSZ may decompose according to equation (1):



Upon cooling, t-ZrO<sub>2</sub> can convert to m-ZrO<sub>2</sub>; hence, the major phase observed at room temperature was m-ZrO<sub>2</sub>. It is known that t'-7YSZ decomposes at temperature above 1500 °C<sup>11</sup> into yttria-deficient t-YSZ and yttria-rich c-YSZ according to equation (2):



When TaYSZ and 7YSZ are mixed and annealed together, it is possible that the Y<sup>3+</sup> ion partially diffuses into t-ZrO<sub>2</sub> obtained from Eq. (1). But this would result in a charge imbalance in the t-ZrO<sub>2</sub> solid solution. Neutrality can be achieved by forming oxygen vacancies or by taking a Ta<sup>5+</sup> ion. If the achievement of neutrality is favored by Ta<sup>5+</sup> ion consumption, then it can be expected that YTaO<sub>4</sub> can act as source of Ta<sup>5+</sup> ion. Hence Ta<sup>5+</sup> from YTaO<sub>4</sub> and Y<sup>3+</sup> from 7YSZ can form stable YTaO<sub>4</sub> in t-ZrO<sub>2</sub> resulting in the stable t-TaYSZ. A schematic illustrating the steps of the stabilization process is shown in Fig. 5. Charge compensation from the YTaO<sub>4</sub> was confirmed by the fact that there is a reduction in the YTaO<sub>4</sub> content (4.19 mol% in the absence of 7YSZ in contrast to 1.31 mol% in the presence of 7YSZ).

In order to confirm this stabilization mechanism, additional annealing experiments were done under high vacuum conditions (10<sup>-8</sup> bar). It is expected that the oxygen vacancy formation will be promoted under vacuum and that the charge neutrality in the above mentioned reaction would be reached by oxygen vacancy formation, rather than by consuming Ta<sup>5+</sup> ion.

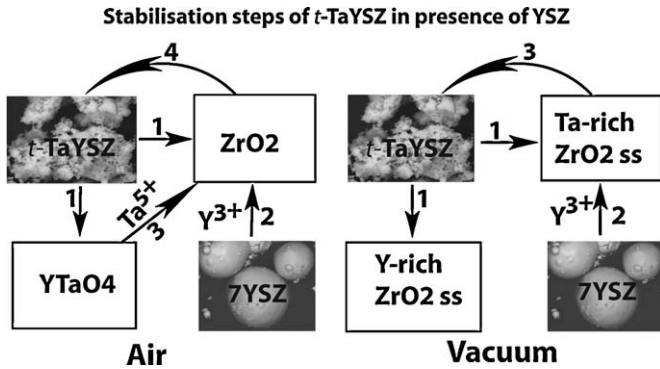
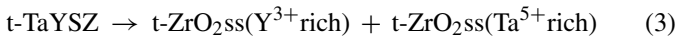


Fig. 5. Schematic showing the stabilization mechanism of *t*-TaYSZ in presence of 7YSZ, both in air and in vacuum. Steps in the stabilization processes are marked with numerals.

XRD analysis of the products of the high temperature annealing showed that under vacuum the TaYSZ decomposition was suppressed. The major resulting phase was *t*-TaYSZ with some minor *m*-ZrO<sub>2</sub> and YTaO<sub>4</sub> phases. The XRD patterns of TaYSZ treated at 1250 °C for 600 h in air and in vacuum are shown in Fig. 6.

It is assumed that the decomposition of TaYSZ follows different mechanisms in air and in vacuum. Under vacuum, the oxygen vacancy formation is promoted leading to the separation of Y-rich *t*-ss and Ta-rich *t*-ss phases. Ytria-rich *t*-ss is stabilized by the oxygen decrowding around the Zr ion and Ta-rich *t*-ss converts to monoclinic ss upon cooling to room temperature.

The decomposition of TaYSZ in vacuum can be described by Eq. (3):



7YSZ, which acts as a source of Y<sup>3+</sup> ion, was found to stabilize the TaYSZ even in vacuum. Excess Ta<sup>5+</sup> in *t*-ZrO<sub>2</sub> ss and Y<sup>3+</sup> from 7YSZ stabilize the *t*-TaYSZ phase, as depicted in Fig. 5. The final *m*-ZrO<sub>2</sub> content was higher in vacuum compared to that in atmospheric air, as can be seen in Fig. 7. Also, there was no decrease of the YTaO<sub>4</sub> content in vacuum, indicating that no charge balance from YTaO<sub>4</sub> has occurred. It was obvious, as in

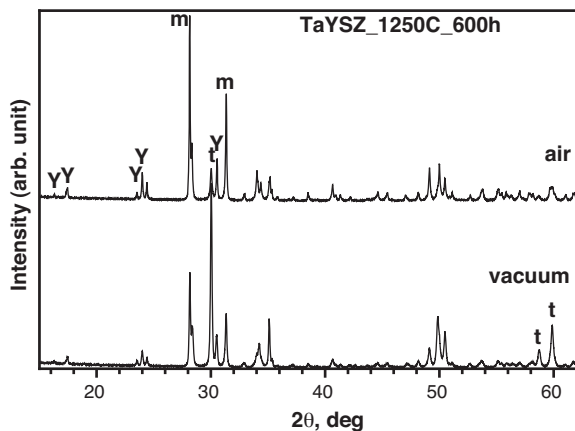


Fig. 6. XRD patterns of TaYSZ treated in air and in vacuum for 600 h at 1250 °C. Y: YTaO<sub>4</sub>, t: *t*-TaYSZ, m: *m*-ZrO<sub>2</sub>.

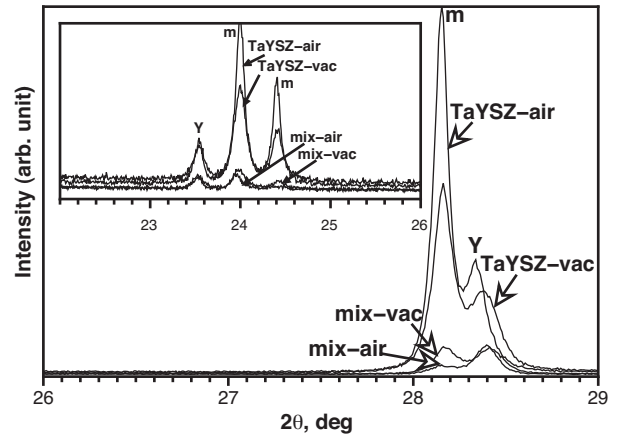


Fig. 7. XRD patterns of a TaYSZ and TaYSZ-7YSZ mixture after a 600 h treatment at 1250 °C in air and in vacuum. m: *m*-ZrO<sub>2</sub>, Y: YTaO<sub>4</sub>.

vacuum charge compensation should be favored by the oxygen vacancies formation rather than by Ta<sup>5+</sup> consumption.

As decomposition of TaYSZ was suppressed in vacuum, it can be concluded that the promoting oxygen vacancy formation can further stabilize the tetragonal structure of TaYSZ. In other words, compounds with compositions Ta<sub>0.16</sub>Y<sub>0.16+x</sub>Zr<sub>0.68-x</sub>O<sub>2</sub> (with *x* mol% excess yttria in the system) could be a new prospective TBC system. This finding agrees with our modeled Ta<sub>2</sub>O<sub>5</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> phase diagram, reported in our previous publication<sup>10</sup>. It was shown that the tetragonal ss region consists of unequal Y<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> concentrations with the Y<sub>2</sub>O<sub>3</sub> content being higher. Excess of yttria helps in creating oxygen vacancies within the TaYSZ system.

The TaYSZ sample pretreated at 1500 °C, did not show any interaction with 7YSZ, except a slight increase in the monoclinic content. The increase in the monoclinic content could be due to the diffusion of oxygen ions from TaYSZ15 into 7YSZ, annihilating oxygen vacancies and rendering YSZ more tetragonal. It is also possible that some Ta<sup>5+</sup> ion can diffuse into 7YSZ making it unstable. As a result, more monoclinic phase was observed in the mixture.

### 3.3. Sintering TaYSZ

A TaYSZ sample was annealed at different temperatures and it was observed that the grain growth starts after 1250 °C, but significant growth was observed at 1500 °C. The sintering temperature of the TaYSZ sample was found to be ~1230 °C and the coefficient of thermal expansion  $11.24 \times 10^{-6} \text{ K}^{-1}$  as determined from the dilatometer curves. The sintering temperature and CTE for 7YSZ were determined to be ~1190 °C and  $10.41 \times 10^{-6} \text{ K}^{-1}$ , respectively. Both the sintering temperature and CTE values are comparatively better for TaYSZ system.

## 4. Conclusion

TaYSZ is unstable at 1250 °C for long duration and decomposes completely to *m*-ZrO<sub>2</sub> and YTaO<sub>4</sub>. However, this

decomposition is suppressed in the presence of 7YSZ. At 1250 °C, diffusion of  $Y^{3+}$  from 7YSZ and  $Ta^{5+}$  from  $YTaO_4$  into the decomposed t- $ZrO_2$  product stabilizes the structure further into t-TaYSZ, even at room temperature. Under vacuum condition, the decomposition reaction was highly suppressed compared to that in air. Excess of  $Y^{3+}$  or  $O^{2-}$  vacancies are supposed to stabilize the TaYSZ structure and hence a system comprising a slight excess of  $Y^{3+}$  can be a prospective stable system. TaYSZ once pretreated at 1500 °C is resistant to any such decomposition. It should be noted that particle size can have an effect on the reactivity of the TaYSZ system and a detailed study of the effect of particle size on the reactivity between TaYSZ and YSZ is proposed for future study. The sintering temperature and CTE of TaYSZ are higher than for 7YSZ. Hence, TaYSZ can be used as a prospective TBC material, either as a single coat or as a topcoat.

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