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Original article

Phase equilibria in the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ system at 1250 °C

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ABSTRACT

The phase relationships in the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ (ZYTO) system at 1250 °C—a temperature of interest for thermal barrier coatings applications—were investigated using precursor-derived powders. The system is bisected by a quasi-binary joining the tetragonal (*t*) ZrO_2 and monoclinic (*M'*) $YTaO_4$ solid solutions. The mutual solubility limits for these phases differ significantly depending on whether the third phase in equilibrium with *t* and *M'* is fluorite or the orthorhombic (*O*) $Zr_6Ta_2O_{17}$. More importantly, the tetragonal phase in equilibrium with fluorite is non-transformable to the monoclinic form upon cooling, whereas that in equilibrium with *O*, which has lower stabilizer content, is transformable. The behavior contrasts with that previously observed for the equilibrium at 1500 °C, wherein the *t* phase on both sides of the quasi-binary is non-transformable. The fluorite solid solution extends from the ZrO_2-$YO_{1.5}$ binary to the $YO_{1.5}$-$TaO_{2.5}$ binary at 1250 °C, as previously shown for 1500 °C.

1. Introduction

Alternative thermal barrier coating (TBC) materials to the current ZrO_2-8 ± 1%$YO_{1.5}$[3] stabilized zirconia (8YSZ) must be identified to meet the demands of more energy efficient, next-generation gas turbine engines. Compositions in the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ (ZYTO) system have previously been proposed as potential TBC candidates due to their low thermal conductivity [1–4], phase stability [5–7] and adequate toughness [8]. The ZYTO system is also of interest for functional applications such as phosphors [9–11], microwave dielectrics [12], lasers [13,14] and ionic conductors [15].

Despite the wealth of potential technological applications, previous work in the ZYTO system has primarily focused on materials synthesized at temperatures above 1400 °C [5,16,17]. There is a lack of information on phase equilibria and transformations at 1250 °C, which are particularly relevant to current processing and operating conditions for thermal barrier coatings. Therefore, the purpose of the present investigation is to advance the understanding of the equilibrium relationships in the ZYTO system at 1250 °C by examining binary and ternary oxide specimens. A foundation is provided by a recently published analysis of the 1500 °C [17], reproduced in Fig. 1(a). It is anticipated that this study will add to the database needed to improve the accuracy of future thermodynamic assessments.

2. Background on phase relations

A thorough review of the constituent binary phase diagrams and available literature on the ternary system were recently described in [17]. Thus only additional studies specific to 1250 °C and new insights are presented below. The relevant phases in the ZYTO system and their shorthand notation are listed in Table 1.

2.1. Terminal oxide phases

While all terminal oxides have multiple allotropes, most phase transitions are above 1250 °C A notable exception, ZrO_2 transforms from the tetragonal ($P4_2/nmc$) to the monoclinic form (baddeleyite, $P2_1/c$) below ~1205 °C [18]. At 1250 °C Y_2O_3 is expected to be bixbyite ($Ia\bar{3}$), an ordered form of fluorite [19], while Ta_2O_5 is expected to be stable in its low temperature orthorhombic (β, *Pmm2*) structure [20].

2.2. $YO_{1.5}$-ZrO_2 binary

The most significant change in the $YO_{1.5}$-ZrO_2 binary between 1500 °C and 1250 °C is the presence of the rhombohedral phase, δ-$Y_4Zr_3O_{12}$ ($R\bar{3}$), at the lower temperature. This phase can be viewed as an ordered derivative of fluorite [21] and disorders congruently at

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[3] Unless otherwise specified, all compositions are given in mole percent of oxide based on single cation formula units. This provides insight into the level of dopant substitution in the cation network.

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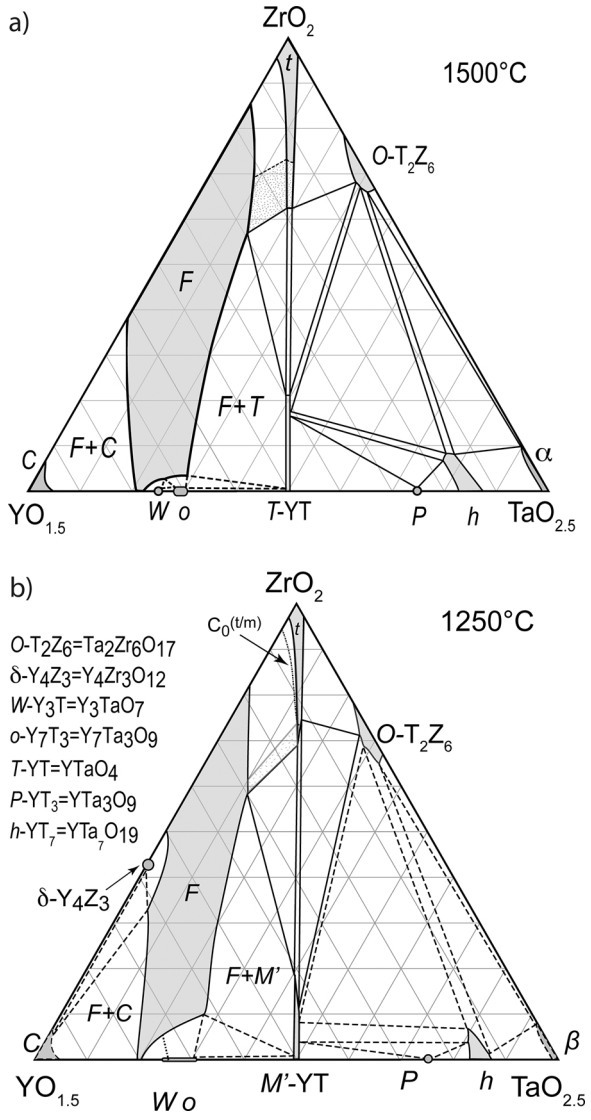

Fig. 1. (a) The previously published isothermal section of the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ (ZYTO) system at 1500 °C [17]. (b) The proposed ternary isothermal section that has resulted from this work.

Table 1
Phase identification reference.

Compound	Structure	Group	Abbr.	PDF number
$YO_{1.5}$ (Y)	bixbyite (cubic)	$Ia\bar{3}$	*C*	00-041-1105
	hexagonal	$P\bar{3}m1$	*H*	
$TaO_{2.5}$	tetragonal	$I4_1/amd$	*α*	01-075-9704
	orthorhombic	*Pmm2*	*β*	00-025-0922
ZrO_2 (Z)	fluorite (cubic)	$Fm\bar{3}m$	*F*	01-077-2115(6)
	tetragonal	$P4_2/nmc$	*t*	00-043-0308
	baddeleyite (monoclinic)	$P2_1/a$	*m*	00-037-1484
$YTaO_4$ (YT)	scheelite (tetragonal)	$I4_1/a$	*T*	
	met. fergusonite (monoclinic)	*I2*	*M*	00-024-1415
	fergusonite (monoclinic)	P2/a	*M'*	00-024-1425
Y_3TaO_7 (Y_3T)	weberite (orthorhombic)	*Ccmm*	*W*	
$Y_7Ta_3O_{18}$ (Y_7T_3)	orthorhombic	*Cmmm*	*o*	
YTa_3O_9 (YT_3)	perovskite (orthorhombic)	*Cmmm*	*P*	01-072-2030
	tetragonal	*P4/mmm*	*τ*	
YTa_7O_{19} (YT_7)	hexagonal	$P\bar{6}c2$	*h*	00-030-1465
$Ta_2Zr_6O_{17}$	orthorhombic	*Ima2c*	*O*	01-072-1745
$Y_4Zr_3O_{12}$	rhombohedral	$R\bar{3}$	*δ*	

~1384 °C [22]. To describe the ordering of fluorite to δ as "sluggish" would be an understatement as the δ phase has only been observed after heat treatments of 3–6 months at temperatures below 1300 °C [21,23]. Therefore δ is not expected to form at 1250 °C even after several hundred hours; however, it is included in the isothermal section because it is a known equilibrium phase.

The fluorite field is reported to extend from 50 to 84% ZrO_2 in the binary at 1250 °C [22]. Also at that temperature the solubility of ZrO_2 in $YO_{1.5}$ is 6% and that of $YO_{1.5}$ in ZrO_2 is 4% $YO_{1.5}$ [22].

2.3. $TaO_{2.5}$-$YO_{1.5}$ binary

Recent work by the authors [24] has re-evaluated the sub-solidus equilibria in this binary system, clarifying discrepancies in prior studies [25,26]. The mutual solubility of the terminal phases is marginal, ~5% of $TaO_{2.5}$ in $YO_{1.5}$, and < 1.5% of $YO_{1.5}$ in $TaO_{2.5}$ [27]. It was found that the fluorite phase reported at high temperatures is stable within a small composition range, ~20 ± 0.5%$TaO_{2.5}$ at 1250 °C, in contrast with previous studies where the reported minimum temperature of stability was above 1500 °C [25,26]. Compositions in the range $Y_{3-x}Ta_{1+x}O_{7+x}$ were found to be stable in the range $0 \leq x < 0.2$ with no miscibility gap but with the ordering evolving from a weberite-like (*W*) *Ccmm* pattern to an orthorhombic (*o*) *Cmmm* pattern through a second order transformation at $x \approx 0.07$. The next phase appears at the equimolar composition, $YTaO_4$ (YT), which does not exhibit a significant homogeneity range. YT has a monoclinic fergusonite structure, *M'* (*P2/a*) from room temperature to ~1425 °C, at which it undergoes a first order transformation to a scheelite-type structure, *T* ($I4_1/a$) [9,28–30]. On cooling, YT undergoes a second order transformation to metastable monoclinic fergusonite, *M* (*I2/a*) that resists transformation to *M'* which is the acknowledged equilibrium structure [31,32]. Thus, *M'* is in equilibrium with the orthorhombic (*o*) phase for compositions between ~30 and 50%$TaO_{2.5}$, and with a defect-perovskite phase YTa_3O_9 (*P*-YT_3) between ~50 and 75%$TaO_{2.5}$. The perovskite phase does not exhibit a significant solubility range within the range of temperatures investigated. Finally, the hexagonal YTa_7O_{19} (*h*-YT_7) phase, stable in the range 85.5–87.5 %$TaO_{2.5}$, below which it is in equilibrium with *P* and above with *β*-$TaO_{2.5}$ [24,26,27].

2.4. $TaO_{2.5}$-ZrO_2 binary

Only one intermediate phase, orthorhombic, *O*, $Ta_2Zr_6O_{17}$ (*Ima*2c), is reported in the $TaO_{2.5}$-ZrO_2 binary at 1500 °C [5,33]. This phase is apparently stable above 750 °C and isostructural with $Nb_2Zr_6O_{17}$ [12,34]. The solubility range at 1500 °C has been claimed as either 20–29% $TaO_{2.5}$ [33] or 21.7–31.7% $TaO_{2.5}$ [5], but that at 1250 °C is unknown. The maximum solubility of $TaO_{2.5}$ in ZrO_2 at 1500 °C is reported as 3.9% and that of ZrO_2 in $TaO_{2.5}$ as ~7% [33]; however, the equilibrium solubility has not been rigorously studied at lower temperatures.

2.5. ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ ternary diagram

The ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ isothermal section at 1250 °C has not been experimentally determined. One preliminary thermodynamic assessment with isothermal sections at 1200 °C and 1500 °C has been published [16] but, with the exception of stoichiometric $YTaO_4$, none of the Ta containing phases were included in the optimization owing to insufficient data. Consequently, the predicted shape of the tetragonal Zr(Y,Ta)O_x field in [16] is not consistent with the model for zirconia stabilization by charge-compensating co-dopants [35] or experimental observations [5,8]. A preferred foundation including the missing phases is provided by the recently published experimental section at 1500 °C [17], Fig. 1(a).

There is a paucity of information on the ternary solubility of phases in the ZYTO system at 1250 °C. In one of the few studies at temperatures