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Original Article

Phase equilibria in the zirconia–yttria/gadolinia–silica systems

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ABSTRACT

Phase equilibria in $\text{ZrO}_2\text{-YO}_{1.5}\text{-SiO}_2$ (ZYS) and $\text{ZrO}_2\text{-GdO}_{1.5}\text{-SiO}_2$ (ZGS) were experimentally assessed at 1400 °C and 1600 °C as they can offer insight on reactions between thermal barrier coatings (TBCs) based on $\text{ZrO}_2\text{-YO}_{1.5}/\text{GdO}_{1.5}$ and molten silicate deposits in gas turbine engines. Features shared in both systems include the absence of ternary compounds and no ternary solubility in the binary phases. In ZYS however, a quaternary invariant reaction was observed that eliminates the zircon–disilicate equilibrium at higher temperatures. The results suggest no appreciable difference in the reactions between silica and thermal barrier oxides based on $\text{ZrO}_2\text{-YO}_{1.5}$ or $\text{ZrO}_2\text{-GdO}_{1.5}$, or environmental barrier coatings based on the corresponding Y/Gd silicates. The phase diagrams derived from these experiments are part of a broader effort to develop thermodynamic databases that can help guide the design of next-generation TBCs.

1. Introduction

Ceramic coatings are vital in the operation of modern gas-turbine engines. Thermal barrier coatings (TBCs) based on $\text{ZrO}_2\text{-REO}_{1.5}$ oxides (RE = Y, Gd, etc.) are applied to critical metallic components to provide thermal protection during engine operation [1–4]. Additionally, the emergence of Si-based ceramics as candidates for structural components in next-generation gas turbines has created the need for environmental barrier coatings (EBCs) [5]. These are dense RE silicate layers that mitigate water vapor induced volatilization of the protective thermally grown SiO_2 layer [5,6].

An important factor limiting further improvements in the energy efficiency of gas turbines is the degradation of the TBCs and EBCs by molten deposits generically known as calcium–magnesium–aluminum–silicates (CMAS) [7–9]. These deposits originate from siliceous debris ingested with the intake air, which melt at temperatures on the order of 1200 °C [7,9] leading to deleterious interactions with the TBC and/or EBC layers [10]. In TBCs, molten CMAS infiltrates the porous compliant microstructure, and upon solidification, compromises the strain tolerance during thermal cycling [9,11]. CMAS interactions with EBCs, on the other hand, yield a reaction layer that is thermally mismatched with the substrate, leading to coating loss by both chemical and thermo-mechanical damage mechanisms [11–14]. Accordingly, CMAS attack represents a fundamental barrier that hinders future progress in gas turbine technology [8]. Chemical reactions are generally undesirable in EBCs, but can be used to advantage in TBCs wherein the reaction

products can precipitate within the flow channels and arrest further infiltration [8,15,11,15]. A notable implementation is based on $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO) which induces dynamic crystallization of the melt into a highly stable oxy-apatite product. The concept could be extended to create an active protection layer on EBC systems [16,17].

An effective CMAS mitigation strategy requires an understanding of the possible chemical reactions between the candidate thermal or environmental barrier oxides (T/EBOs) and the wide range of possible siliceous debris that can be ingested by the engine. For example, recent investigations have shown that the amount of RE oxide available to consume the melt via a reactive crystallization pathway is inversely related to the RE cation ion size in the coating material [11,15,18]. Therefore, elucidating the phase equilibria between T/EBC oxides and CMAS is an important component in developing tools that can guide the design of next-generation coating systems. The present work is part of a broader initiative to develop a thermodynamic database for the system containing the oxides of Al, Ca, Fe, Gd, Mg, Si, Y, and Zr [11]. Prior work has elucidated the ternaries for the Ca–O–Y $\text{O}_{1.5}\text{-SiO}_2$ and CaO– $\text{GdO}_{1.5}\text{-SiO}_2$ systems [19,20], as well as select equilibria in higher order systems [15]. This article focuses on the ternaries between SiO_2 and the $\text{ZrO}_2\text{-YO}_{1.5}$ and $\text{ZrO}_2\text{-GdO}_{1.5}$ binaries, which are an essential part of the wider effort.

2. Background on phase equilibria

The current understanding of the relevant terminal phases and

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Table 1
Relevant phases in ZrO_2 - $YO_{1.5}$ - SiO_2 and ZrO_2 - $GdO_{1.5}$ - SiO_2 at 1400 °C and 1600 °C.

Formula	Abbrev.	Phase Name	Structure	Space Group
ZrO_2	F	Fluorite	cubic	$Fm\bar{3}m$
	t		tetragonal	$P4_2/nmc$
	m	baddeleyite	monoclinic	$P2_1/c$
$YO_{1.5}$	CY	Bixbyite	cubic	$Ia\bar{3}$
$GdO_{1.5}$	BG		monoclinic	$C2/m$
	CG	Bixbyite	cubic	$Ia\bar{3}$
SiO_2	β -Cr	β -cristobalite	cubic	$Fd\bar{3}m$
	α -Cr	α -cristobalite	tetragonal	$P4_12_12$
	β -Tr	β -tridymite	hexagonal	$P6_3/mmc$
$ZrSiO_4$	ZS	zircon	tetragonal	$I4_1/amd$
$Y_2Si_2O_7$	α -YDS	Y disilicate (α)	triclinic	$P1$
	β -YDS	Y disilicate (β)	monoclinic	$C2/m$
	γ -YDS	Y disilicate (γ)	monoclinic	$P2_1/a$
	δ -YDS	Y disilicate (δ)	orthorhombic	$Pna2_1$
Y_2SiO_5	X_1 -YMS	Y monosilicate (X_1)	monoclinic	$P2_1/c$
	X_2 -YMS	Y monosilicate (X_2)	monoclinic	$C2/c$
$Gd_2Si_2O_7$	α -GDS	Gd disilicate (α)	triclinic	$P1$
	δ -GDS	Gd disilicate (δ)	orthorhombic	$Pna2_1$
Gd_2SiO_5	GMS	Gd monosilicate	monoclinic	$P2_1/c$
$Gd_{9.33}(SiO_4)_6O_2$	Ap	apatite	hexagonal	$P6_3/m$
$Gd_2Zr_2O_7$	Py	pyrochlore	cubic	$Fd\bar{3}m$

constituent binaries is reviewed to provide a foundation for the experimental assessments of the ZrO_2 - $YO_{1.5}$ - SiO_2 (ZYS) and ZrO_2 - $GdO_{1.5}$ - SiO_2 (ZGS) systems. No ternary phases are reported in the literature for these or related systems (i.e. those containing other rare earth oxides, or HfO_2), so it is expected that ternary equilibria would be based on the relationships between the phases in the binary systems. The phases of interest are summarized in Table 1.

2.1. Terminal oxide phases

All terminal oxides in the ternary systems have multiple allotropes that may become stabilized or de-stabilized as their compositions are modified. Silica is particularly complex in the large number of crystalline phases and the ease with which the transformations between them are suppressed upon cooling. In the temperature range of interest to this study (1400–1600 °C), SiO_2 is stable as β -cristobalite ($Fm\bar{3}m$), which melts at 1723 °C and can be retained as a metastable phase down to ~250 °C, where it transforms to α -cristobalite ($P4_12_12$) [21]. Under equilibrium, β -cristobalite should transform at 1470 °C to β -tridymite ($P6_3/mmc$, subsequently to β -quartz ($P6_222$) at 867 °C and finally to α -quartz ($P3_221$) at 574 °C; more commonly, however, β -tridymite transforms to one of its multiple metastable allotropes upon cooling [22]. For the purposes of this study β -cristobalite and β -tridymite are the only relevant phases of SiO_2 .

Zirconia is tetragonal (t , $P4_2/nmc$) at the temperatures of interest, but transforms to a fluorite form (F , $Fm\bar{3}m$) above 2377 °C, which melts at ~2710 °C, and to the monoclinic form (baddeleyite, m , $P2_1/c$) below ~1205 °C [23]. $YO_{1.5}$ adopts the C-type rare earth oxide (REO) structure, an anion-ordered form of fluorite known as bixbyite (Y , $Ia\bar{3}$), from ambient to 2325 °C, where it transforms to a hexagonal structure (H , $P\bar{3}ml$) before melting at 2430 °C [24]. Finally, $GdO_{1.5}$ has the B-type REO structure (B , $C2/m$) at the temperatures of interest and the C-type below ~1226 °C. Upon heating, it transforms to the A-type REO ($P\bar{3}ml$) at 2170 °C, then to H ($P6_3/mmc$) at 2208 °C, and finally to X ($Im\bar{3}m$) at 2370 °C before melting at 2426 °C [25].

Table 2
Sample compositions investigated and phases present.

Sample Number	Bulk Composition [mol%]				Phases	
	ZrO	YO _{1.5}	GdO _{1.5}	SiO ₂	1400 °C	1600 °C
Y1	84	6		10	t + ZS + F	t + F + ZS
Y2	60	10		30	ZS + F + β -YDS	ZS + F + SiO_2
Y3	50	30		20	ZS + F + β -YDS	SiO_2 + F + γ -YDS
Y4	35	45		20	F + β -YDS + X_2 -YMS	F + γ -YDS + X_2 -YMS
Y5	15	75		10	F + X_2 -YMS + CY	F + X_2 -YMS + CY
G6	83		7	10	F	t + F + ZS
G7	60		20	20	F + ZS + α -GDS	F + ZS + γ -GDS
G8	40		40	20	F + α -GDS	F + γ -GDS + Ap
G9	50		46	4	F + α -GDS + Py	F + Ap
G10	30		50	20	α -GDS + Py + Ap	F + Ap
G11	20		60	20	Py + Ap + GMS	Ap + F + GMS
G12	10		80	10	F + GMS + CG	F + GMS + CG

2.2. ZrO_2 - $YO_{1.5}$ Binary

Phase relationships in the ZrO_2 - $YO_{1.5}$ binary have been widely studied [26–29] owing to their relevance to transformation toughened ceramics [30], solid oxide fuel cells [31], and TBC technology [32]. There is only one intermediate compound, δ - $Y_4Zr_3O_{12}$ (rhombohedral $R\bar{3}$), stable below ~1350 °C [27] which forms by anion and cation ordering within the higher temperature fluorite phase [33]. An additional compound with stoichiometry Y_6ZrO_{11} has been reported in earlier studies [34] but dismissed as a metastable compound by subsequent work [35]. In contrast with the δ -phase, which is reported as a line compound, all terminal phases exhibit some degree of mutual solubility. Specifically, at 1400 °C the tetragonal phase is reportedly stable between 0 and ~4.7% $YO_{1.5}$, the fluorite phase from ~14.2% to ~63.4% $YO_{1.5}$, and the bixbyite phase in the range 92.1%–100% $YO_{1.5}$. At 1600 °C the stability ranges are 0–4.5 % $YO_{1.5}$ for the tetragonal phase, 12.3–64.2 % $YO_{1.5}$ for fluorite, and 90.1–100 % $YO_{1.5}$ for bixbyite [32].

2.3. ZrO_2 - $GdO_{1.5}$ Binary

The only intermediate compound in the ZrO_2 - $GdO_{1.5}$ binary system is the $Gd_2Zr_2O_7$ pyrochlore (Py, $Fd\bar{3}m$), stable up to ~1530 °C [32,36,37], above which it disorders to a defect-fluorite. The pyrochlore phase is a fluorite derivative with stoichiometry $(A,B)_4(O_7\Box)_1$, wherein \Box denotes anion vacancies; the larger A and smaller B cations are ordered in alternate rows along $\langle 110 \rangle$ directions on the cation FCC lattice. There are three ordered anion sites, one coordinated by 4 A cations, a second one by 2 A + 2 B cations, and the vacant site coordinated by 4 B cations. The ordering is driven by the cation radii ratio, with $r_{Gd}^{3+}/r_{Zr}^{4+} \sim 1.46$ being at the lower limit of stability [38,39]. Unlike the δ - $Y_4Zr_3O_{12}$ phase, the $Gd_2Zr_2O_7$ pyrochlore is not a line compound. The extent of solubility is somewhat uncertain owing to the ambiguity of the fluorite-pyrochlore equilibrium [40]. Some studies consider that the ordering transformation is first order [32], with distinct two phase fields between fluorite and pyrochlore, whereas others consider the transition as second order [41]. Nevertheless, the homogeneity range of the pyrochlore phase at ~1400 °C is generally accepted as approximately ~45–55% $GdO_{1.5}$ [40,42–44]. Other solid solution fields in ZrO_2 - $GdO_{1.5}$ at 1400 °C include tetragonal ZrO_2 , stable from 0 to 2.7 % $GdO_{1.5}$, an extensive fluorite field at 13.4–43.3 % $GdO_{1.5}$ and 58–70.2 % $GdO_{1.5}$ [32]; the C- $GdO_{1.5}$ and B- $GdO_{1.5}$ phases are stable within 89–95 % $GdO_{1.5}$ and 99.9–100

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