1
2
3
4 **Interaction Between Ceramic Powder and Molten Calcia-Magnesia-Alumino-Silicate**
5
6 **(CMAS) Glass, and Its Implication on CMAS-Resistant Thermal Barrier Coatings**
7
8
9

10
11 **Amanda R. Krause, Xing Li[§], and Nitin P. Padture^{*}**
12

13
14 School of Engineering, Brown University, Providence RI, 02912, USA
15
16
17

18
19 For: Scripta Materialia
20
21
22
23
24

25
26 **Abstract**
27

28 Calcia-magnesia-alumino-silicate (CMAS)-attack mitigation mechanisms of
29 $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ composition TBCs are investigated through a ‘model’ study where
30 $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ ceramic powders are immersed in molten CMAS glass for various durations at 1300
31 °C. The key insight gained from this study is that the formation of the CMAS-blocking apatite
32 phase requires high concentration of Y^{3+} within a confined volume of CMAS, whereas the
33 presence of a large-volume CMAS sink for Y^{3+} precludes the formation of apatite. It is
34 also demonstrated that the ceramic microstructure has a profound effect on its dissolution and
35 penetration by CMAS, and on the concomitant crystallization of apatite.
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53 [§] On leave from Beijing Institute of Technology, Beijing, 100081, P.R. China
54

55 ^{*} Author to whom correspondence should be addressed. Email: nitin_padture@brown.edu
56
57
58
59
60
61
62
63
64
65

Thermal barrier coatings (TBCs) made of the typical 7wt.% Y_2O_3 -stabilized ZrO_2 (7YSZ) composition are commonly used to insulate and protect hot-section metallic components in gas-turbine engines used for aircraft propulsion and electricity generation.[1-4] While TBCs allow higher operating temperatures in engines for improved performance and efficiency, the rising engine temperatures introduce new materials requirements.[3, 4] For example, calcia-magnesia-alumino-silicates (CMASs) entering engines in the form of sand, fly ash, volcanic ash, runway debris, *etc.* melt at temperatures greater than $\sim 1200^\circ\text{C}$ and damage the TBCs causing them to spall.[5-12] The molten CMAS glass infiltrates pores/cracks in the TBCs and dissolves the 7YSZ grains.[13] Reprecipitation of Y-depleted ZrO_2 grains occurs due to the low solubility of Zr^{4+} in the CMAS glass compared with Y^{3+} , consequently enriching the CMAS in Y^{3+} . [12-16] However, the small amount of Y^{3+} solute available in 7YSZ TBCs (0.08:1::Y:Zr atomic ratio) is not sufficient to alter the composition of the CMAS and its flow behavior significantly, resulting in full TBC penetration by the CMAS. Thus, conventional 7YSZ composition is ill-suited for TBC application at higher temperatures when CMAS is present. In this context, we recently showed that by increasing the Y^{3+} solute content in YSZ TBCs — $2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ (1:1::Y:Zr atomic ratio) — the CMAS penetration is arrested at high temperature (1340°C). [17, 18] This is attributed to the introduction of a sufficient amount of Y^{3+} into the CMAS during the dissolution-reprecipitation process, which induces crystallization of an apatite phase from the CMAS and the reprecipitation of Y^{3+} -lean ZrO_2 grains. [18-20] The refractory apatite phase essentially ‘seals’ the coating, blocking further penetration of the CMAS. [18-20] TBCs made of other ceramics, such as rare-earth (RE) zirconates ($\text{RE}_2\text{Zr}_2\text{O}_7$), also induce precipitation of apatite and other secondary phases during CMAS-mitigation. [9, 10, 13, 19, 21-23] While this effect is dramatic and it is of practical use, there are gaps in our understanding of the basic mechanisms involved. In

1
2
3
4 particular, the transport behavior of Y^{3+} and Zr^{4+} at the ceramic/CMAS interface and within the
5
6 CMAS glass has not been studied. Yet this transport behavior is known to govern the nucleation
7
8 and growth of the crystallizing phases, which in turn control the TBCs' CMAS-mitigating
9
10 capability.[23] Analyzing the transport behavior and solution-precipitation process is difficult
11
12 in TBC/CMAS interaction studies due to the lack of well-defined interfaces. To circumvent this
13
14 issue, we have performed 'model' experiments involving high-temperature interactions between
15
16 $2ZrO_2 \cdot Y_2O_3$ polycrystalline ceramic powders and CMAS glass. The key insight provided by this
17
18 study is that the formation of the desirable apatite phase requires high concentration of Y^{3+}
19
20 within a confined volume (pocket) of CMAS, whereas the presence of a large-volume CMAS
21
22 sink for Y^{3+} precludes the formation of the apatite phase.
23
24
25
26
27

28
29 Hollow-sphere plasma-densified (HOSP) powder of $2ZrO_2 \cdot Y_2O_3$ (Oerlikon-Metco,
30
31 Westbury, NY) from the previous study was used (Fig. 1a).[17] CMAS of composition
32
33 $39.2CaO \cdot 5.2MgO \cdot 4.1Al_2O_3 \cdot 51.5SiO_2$ (mol.%) from a previous study[19] was prepared by mixing
34
35 the respective reagent-grade oxide constituents, and heating the mixture at $1550^\circ C$ for 4 h in a Pt
36
37 crucible before quenching to room temperature in water. The CMAS glass was then crushed and
38
39 reheated under the same conditions to ensure a homogeneous glass. The crushed CMAS glass
40
41 was then ball-milled for 72 h in ethanol to produce a glass frit. A small amount of the glass frit
42
43 (70 mg) was then placed in a small Pt crucible and heated to $1350^\circ C$ for 4 h before quenching in
44
45 air to room temperature. The heat-treatment was repeated to remove any air bubbles and produce
46
47 a homogeneous glassy reservoir at the bottom of the crucible. $2ZrO_2 \cdot Y_2O_3$ powder (10.5 mg;
48
49 13% wt.% of the CMAS) was placed on top of the glass surface, and the samples were then heated
50
51 at $1300^\circ C$ for 1, 4, or 24 h in a box furnace in air before being quenched to room temperature. (The
52
53 13 wt.% amount was chosen based on some preliminary experiments, where 11-12 wt.% was
54
55
56
57
58
59
60
61
62
63
64
65

found to be the ‘solubility’ limit of $2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ powder in CMAS glass heat-treated at 1300 °C for 24 h.) The Pt crucibles with the samples were cut in half using a diamond saw, mounted in epoxy, and the cross-sections were polished to 1 μm finish using standard metallographic techniques.

The cross-sections were characterized using a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Germany) equipped with an energy dispersive spectrometer (EDS; Inca, Oxford Instruments, UK) and a transmission electron microscope (TEM; 2100F, JEOL, Japan or CM20, FEI, Hillsboro, OR), operated at 200 kV accelerating voltage, and also equipped with EDS. The TEM specimen was obtained using focused ion beam (FIB; Helios 600, FEI, Hillsboro, OR). Electron probe micro-analysis (EPMA; Cameca SX-100, Cameca Instruments Inc., France), operated with a wavelength dispersive spectrometer (WDS) in conjunction with elemental standards, was used to measure the local chemical compositions of the CMAS and the grains more accurately.

In separate experiments, the solubility limit of Y^{3+} in the CMAS glass was determined by heat-treating several batches of Y_2O_3 powder and CMAS glass frit mixture, with increasing Y_2O_3 :CMAS ratios, at 1300 °C for 24 h in air, followed by quenching. The resulting materials were crushed and analyzed using X-ray diffraction (XRD; D8 Advance, Bruker AXS, Germany). The mixture in which the first appearance of discernible Y_2O_3 and/or apatite peaks above the amorphous hump was identified as the solubility limit. Similar experiments were performed using 7YSZ powder to determine the solubility limit of Zr^{4+} .

Figure 1A is a SEM micrograph of the starting $2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ powder showing a combination of densified and partially-densified spheres (some hollow). Also, note the wide porosity and size

1
2
3
4 distribution. Fortuitously, this diversity in the morphology and size allows us to study a rich
5
6 variety of effects in a few experiments.
7

8
9 Figures 1B and 1C are cross-sectional SEM micrographs showing interactions
10 between $2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ powder and CMAS glass heat-treated at 1300 °C for 1 h. Figure 1B shows
11 the overall view where the powder particles are in a cluster and are starting to settle in the CMAS
12 glass (dark gray) under gravity. Figure 1C is a higher-magnification SEM image of a region in
13 the middle of the particle cluster showing different particle morphologies. One particle type,
14 *e.g.* P1 in Fig. 1C (light gray), shows limited interaction with little to no CMAS glass infiltration
15 into the particle and a composition very similar to that of the original powder (*e.g.* Z1 in Fig. 1C
16 and Table 1). The faceted rod-like crystals (*e.g.* A1 in Fig. 1C) at the surface of these particles are
17 apatite (medium gray), as identified by the chemical composition (Table 1). Other smaller,
18 partially-densified particles, *e.g.* P2 in Fig. 1C, show evidence of extensive interaction with the
19 CMAS glass. The initial particle morphology is no longer recognizable, and there is extensive
20 formation of apatite. Some particles, *e.g.* P3 in Fig. 1C, show a mixed behavior, where the
21 periphery has interacted with the CMAS glass extensively and is Y-depleted (composition Z2 in
22 Table 1), with concomitant formation of apatite, while the interior is intact with no change in
23 composition. A TEM specimen was extracted from the region specified (dashed rectangle) in
24 Fig. 1c to investigate further the interactions between $2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ particles and CMAS glass.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

48 Figure 2A is a bright-field TEM micrograph showing the CMAS attack front (dashed
49 curve), which appears to be relatively even with no significant penetration into the grain
50 boundaries of the interior of the grain. In the interaction region there are several examples of
51 faceted apatite grains surrounded by Y-lean, rounded c-ZrO_2 grains (Figs. 2B and 2C). The
52 elemental compositions of the grains A2 and Z4 are given in Table 1. The indexed selected area
53
54
55
56
57
58
59
60
61
62
63
64
65

electron diffraction patterns (SAEDPs) in Fig. 2C confirm the phases A3 and Z3, to be apatite and *c*-ZrO₂, respectively, and their chemical compositions are given in Table 1.

The extent of the reaction with a particle, or the particle's morphology as observed in Fig. 1C, is depends on its initial surface area. Small, porous particles have sufficient surface area for rapid dissolution, inducing the precipitation of rounded, Y-depleted *c*-ZrO₂ grains and faceted apatite grains. Large particle with a dense exterior have a planar interface, in part due to the lack of grain boundary penetration, as observed in Fig. 2B. Therefore, the dissolution rate is controlled by the transport to and from the interaction interface. From these observations two important implications on TBCs can be derived. First, in air plasma sprayed (APS) TBCs, the adhesion and bonding of splat boundaries may play an important role in the CMAS-penetration behavior. Second, microstructure features influence the dissolution rate. This suggests that an optimum microstructure will need to be designed that will allow sufficient dissolution in the CMAS glass to allow apatite formation, but prevent significant CMAS penetration.

Previously, the apatite composition has been used to access CMAS mitigation capability.[19]The general formula for silicate-apatite is $A_4^I A_6^{II} (SiO_4)_6 O_x$ [24], where the larger Ca^{2+} occupies the larger A^I site (coordination (CN)# 9), and the smaller Y^{3+} occupies the smaller A^{II} site (CN# 7) but it can also occupy the A^I site. The oxygen content, x , is dependent on the cumulative valency of the cations; $x=2$ when all oxygen sites are occupied.[24-26]Theoretically, the composition of silicate-apatite can range between $Ca_2Y_8(SiO_4)_6O_2$ and $Ca_4Y_6(SiO_4)_6O$ (listed in Table 1)[27]. The latter composition is thought to be less stable due to the high concentration of O^{2-} vacancies needed, but in this study the composition of apatite grains is closer to $Ca_4Y_6(SiO_4)_6O$. It is also noted that the apatite grains contain Zr^{4+} (Table 1), presumably in solid solution, which has also been observed in Gd-based silicate apatite[22]. It is

suggested that Zr^{4+} may substitute for Ca^{2+} and/or Y^{3+} , and will reduce the O^{2-} vacancy concentration by virtue of its higher valency.

An interesting observation in the overall view in Fig. 3A is that the particles at the periphery of the cluster have dramatically different morphologies relative to the particles in the interior. More importantly, there is a big difference in the morphology of the side of individual particles facing the open CMAS glass and the side facing the cluster, as seen in Figs. 3B and 3C. The CMAS-side is heavily infiltrated with extensive exfoliation, and dissolution/precipitation of Y-depleted $c\text{-ZrO}_2$ grains (see composition of Z5 in Table 1). However, there is little evidence of apatite growth in that region. In contrast, there is no significant dissolution/exfoliation on the cluster-side of the $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ particles (see Z6 in Table 1), but faceted apatite grains (medium gray) are found in the regions between particles, away from the periphery. Figure 3D plots the WDS elemental composition (Si, Y, Zr) of the CMAS glass as a function of distance away from the edge (bottom) of the particle cluster. The dashed lines in Fig. 3D indicate the measured CMAS glass composition (WDS) in the interior of the particle cluster. These data indicate that Zr^{4+} has a lower solubility in the CMAS glass compared with Y^{3+} . Quantitatively, these results are also consistent with the independently determined solubility limit of Y^{3+} and Zr^{4+} in the CMAS glass of ~6 at.% and ~3 at.% (cation basis), respectively, under the same heat-treatment conditions. The most striking feature of these data is that the Zr^{4+} concentration is homogenous in the CMAS, whereas the Y^{3+} concentration shows a significant concentration gradient. These observations indicate that confinement of Y^{3+} in the CMAS melt plays a key role in apatite formation, which has important implications for the CMAS-resistance in actual TBCs. In other words, large glass pockets, which could serve as large sinks for Y^{3+} , are not desirable for the formation of CMAS-blocking apatite phase in TBCs.

The following explanation for this behavior is proposed. When a $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ grain dissolves in the CMAS glass, locally the glass is saturated in Y^{3+} and Zr^{4+} . Since solubility of Zr^{4+} in the CMAS glass is about half of that for Y^{3+} , Y-depleted $c\text{-ZrO}_2$ will nucleate heterogeneously and grow. The Y-content in the $c\text{-ZrO}_2$ is likely to depend on various factors such as the partition (distribution) coefficient, which is not known for this system, and the amount of Y^{3+} available locally. For this system, the net gain of Y^{3+} in the glass is determined by the dissolution rate, transport of Y^{3+} to the glass sink, and its solubility limit. Apatite formation becomes favorable only when the Y-content exceeds ~ 6 at.%. On the cluster-side, simultaneous dissolution of multiple particles introduces a high flux of Y^{3+} and Zr^{4+} into an effectively small volume of glass. The solubility limit of Y is exceeded due to the inefficiency of transport to the glass sink. Once again, the composition of the apatite will depend on the relative availability and activity of the necessary elements in the CMAS glass. On the periphery, apatite growth is suppressed due to insufficient amount of Y^{3+} in the glass, resulting from the transport of Y^{3+} into the large glass sink. Thus, CMAS glass can continue to penetrate the CMAS-side of the particles but not the cluster-side, as seen in Figs. 3A-3C.

A similar effect is observed in Fig. 4A in samples heat-treated for a longer duration (4 h at 1300°C). The CMAS-side region Z7 is Y-depleted with no evidence of apatite crystallization, whereas on the cluster-side apatite is observed and the region Z8 is not Y-depleted. Similarly, in the middle of the particles cluster, porous $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ particles are completely penetrated by CMAS with extensive apatite crystallization (e.g. P4 in Fig. 4B), while dense particles are only partially penetrated by CMAS, with some evidence of apatite crystallization. After 24 h heat-treatment at 1300°C most of the particles, and all of the apatite crystals, have dissolved in the CMAS glass (Figs 4C and 4D). Only remnants of Y-depleted $c\text{-ZrO}_2$ grains are found settled to

the bottom of the Pt crucible (*e.g.* Z9 in Fig. 4D and Table 1). The 24-h heat-treatment duration is sufficient for the Y^{3+} in the CMAS-glass to dissipate throughout, with total Y^{3+} content in the CMAS glass well below the solubility limit.

The lack of apatite phase after 24-h heat-treatment exemplifies the transient nature of the TBC/CMAS interaction, and it is important to recognize that the precipitates may be metastable and their compositions can alter with time. In this context, Mechnich *et al.*[22] provided evidence for a change in the Gd-apatite composition with time in a $Gd_2Zr_2O_7$ /CMAS interaction study. A change in the apatite and Y-depleted c - ZrO_2 compositions with time has also been observed in an interaction study of $2ZrO_2 \cdot Y_2O_3$ free-standing APS coatings with CMAS at 1340 °C (not published). Therefore, it is difficult to predict the CMAS-mitigating capability of a TBC ceramic just based on the composition of the precipitates at a particular heat-treatment condition.

In closing, we have demonstrated the usefulness of model studies involving interactions between ceramic powders and CMAS glass in gaining insights into the CMAS-resistance of TBCs. The key insight gained in this study is that the formation of the desirable CMAS-blocking apatite phase requires high concentration of Y^{3+} within a confined volume (pocket) of CMAS glass, whereas the presence of a large-volume CMAS-glass sink for Y^{3+} precludes the formation of the apatite phase. In addition, it is shown that the ceramic microstructure has a profound effect on the dissolution and the penetration of the ceramic by the CMAS glass. Ultimately, the relative rates of the dissolution and the transport of the relevant species will control the formation and the growth of the CMAS-attack-mitigating phases such as apatite. This understanding has far-reaching implications for the design of CMAS-resistant TBCs of the future.

1
2
3
4 The support from the Office of Naval Research (grant no. N00014-15-1-2375, monitored
5
6 by Dr. D. Shifler) is gratefully acknowledged. We thank Dr. H.F. Garces for experimental
7
8 assistance.
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 1: Chemical compositions of grains and regions marked in Figs.1,2, 3, and 4 and theoretical compositions of important apatite phases.

At.% Cation Basis	Ca	Si	Y	Zr
$2\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3$ Powder*	-	-	50.0	50.0
$\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{O}^*$	25.0	37.5	37.5	-
$\text{Ca}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2^*$	12.5	37.5	50.0	-
A1**	19.3	36.6	38.4	5.7
Z1**	-	-	47.1	52.9
Z2**	2.5	0.7	20.9	75.9
A2	15	40	41	4
Z3	3	-	22	75
A3	17	39	40	4
Z4	3	-	19	78
Z5	4	-	18	77
Z6**	-	-	52.3	47.7
Z7	5	2	17	76
Z8	-	-	49	51
Z9	3	-	15	82

* Ideal composition

** Measured using WDS. All others measured using EDS.

References

- [1] N.P. Padture, M. Gell, E.H. Jordan, *Science* 296 (2002) 280-284.
- [2] A.G. Evans, D.R. Clarke, C.G. Levi, *J. Eur. Ceram. Soc.* 28 (2008) 1405-1419.
- [3] D.R. Clarke, M. Oechsner, N.P. Padture, *MRS Bull.* 37 (2012) 891-898.
- [4] R. Darolia, *Intl. Mater. Rev.* 58 (2013) 315-348.
- [5] F.H. Stott, D.J. DeWet, R. Taylor, *MRS Bull.* 19 (1994) 46-49.
- [6] J.L. Smialek, F.A. Archer, R.G. Garlick, *JOM* 46 (1994) 39-41.
- [7] M.P. Borom, C.A. Johnson, L.A. Peluso, *Surf. Coat. Technol.* 86-87 (1996) 116-126.
- [8] S. Krämer, S. Faulhaber, M. Chambers, D.R. Clarke, C.G. Levi, J.W. Hutchinson, A.G. Evans, *Mater. Sci. Engr. A* 490 (2008) 26-35.
- [9] J.M. Drexler, A.D. Gledhill, K. Shinoda, A.L. Vasiliev, K.M. Reddy, S. Sampath, N.P. Padture, *Adv. Mater.* 23 (2011) 2419-2424.
- [10] A.D. Gledhill, K.M. Reddy, J.M. Drexler, K. Shinoda, S. Sampath, N.P. Padture, *Mater. Sci. Engr. A* 528 (2011) 7214-7221.
- [11] M.H. Vidal-Setif, N. Chellah, C. Rio, C. Sanchez, O. Lavigne, *Surf. Coat. Technol.* 208 (2012) 39-45.
- [12] C.G. Levi, J.W. Hutchinson, M.-H. Vidal-Setif, C.A. Johnson, *MRS Bull.* 37 (2012) 932-941.
- [13] S. Krämer, J. Yang, C.G. Levi, C.A. Johnson, *J. Am. Ceram. Soc.* 89 (2006) 3167-3175.
- [14] A. Aygun, A.L. Vasiliev, N.P. Padture, X. Ma, *Acta Mater.* 55 (2007) 6734-6745.
- [15] M.H. Vidal-Setif, C. Rio, D. Boivin, O. Lavigne, *Surf. Coat. Technol.* 239 (2014) 41-48.
- [16] H.F. Garces, B.S. Senturk, N.P. Padture, *Scripta Mater.* 76 (2014) 29-32.

- [17] A.R. Krause, B.S. Senturk, H.F. Garces, G. Dwivedi, A.L. Ortiz, S. Sampath, N.P. Padture, J. Am. Ceram. Soc. 97 (2014) 3943-3949.
- [18] A.R. Krause, B.S. Senturk, N.P. Padture, J. Am. Ceram. Soc. 97 (2014) 3950-3957.
- [19] J.M. Drexler, A.L. Ortiz, N.P. Padture, Acta Mater. 60 (2012) 5437-5447.
- [20] N.K. Eils, P. Mechnich, W. Braue, J. Am. Ceram. Soc. 96 (2013) 3333-3340.
- [21] U. Schulz, W. Braue, Surf. Coat. Technol. 235 (2013) 165-173.
- [22] P. Mechnich, W. Braue, J. Am. Ceram. Soc. 96 (2013) 1958-1965.
- [23] D.L. Poerschke, C.G. Levi, J. Eur. Ceram. Soc. 35 (2015) 681-691.
- [24] J. Felsche. The Crystal Chemistry of the Rare-Earth Silicates. Structure and Bonding Volume 13. Berlin: Springer; 1973.
- [25] J. Ito, Am. Min. 53 (1968) 890-907.
- [26] R.D. Shannon, Acta Cryst. A 32 (1976) 751-767.
- [27] T. Nagasawa, H. Yamane, S. Kubota, M. Shimada, J. Ceram. Soc. Jpn. 106 (1998) 1238-1241.

Figure Captions

1. (A) SEM image of the as-received $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ HOSP powder. Cross-sectional SEM images CMAS glass with the of the $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ in a Pt crucible heat-treated at 1300 °C for 1 h at: (B) low and (C) high magnifications, where the $2\text{ZrO}_2\cdot\text{Y}_2\text{O}_3$ HOSP powder is clustered near the surface of the CMAS glass. The dashed box indicates the region from where the TEM sample was extracted using FIB.
2. (A) Bright-field TEM images of the surface of particle P3 from Fig. 1C. The white dashed line indicates the CMAS-attack front. (B-C) Higher magnification TEM micrographs from the

1
2
3
4 interaction regions in (a). Indexed SAEDPs of A3 and Z3 are included as insets in (C), where 'B'
5
6 indicates the zone axis and the transmitted beam is circled.
7
8

9
10 **3.**Cross-sectional SEM images of the sample from Fig. 1(B) (1300 °C, 1 h) showing region near
11 the particle-cluster periphery (denoted by the dashed curves): (A) at low magnification and (B)-
12 (C) at higher magnifications. (D) The elemental Si, Y, and Zr content in the glass, measured by
13 WDS, as a function of distance from the particle-cluster edge. The dashed lines indicate the
14 composition of the CMAS glass pockets within the interior of the particle-cluster.
15
16
17
18
19
20
21

22 **4.**Cross-sectional SEM images for sample heat-treated at 1300 °C for 4 h: (A) the particle-cluster
23 periphery (dashed curve) region and (B) within the particle-cluster. Cross-sectional SEM images
24 for sample heat-treated at 1300 °C for 24 h showing remaining ceramic particles at the bottom of
25 the Pt crucible at: (C) low and (D) high magnifications.
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure(s)

Figure(s)

Figure(s)

Figure(s)

'Model' studies of high-temperature interaction between ceramic powder and calcia-magnesia-alumino-silicate (CMAS) glass for understanding mechanisms of CMAS-resistance in thermal barrier coatings.