

Thermochemistry of CaO-MgO-Al₂O₃-SiO₂ (CMAS) and Advanced Thermal and Environmental Barrier Coating Systems

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Introduction

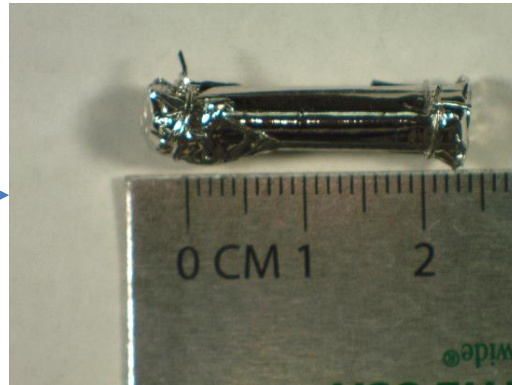
CaO-MgO-Al₂O₃-SiO₂ (CMAS) oxides are constituents in a broad number of materials and minerals which have recently inferred to discussions in materials science, planetary science, geochemistry and cosmochemistry communities. In materials science, there is increasing interest in the degradation studies of thermal (TBC) and environmental (EBC) barrier coatings of gas turbines by molten CMAS. These coatings have been explored to be applied on silicon-based ceramics and composites which are lighter and more temperature capable hot-section materials of gas turbines than the current Ni-based superalloys. The degradation of the coatings occurs when CMAS minerals carried by the intake air into gas turbines, e.g. in aircraft engines, reacts at high temperatures (>1000°C) with the coating materials. This causes premature failure of the static and rotating components of the turbine engines. We discuss some preliminary results of the reactions between CMAS and Rare-Earth (RE – Y, Yb and Gd) oxide stabilized ZrO₂ systems, and stability of the resulting oxides and silicates.

Experimental

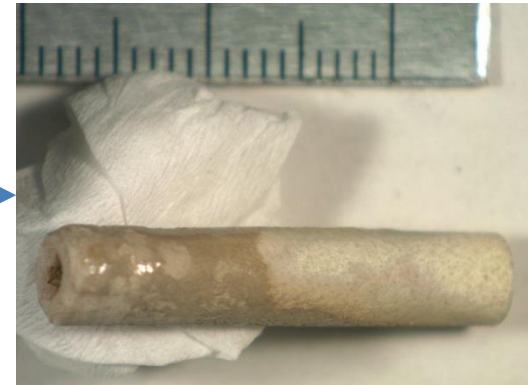
Samples studied in this scientific work were Plasma sprayed hollow tubes ($\sim \varnothing = 2.2$ mm and 26 mm height) provided by Prior the reaction the hollow tube samples were sintered at 1500 °C for 10 h. Then the hollow tube samples were half filled with CMAS powder (1:10 CMAS to sample mass ratio), wrapped and sealed with platinum foil, and heat treated at 1310 °C for 5h. Samples were characterized by differential scanning calorimetry, X-ray diffraction and. The phase evolution and composition of the samples after the experiments were characterized using X-ray diffraction (XRD) and cross section electron microscopy analysis. The thermal evolution of the samples were probed by differential scanning calorimetry (DSC).



(A)



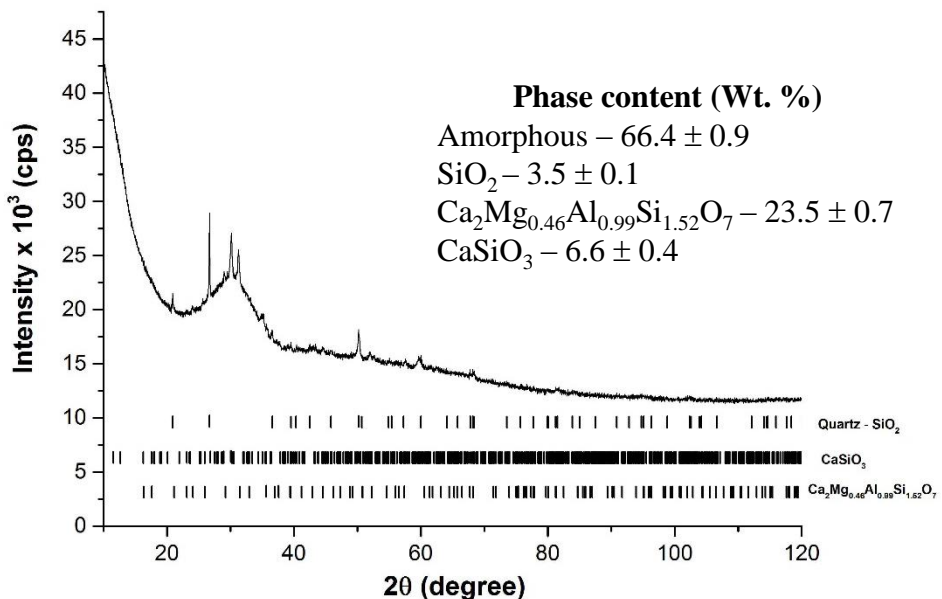
(B)



(C)

Hollow tube samples: (A) pristine; (B) before heat treatment in which it was half filled with CMAS powder, wrapped and sealed with Pt foil; (C) after heat treatment at 1310 °C for 5h and unwrapped.

Results: characterization of CMAS before reaction

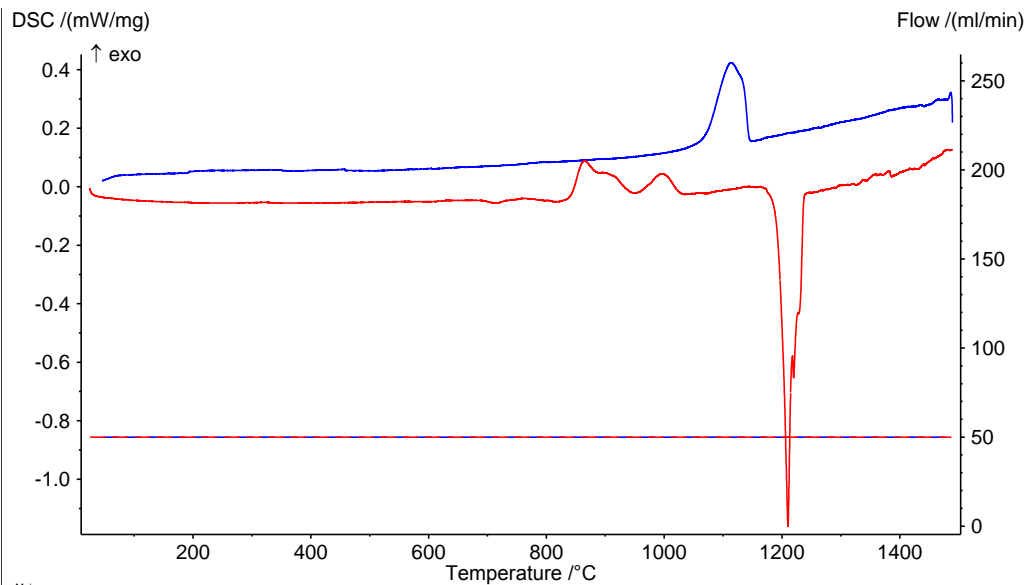


X-ray diffraction patterns of the as-received CMAS sample.

Chemical analysis of the as-received NASA CMAS by ICP-OAS

Element	Amount (wt. %)	±
Ca	21	1
Mg	3.1	0.2
Al	6.1	0.3
Si	19	1
Fe	5.9	0.3
Ni	1.10	0.06

Trace elements found but not quantified are
 Ba, Cr, Cu, K, Mn, Na, Sr, Ti, Zr



BET specific surface area: $0.8 \pm 0.1 \text{ m}^2/\text{g}$.

DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.

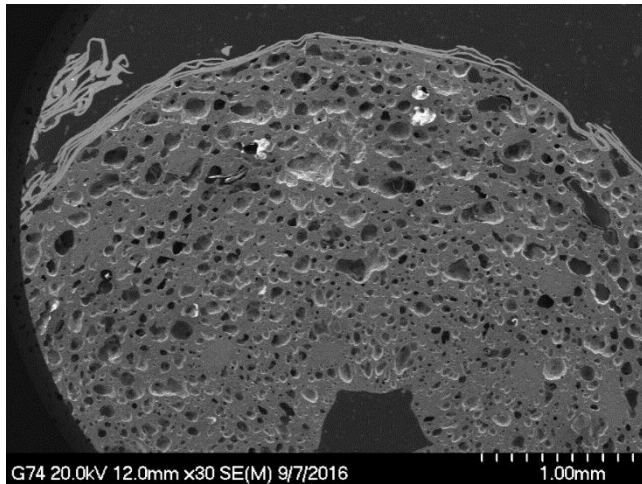
Results: characterization of the hollow tubes before reaction

Table 1 - Initial sample parameters measured by nitrogen adsorption, He picnometry and optical microscopy.

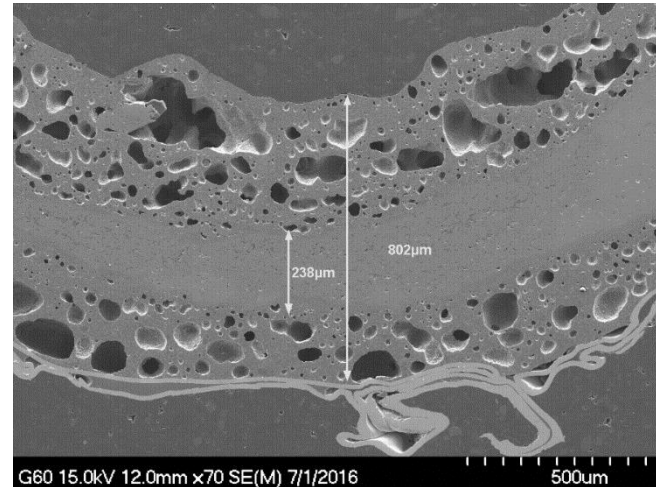
Sample	CMAS Surface concentration (g/cm ²)	BET Specific Surface Area (m ² /g)	Surface area of Pores between 8 Å-150 μm (m ² /g)*	Total pore volume ·10 ⁻⁵ (cm ³ /g)	Density (g/cm ³)	
					Geometric†	Measured by He picnometry
20 YSZ	147 ± 4	0.0384 ± 0.005	0.024 ± 0.003	3.6 ± 0.5	5.134 ± 0.003	5.72 ± 0.04
30 YSZ	69 ± 2	0.307 ± 0.05	0.11 ± 0.02	28.3 ± 4	4.77 ± 0.03	-
ZrO ₂ -13.1Y ₂ O ₃ - 10.5Gd ₂ O ₃ -11.4Yb ₂ O ₃	142 ± 4	0.12±0.02	0.036±0.005	12 ± 2	6.186 ± 0.003	6.19 ± 0.09
ZrO ₂ -15Y ₂ O ₃ - 5.63Gd ₂ O ₃ -5.65Yb ₂ O ₃	104 ± 3	0.12 ± 0.02	0.013 ± 0.002	13 ± 2	6.071 ± 0.003	6.0 ± 0.1

*Cumulative measured by BJH method. †Measured in an optical microscope.

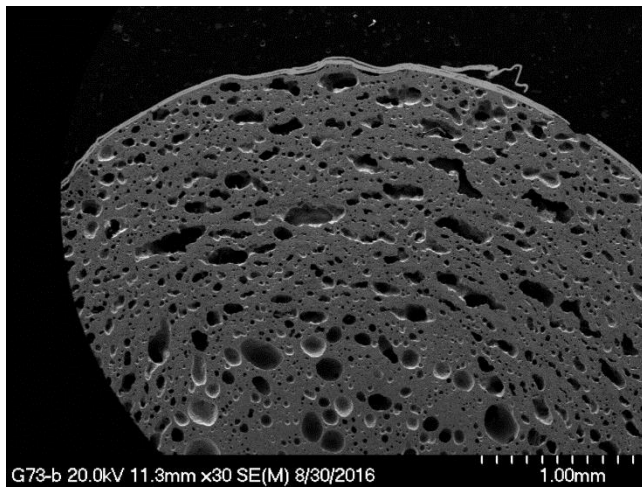
Results: SEM at low magnification (lower cut section)



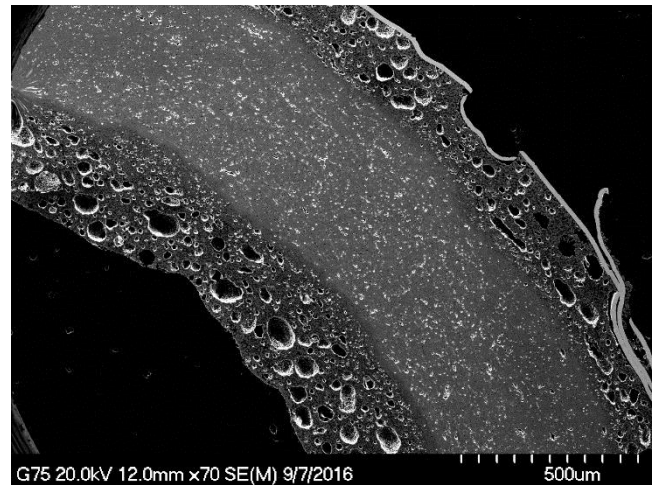
(A) 20YSZ



(B) 30YSZ



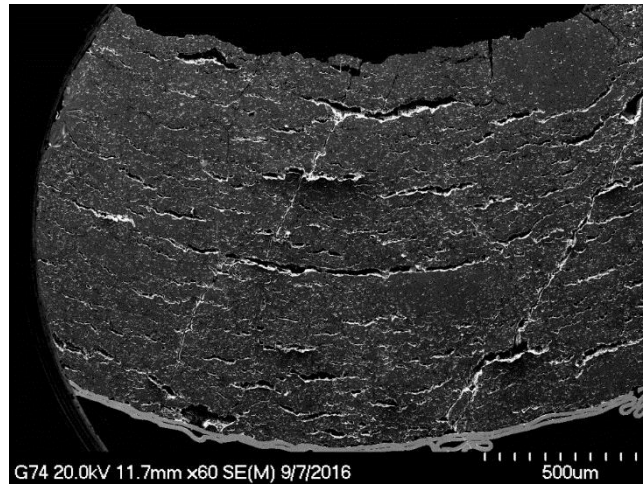
(C) $\text{ZrO}_2\text{-13.1Y}_2\text{O}_3\text{-10.5Gd}_2\text{O}_3\text{-11.4Yb}_2\text{O}_3$



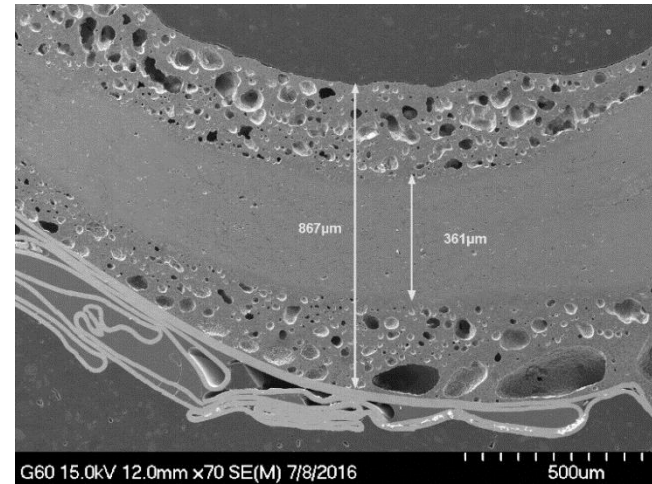
(D) $\text{ZrO}_2\text{-15Y}_2\text{O}_3\text{-5.63Gd}_2\text{O}_3\text{-5.65Yb}_2\text{O}_3$

SEM cross – sectional electron images of the lower section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h. It is clear from these images that CMAS penetrated, reacted and expanded with a large extent the entire bulk cross-section of samples (A) and (C). Samples (B) and (D) apparently seems to be less reactive to CMAS.

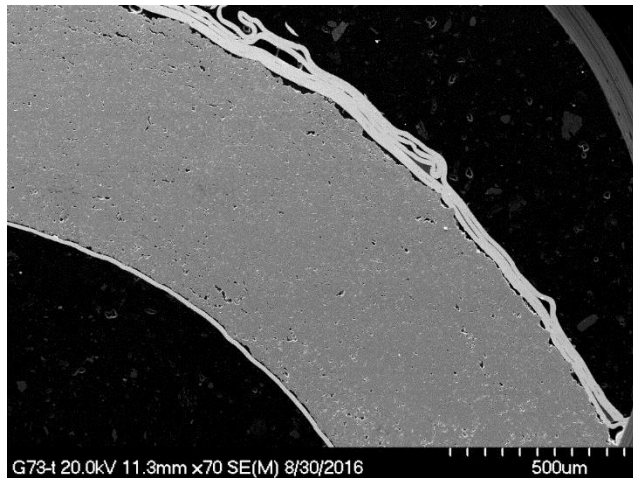
Results: SEM at low magnification (upper cut section)



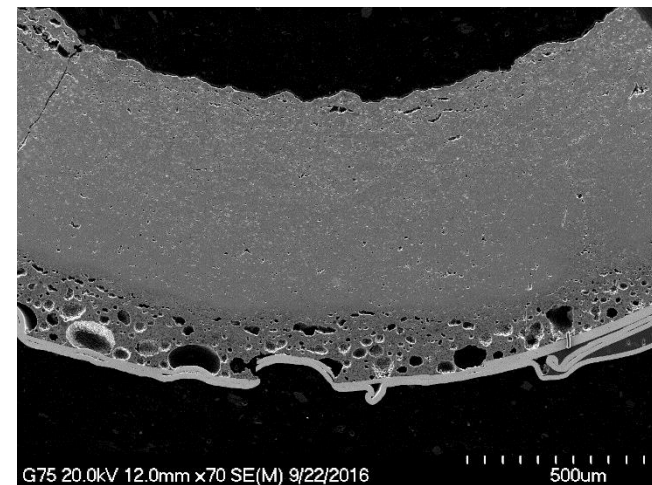
(A) 20YSZ



(B) 30YSZ



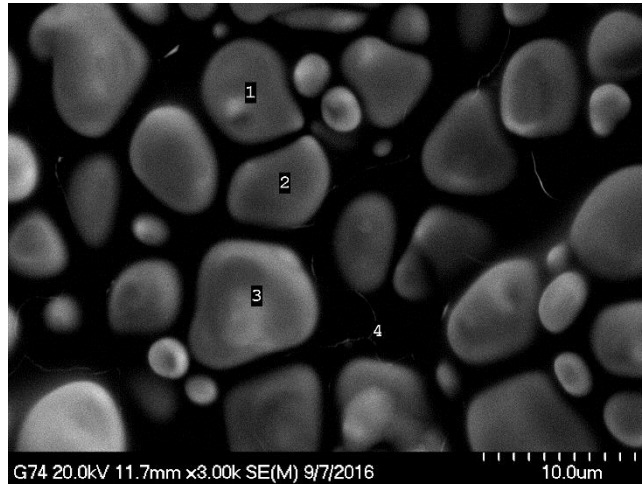
(C) $\text{ZrO}_2\text{-13.1Y}_2\text{O}_3\text{-10.5Gd}_2\text{O}_3\text{-11.4Yb}_2\text{O}_3$



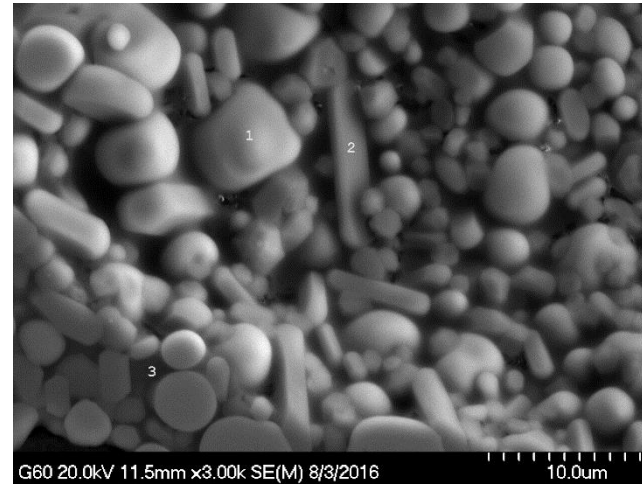
(D) $\text{ZrO}_2\text{-15Y}_2\text{O}_3\text{-5.63Gd}_2\text{O}_3\text{-5.65Yb}_2\text{O}_3$

SEM cross – sectional electron images of the upper section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h. Apparently most of the CMAS melt was consumed in the penetration and reaction with the lower section of the hollow tube samples (A) and (C), and it did not penetrate and react with a large extent in the upper section of these hollow tube samples.

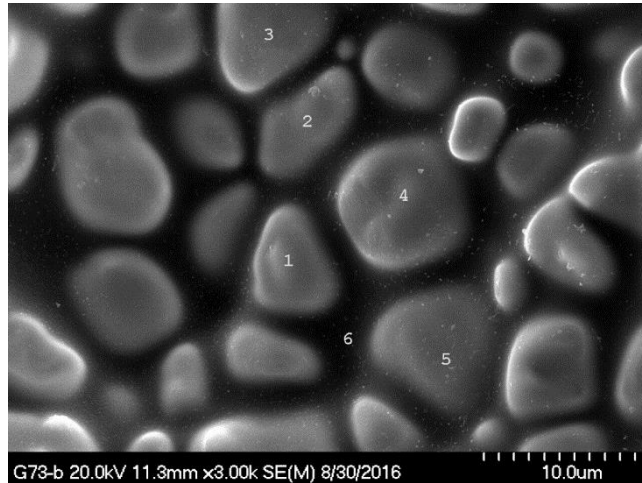
Results: SEM/BSE at high magnification (lower cut section)



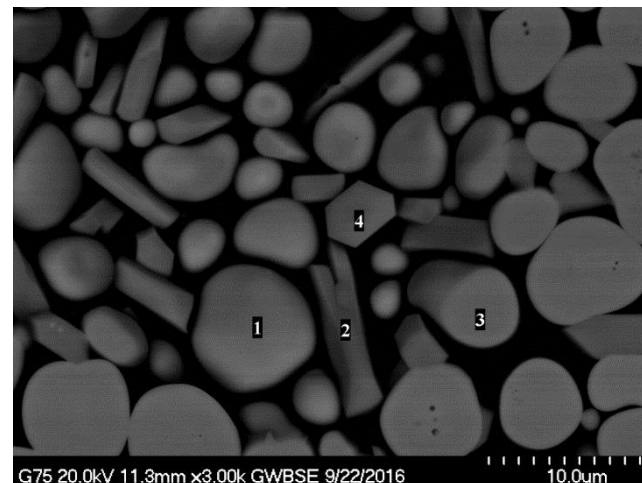
(A) 20YSZ



(B) 30YSZ



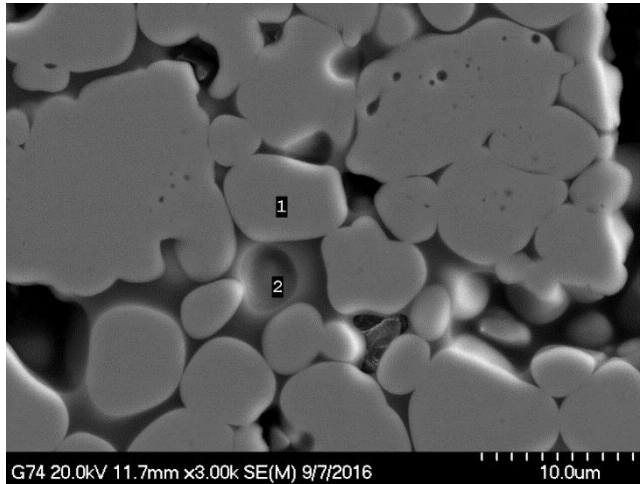
(C) ZrO₂-13.1Y₂O₃-10.5Gd₂O₃-11.4Yb₂O₃



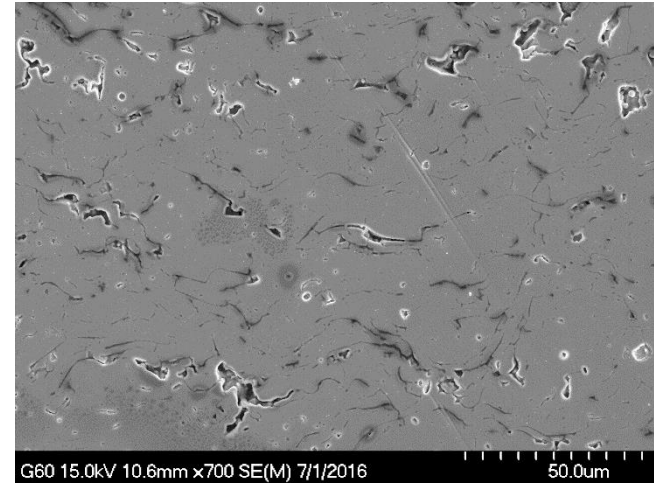
(D) ZrO₂-15Y₂O₃-5.63Gd₂O₃-5.65Yb₂O₃

SEM cross-sectional electron images of the lower section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h. Area probed were those that exhibited large extent of penetration and reaction. EDS analysis results of the numbered spots probed are given in Table 2.

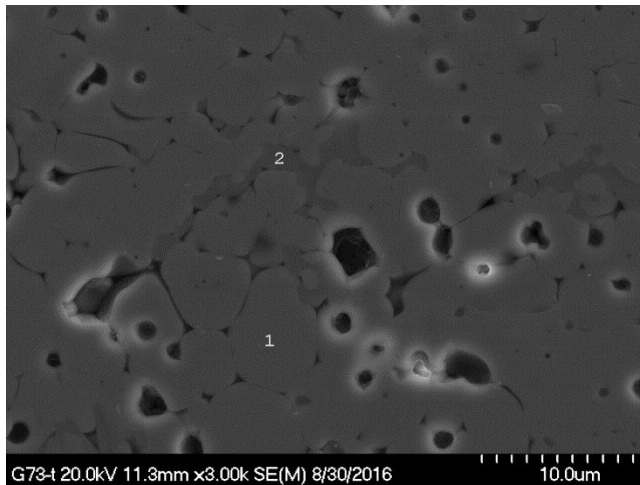
Results: SEM at high magnification (upper cut section)



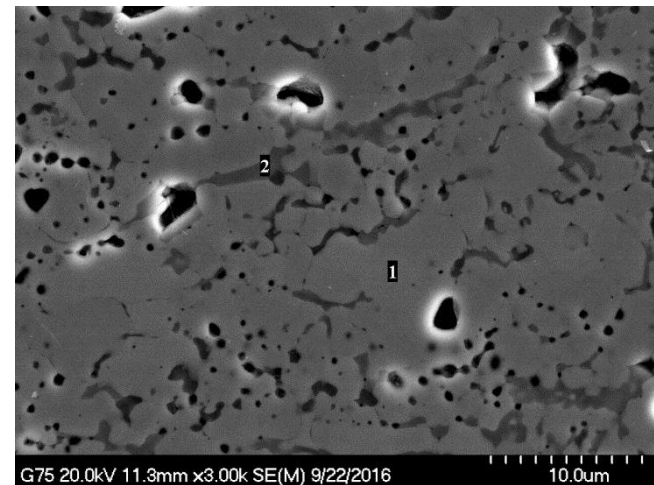
(A) 20YSZ



(B) 30YSZ



(C) $\text{ZrO}_2\text{-13.1Y}_2\text{O}_3\text{-10.5Gd}_2\text{O}_3\text{-11.4Yb}_2\text{O}_3$



(D) $\text{ZrO}_2\text{-15Y}_2\text{O}_3\text{-5.63Gd}_2\text{O}_3\text{-5.65Yb}_2\text{O}_3$

SEM cross – sectional electron images of the upper section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h. Area probed were those that exhibited small extent of penetration and reaction. EDS analysis results of the numbered spots probed are given in Table 3.

Results: EDS analysis (lower cut section)

Table 2 – Elemental composition of grains and grain boundaries of the lower section of the hollow tube samples measured by EDS.

Sample	Weight (%)										
	O	Mg	Al	Si	Ca	Fe	Y	Zr	Yb	Gd	Ni
20YSZ											
1	19.8(5)	0.30(6)	0.22(5)	0.40(5)	0.89(7)	0.67(9)	17.6(3)	60.1(5)	-	-	-
2	12.2(5)	0.17(6)	0.17(6)	0.60(6)	1.11(9)	0.6(1)	18.5(4)	66.6(6)	-	-	-
3	18.2(5)	0.24(6)	0.14(6)	0.42(6)	0.82(7)	0.5(1)	17.9(3)	61.8(5)	-	-	-
4	33.0(7)	2.0(1)	3.8(1)	12.3(2)	12.3(2)	3.3(2)	9.8(4)	22.7(5)	-	-	0.7(2)

30YSZ											
1	13.7(3)	0.24(5)	0.20(5)	0.32(5)	1.04(8)	-	27.7(3)	56.8(5)	-	-	-
2	20.0(4)	0.28(5)	0.36(5)	12.0(1)	8.6(1)	-	55.7(5)	3.0(2)	-	-	-
3	23.1(5)	3.8(1)	1.8(1)	16.3(2)	33.8(3)	-	13.4(4)	7.8(3)	-	-	-

ZrO ₂ -13.1Y ₂ O-10.5Gd ₂ O ₃ -11.4Yb ₂ O ₃											
1	18(1)	0.4(1)	0.8(1)	2.2(2)	2.3(2)	-	1.1(6)	33(1)	29(4)	13(2)	-
2	35(2)	0.7(2)	1.6(2)	4.1(3)	3.8(2)	1.2(3)	2.6(7)	35(1)	12(2)	4(1)	-
3	36(2)	0.7(2)	1.7(3)	4.2(4)	3.7(4)	-	3.0(9)	35(2)	13(3)	3(2)	-
4	16.3(9)	0.3(1)	0.4(1)	1.3(1)	2.2(2)	1.6(3)	3.4(5)	49(1)	18(2)	8(1)	-
5	17.7(4)	0.11(5)	0.01(5)	0.49(5)	1.51(8)	-	5.7(2)	64.6(5)	5.9(6)	4.0(4)	-
6	29(1)	2.0(1)	4.4(1)	14.0(3)	16.7(3)	7.1(3)	1.3(4)	9.1(5)	10(1)	5.9(9)	-

ZrO ₂ -15Y ₂ O ₃ -5.63Gd ₂ O ₃ -5.65Yb ₂ O ₃											
1	17.6(4)	-	0.14(5)	0.26(5)	0.8(1)	-	13.4(3)	53.0(5)	8.6(6)	6.2(4)	-
2	25.6(4)	-	0.3(1)	8.4(1)	4.5(1)	-	27.0(4)	4.4(2)	8.4(6)	21.3(6)	-
3	11.9(4)	-	0.04(1)	0.06(5)	0.79(7)	-	14.0(3)	54.8(4)	10.3(7)	8.1(5)	-
4	18.1(4)	-	0.33(6)	9.1(1)	4.8(1)	-	29.1(5)	2.8(2)	9.1(7)	26.6(7)	-

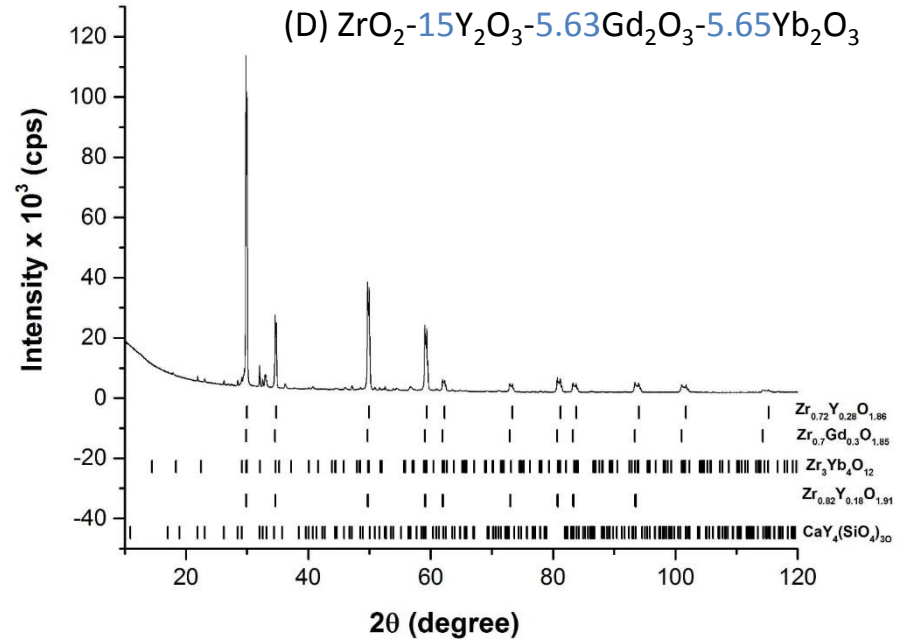
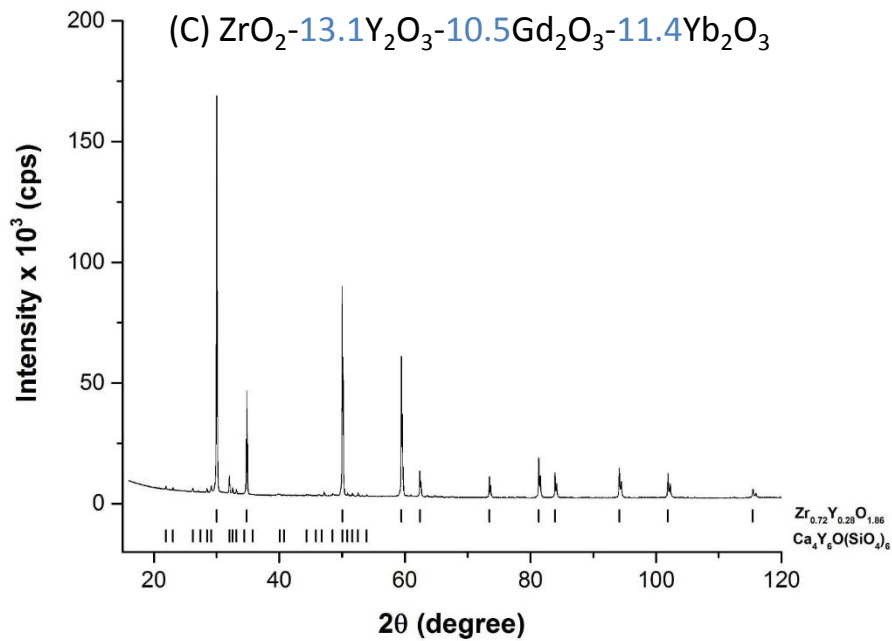
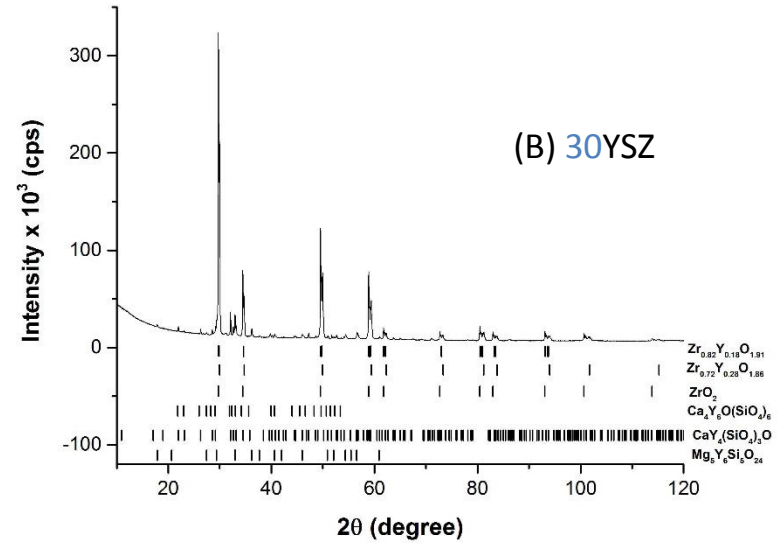
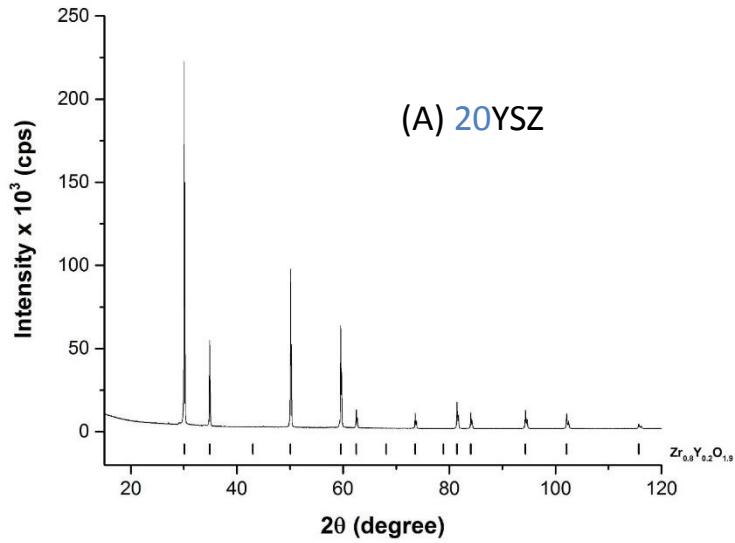
Results: EDS analysis (upper cut section)

Table 3 – Elemental composition of grains and grain boundaries of the upper section of the hollow tube samples measured by EDS.

Sample	Weight (%)										
	O	Mg	Al	Si	Ca	Fe	Y	Zr	Yb	Gd	Ni
20YSZ	-	-	-	-	-	-	-	-	-	-	-
1	14.5(5)	-	-	0.28(5)	-	-	19.4(4)	65.8(6)	-	-	-
2	11.5(5)	0.15(7)	0.25(7)	0.75(8)	1.1(1)	-	20.0(5)	66.3(7)	-	-	-
30YSZ*	-	-	-	-	-	-	-	-	-	-	-
1	33(3)	-	1.5(6)	5.3(8)	4.9(9)	-	20(3)	35(3)	-	-	-
ZrO ₂ -13.1Y ₂ O ₃ -10.5Gd ₂ O ₃ -11.4Yb ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-
1	11.4(4)	-	0.08(6)	0.07(6)	-	-	11.3(3)	53.8(6)	11.2(7)	12.1(6)	-
2	13.5(3)	-	0.10(7)	6.5(1)	3.8(1)	-	19.0(5)	10.3(4)	12.1(8)	34.6(9)	-
ZrO ₂ -15Y ₂ O ₃ -5.63Gd ₂ O ₃ -5.65Yb ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-
1	10.5(3)	-	0.14(5)	0.09(6)	-	-	18.0(4)	42.8(5)	14.2(8)	14.2(6)	-
2	14.2(4)	0.07(6)	0.89(7)	6.8(1)	3.9(1)	-	26.4(5)	10.1(3)	10.5(8)	27.1(8)	-

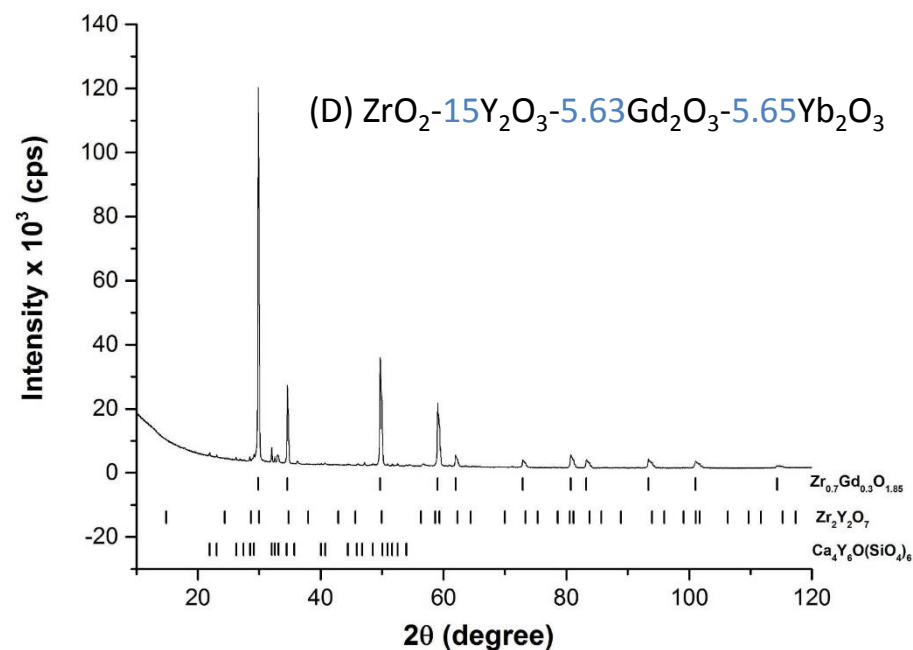
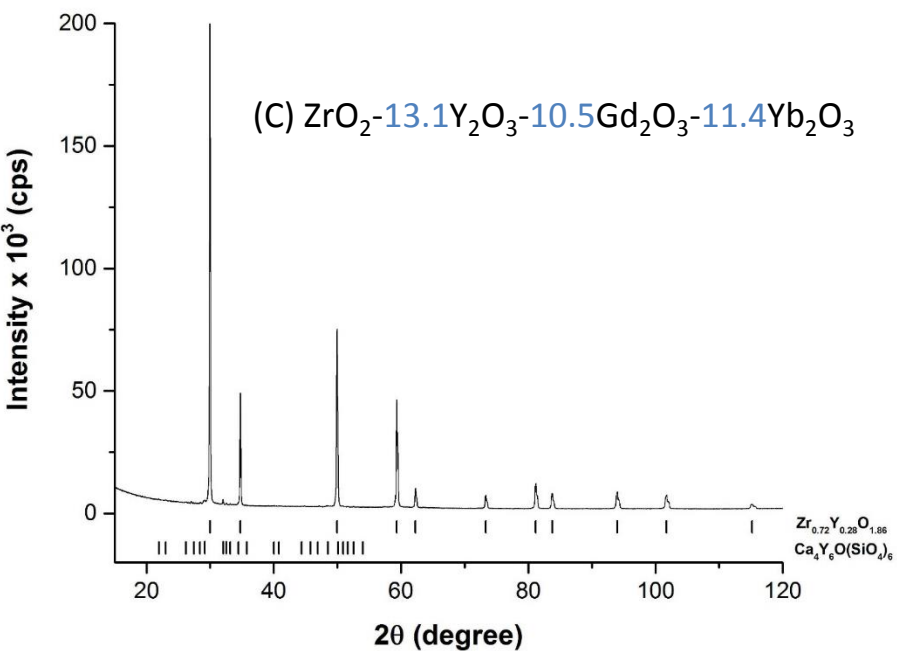
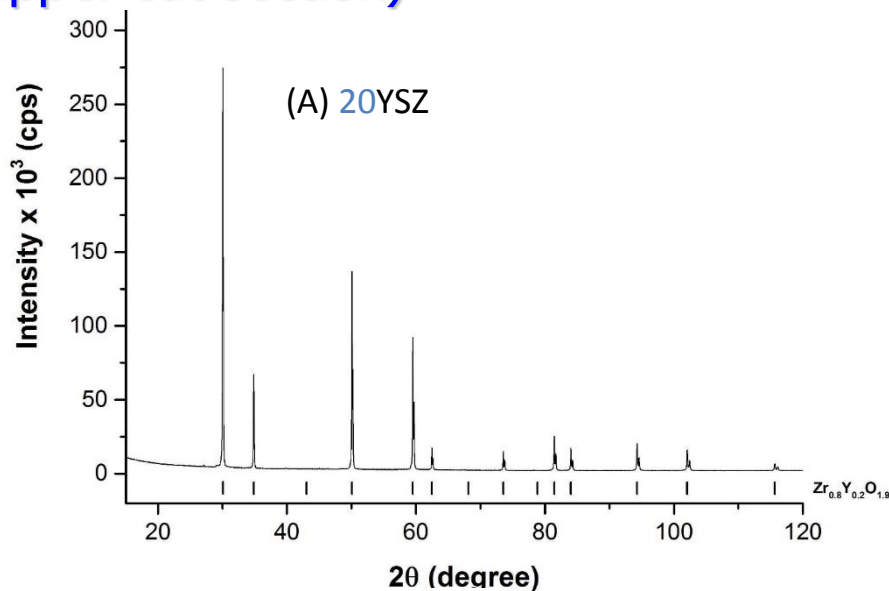
*Rectangular area covering the whole image of the sample was probed by EDS instead of a single spot.

Results: XRD (lower cut section)



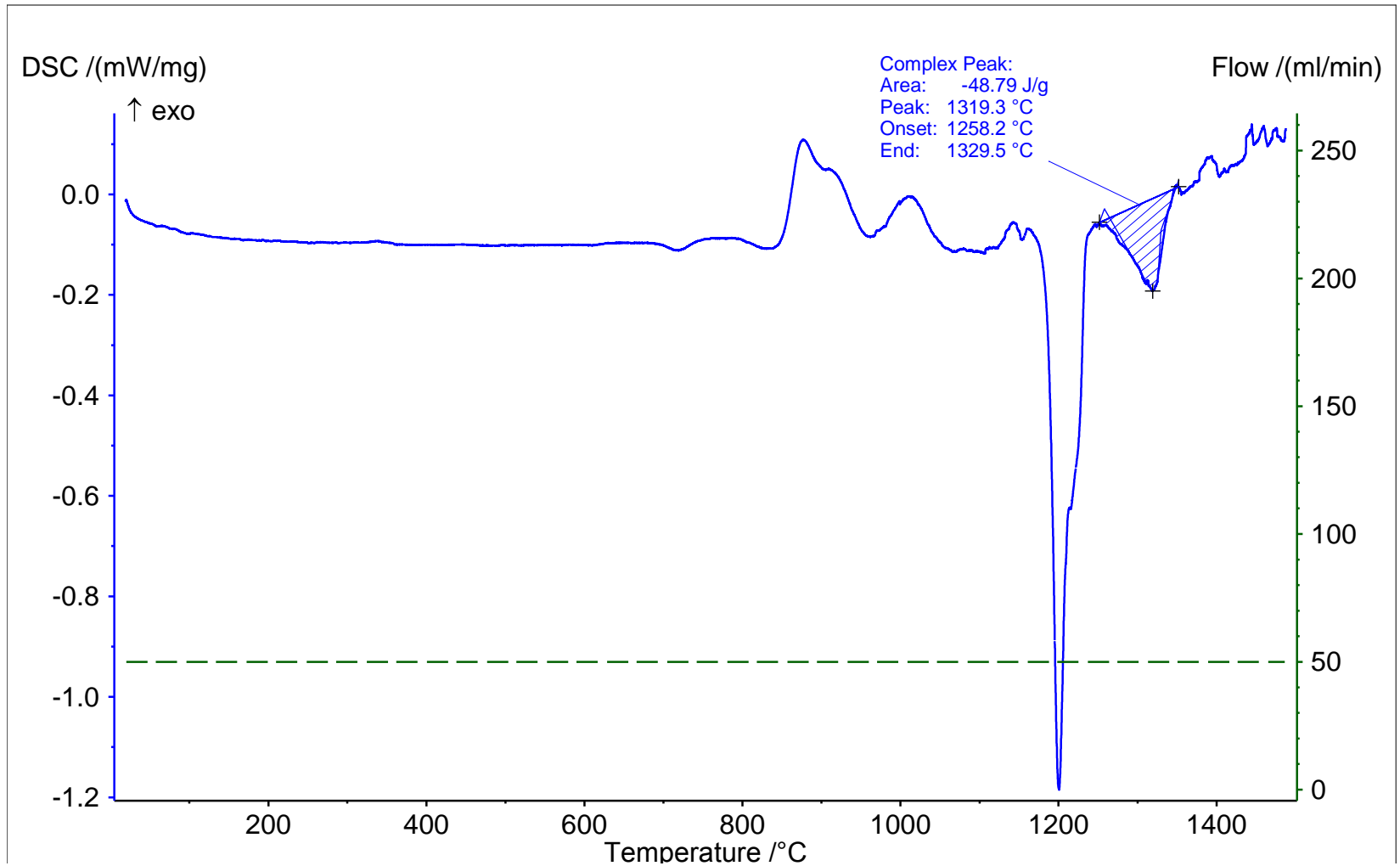
XRD pattern of the lower section of the hollow tube samples half filled with NASA CMAS and heated treated at 1310 °C at 10 °C/min and held for 5 h.

Results: XRD (upper cut section)



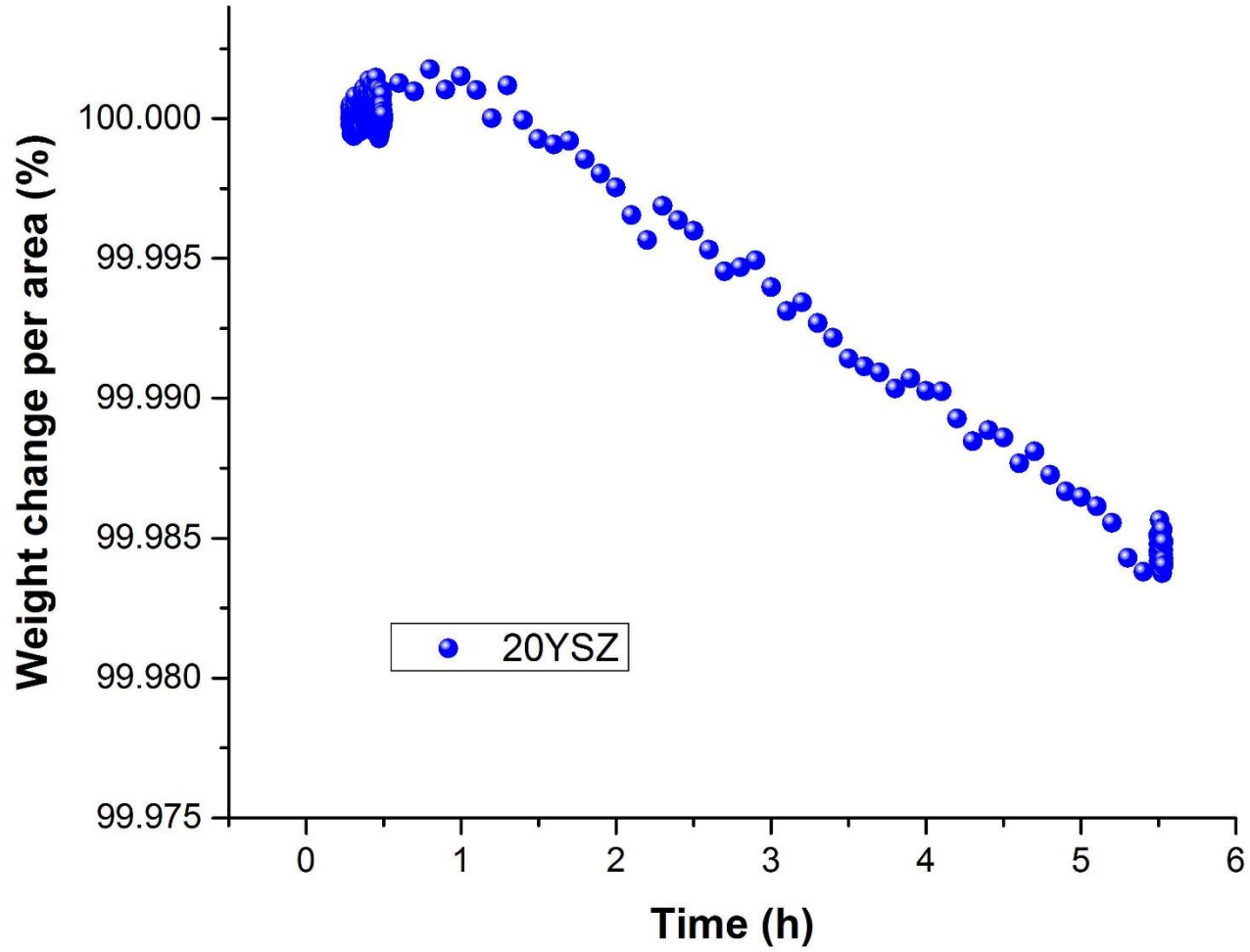
XRD pattern of the upper section of the hollow tube samples half filled with NASA CMAS and heated treated at 1310 °C at 10 °C/min and held for 5 h.

Results: DSC



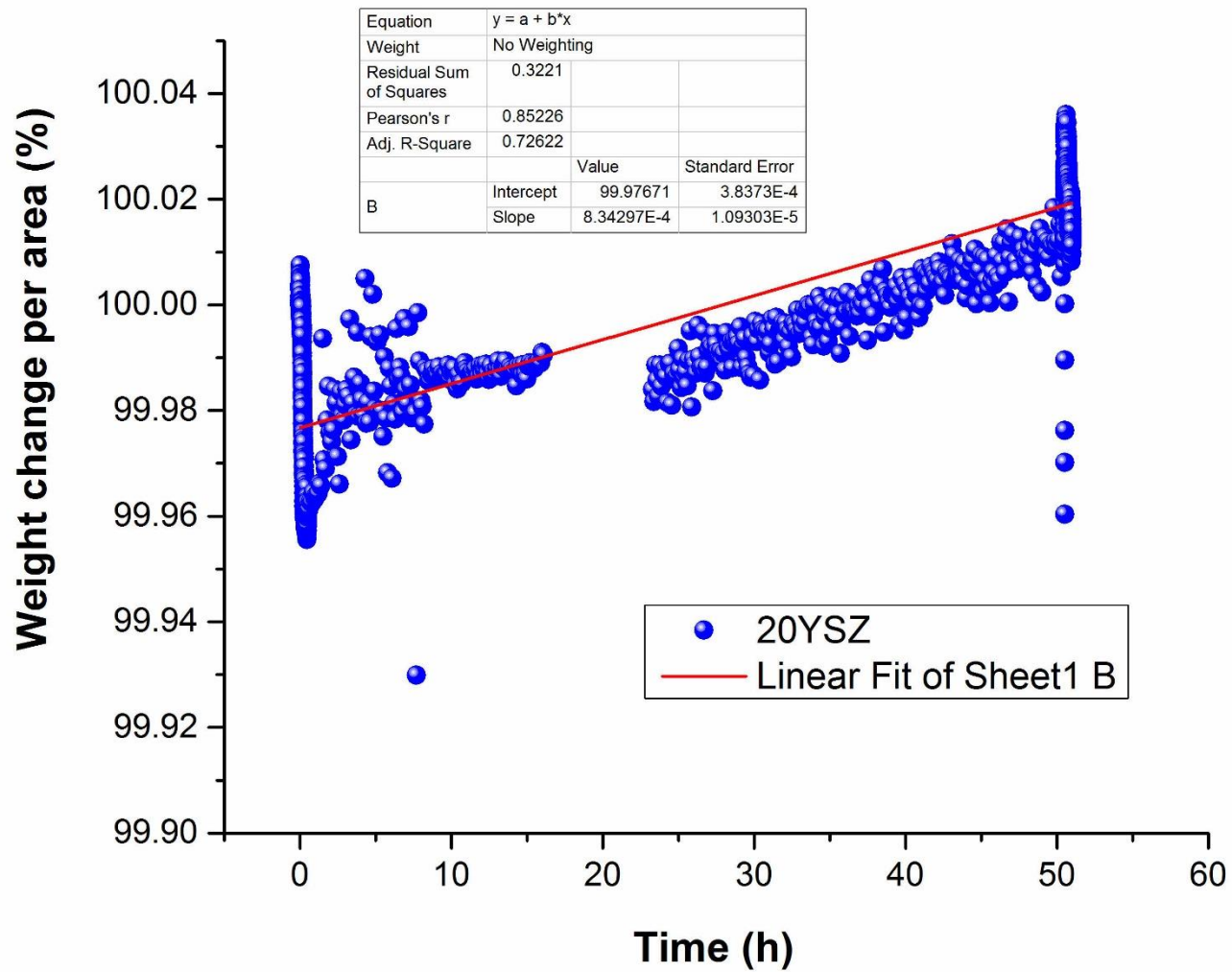
DSC traces during heating and cooling up to 1500 °C at 10 °C/min of the 30YSZ hollow tube ground and mixed with NASA CMAS (1:10 wt. %).

Results: TGA



Thermogravimetric traces of the 20YSZ hollow tube half filled with NASA CMAS at 1300 °C under 100 mL cm⁻³ air flow.

Results: TGA



Thermogravimetric traces of the 20YSZ hollow tube half filled with NASA CMAS at 1300 °C in 50 % H₂O under 100 mL cm⁻³ of air flow. This sample was heat treated before in the TGA balance at 1300 °C under 100 mL cm⁻³ air flow for 5h.

Summary

- Thermochemical reactions between CMAS and EBC and TBC materials were studied at 1310 °C for 5h.
- CMAS penetrated the samples at the grain boundaries and dissolved the EBC/TBC material to form silicate glassy and orthosilicate crystalline phases containing the rare-earth elements.
- 30YSZ and $\text{ZrO}_2\text{-15Y}_2\text{O}_3\text{-5.63Gd}_2\text{O}_3\text{-5.65Yb}_2\text{O}_3$ samples lower reactivity to CMAS than 20YSZ and $\text{ZrO}_2\text{-13.1Y}_2\text{O}_3\text{-10.5Gd}_2\text{O}_3\text{-11.4Yb}_2\text{O}_3$.

Acknowledgements

This work was supported by NASA Transformational Tools and Technologies Project, and also partially supported by the NASA-Army Research Laboratory Collaborative High Temperature Functionally Graded Sandphobic Coating and Surface Modification Research Project under NASA-Army Space Act Agreement SAA3-1460-1.