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Genki Sano

Institute of Science Tokyo

Kazuki Tsukamoto

Institute of Science Tokyo

Takashi Watanabe

Institute of Science Tokyo

Rie Endo

Shibaura Institute of Technology

Masahiro Susa

Institute of Science Tokyo

Miyuki Hayashi

hayashi.m.28eb@m.isct.ac.jp

Institute of Science Tokyo

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Wetting, spreading and interfacial reactions of CaO-MgO-Al₂O₃-SiO₂ melts on yttria-stabilized zirconia

Genki Sano¹, Kazuki Tsukamoto¹, Takashi Watanabe¹, Rie Endo², Masahiro Susa¹ and Miyuki Hayashi^{1*}

¹ Department of Materials Science and Engineering, Institute of Science Tokyo,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

² College of Engineering, Shibaura Institute of Technology
3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan

*Corresponding author: Miyuki Hayashi hayashi.m.28eb@m.isct.ac.jp

ORCID

Miyuki Hayashi: 0000-0001-5449-2651

Takashi Watanabe: 0009-0008-7479-6263

Rie Endo: 0000-0002-4844-4159

Abstract

Yttria-stabilized zirconia (YSZ) is often used as a thermal barrier coating (TBC) material for gas turbines. When calcium-magnesium-aluminum-silicate (CMAS) deposits derived from sand, dust and volcanic ash accumulates on the TBC during operation, the molten CMAS wets and spreads, and reacts with the TBC leading to the formation of Y-depleted ZrO_2 , as a result, compromising the thermal protection of the TBC. In this study, the contact angles of CMAS melts on YSZ and Al_2O_3 substrates were measured using the sessile drop method to observe the effects of interfacial reactions on the wetting and spreading behaviors of CMAS melts. To elucidate the thermodynamics of the formation of Y-depleted ZrO_2 in CMAS melts, the saturation solubility of ZrO_2 in four different CMAS melts was measured. Sessile drop measurements and electron probe microanalyzer observations revealed that the contact angles of CMAS melts on the YSZ substrates continuously decreased owing to the progress of interfacial reaction, leading to the formation of Y-depleted ZrO_2 . On the other hand, the contact angles of CMAS melts on the Al_2O_3 substrates remained constant because anorthite covered the entire interface and the local equilibrium at the interface was reached. The ZrO_2 solubility measurements revealed that the reprecipitation of Y-depleted ZrO_2 is attributed to the reduction in the saturation solubility of ZrO_2 in the CMAS melts near the interface, resulting from a decrease in the CaO and MgO concentrations and an increase in the Y_2O_3 concentration in the CMAS melt owing to the CMAS/YSZ interfacial reaction.

Keywords

calcium-magnesium-aluminum-silicate, yttria-stabilized zirconia, thermal barrier coating, contact angle, ZrO_2 solubility

1. Introduction

Thermal barrier coatings (TBCs) are extensively applied to hot components in gas turbines. [1-3] The TBCs can protect and insulate hot section components so that operating temperatures of gas turbines can be increased leading to the better performance and higher thermal efficiency. The thermal protection system including TBC has multilayer structures composed of a metallic bond coat (BC) in contact with nickel-based superalloy substrate, a ceramic top coat for thermal insulation, i.e., TBC and a thermally grown oxide (TGO), predominantly alumina, that forms between TBC and BC. [3] Yttria-stabilized zirconia (YSZ) is often used as a TBC material owing to its low thermal conductivity with minimal temperature dependence [3-5] and relatively high thermal expansion coefficient closely matching that of underlying nickel-based superalloy substrate. [6,7] YSZ coatings are commonly deposited onto substrates via electron-beam physical vapor deposition (EB-PVD) or air plasma spraying (APS). [8]

However, due to the increasing demand for higher operation temperatures in gas turbines, the following problem is caused by the accumulation of calcium-magnesium-aluminum-silicate (CMAS) deposits derived from sand, dust and volcanic ash on the TBC: CMAS has a relatively low melting temperature (ca. 1260°C or even lower), and melts when it adheres to the TBC during operation. The molten CMAS wets the outer layer, infiltrates the inner porous layer, and reacts with the TBC, causing a loss of porosity and an increase in elastic modulus. The resulting reduction in strain tolerance promotes spallation, compromising the thermal protection provided by the TBC. [9] The wetting properties of CMAS melts on the TBC such as contact angle are directly related to the processes of impact, adhesion, and spreading of CMAS deposits. [10,11] When an interfacial reaction occurs between the TBC and CMAS melts, the interfacial tension decreases, facilitating the spreading of CMAS melts on the TBC. [12] Thus, the wetting and spreading behavior of CMAS melts and the interfacial reaction between the TBC and CMAS melts are important factors in evaluating the CMAS

corrosion resistance of TBCs. [11]

Song et al. used the sessile drop method to observe the wetting and spreading behavior of a CMAS melt on an alumina substrate under non-isothermal conditions. [13] Zhang et al. also employed the sessile drop method to conduct the in-situ observation of the wetting and spreading behaviors of CMAS melts on YSZ coatings deposited by plasma spray physical vapor deposition (PS-PVD) and EB-PVD at different temperatures. [8] The contact angles of CMAS melts on single-crystal YSZ surfaces with different Miller indices were compared using first-principles calculations [14] and the sessile drop method. [15] Yin et al. measured the contact angle of a CMAS melt on polycrystalline YSZ with different surface roughness values using the sessile drop method and reported that the contact angle increased with surface roughness. [16] However, to the best of our knowledge, there are few reports investigating the contact angle of CMAS melts on YSZ substrate from the perspective of CMAS/YSZ interfacial reactions. [17]

Regarding the interfacial reactions between YSZ coatings and CMAS melts, reprecipitation of Y-depleted ZrO_2 has been reported following the dissolution of YSZ into the CMAS melt, resulting in the delamination of the coating from the underlying substrate. [18] In some studies, the single-crystal YSZ has been used to observe the change in microstructure during the interfacial reaction: [19,20] The reprecipitated Y-depleted ZrO_2 forms a cell structure at the interface, followed by the development of fine spherical particles between the cell structure and CMAS melt. However, owing to the lack of a thermodynamic database, the mechanism underlying the reprecipitation of Y-depleted ZrO_2 remains unclear.

Introducing Al_2O_3 to YSZ coating can promote the formation of an anorthite layer, thereby suppressing the interfacial reaction between YSZ and CMAS, [21] and reducing the wettability of the coating. [22]

Therefore, comparing the contact angles of CMAS melts on YSZ and Al_2O_3 substrates may provide insights into the effect of interfacial reactions on contact angles. The objectives of this study were to: (i) compare the time-dependent contact angles of CMAS melts on YSZ and Al_2O_3 substrates using the sessile drop method, and (ii) clarify the correlation between the saturation solubility of ZrO_2 and the interfacial reaction-induced compositional changes in CMAS melts, thereby providing a thermodynamic explanation for the precipitation of Y-depleted ZrO_2 from the CMAS melt.

2. Experimental

2.1. CMAS sample preparation

Reagent-grade SiO_2 , Al_2O_3 , MgO and CaCO_3 were used as starting materials, and CaCO_3 was heated at 1373 K for 12 h in air to generate CaO . **Table 1** lists the chemical compositions of the CMAS samples. The composition of CMAS1 was adopted from a previous study. [8] CMAS2 and CMAS3 were prepared by substituting CaO and MgO with Al_2O_3 and SiO_2 , while keeping the CaO/MgO and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios constant. In CMAS4, CaO , MgO , Al_2O_3 , and SiO_2 were substituted with Y_2O_3 while maintaining a constant $\text{CaO/MgO/Al}_2\text{O}_3/\text{SiO}_2$ ratio. These reagents were weighed according to the compositions listed in Table 1 and mixed using an alumina mortar and pestle for 30 min. Approximately 20 g of the resulting mixture was placed in a platinum crucible and melted at 1723 K for 1 h in air.

Table 1 Chemical compositions of the CMAS samples (mol%).

	CaO	MgO	Al_2O_3	SiO_2	Y_2O_3	CaO/MgO	$\text{SiO}_2/\text{Al}_2\text{O}_3$
CMAS1	31.0	11.2	5.8	52.0	-	2.77	8.96
CMAS2	25.9	9.3	6.5	58.3	-	2.77	8.96
CMAS3	20.8	7.5	7.2	64.5	-	2.77	8.96
CMAS4	31.0	11.2	5.42	48.58	3.8	2.77	8.96

2.2 Sessile drop method

Approximately 18 – 23 mg of CMAS1 melt was attached to the tips of an R-type thermocouple. The thin Pt and Pt-13mass%Rh wires (0.15 mm in diameter and ca. 7 mm in length) of the thermocouple were extended using thicker Pt and Pt-13mass%Rh wires (0.5 mm in diameter and ca. 500 mm in length), respectively. The thermocouple except for the thin wires was inserted into a mullite tube with an inner diameter of 4 mm and outer diameter of 6 mm. The thermocouple with the attached CMAS1 sample was used for the sessile drop measurement on polycrystalline and single-crystal YSZ substrates and polycrystalline Al_2O_3 substrates. The details of these substrates are (i) single-crystal ZrO_2 - 23 mol% $\text{YO}_{1.5}$ (ZrO_2 - 21.5 mass% $\text{YO}_{1.5}$) with (100) orientation and a dimension of $10 \times 10 \times 0.5$ mm, (ii) polycrystalline ZrO_2 - 18.8 mol% $\text{YO}_{1.5}$ (ZrO_2 - 17.5 mass% $\text{YO}_{1.5}$) with a dimension of $10 \times 10 \times 1.5$ mm, and (iii) polycrystalline Al_2O_3 with a dimension of $10 \times 10 \times 1.5$ mm. **Fig. 1** shows a schematic of the sessile drop apparatus with the enlarged views of the area near the CMAS1 sample from the directions perpendicular and parallel to the longitudinal axis of the furnace tube. The substrate was placed horizontally in the uniform-temperature zone of an electric furnace. After the furnace temperature reached 1573 K, the thermocouple with the attached CMAS1 was inserted into the furnace. After the sample had reached 1573 K, the CMAS1 melt was dropped onto the substrate. The contact angles were measured by recording images of the CMAS1 droplet using a He-Ne laser as the light source.

As shown in Fig. 1, a He-Ne laser was used as the light source. The laser beam was magnified 10 times using a beam expander and irradiated onto the samples. A CMOS camera was placed on the opposite side of the furnace, and the laser beam irradiating the sample was transmitted through a bandpass filter with a wavelength of 632 nm to clearly capture the outline of the droplet. In this study, the droplet masses ranged from 18.6 mg to 23 mg, well below the 100 mg threshold for which gravitational deformation can be considered negligible. [23,24] Therefore, the $\theta/2$ method was applied

[25] to calculate the contact angle θ from the digital images captured from the recordings using Eq.

(1).

$$\frac{\theta}{2} = \tan^{-1} \left(\frac{h}{r} \right) \quad (1)$$

where h is the height, and r is the radius of the contact circle, as shown in Fig. 2.

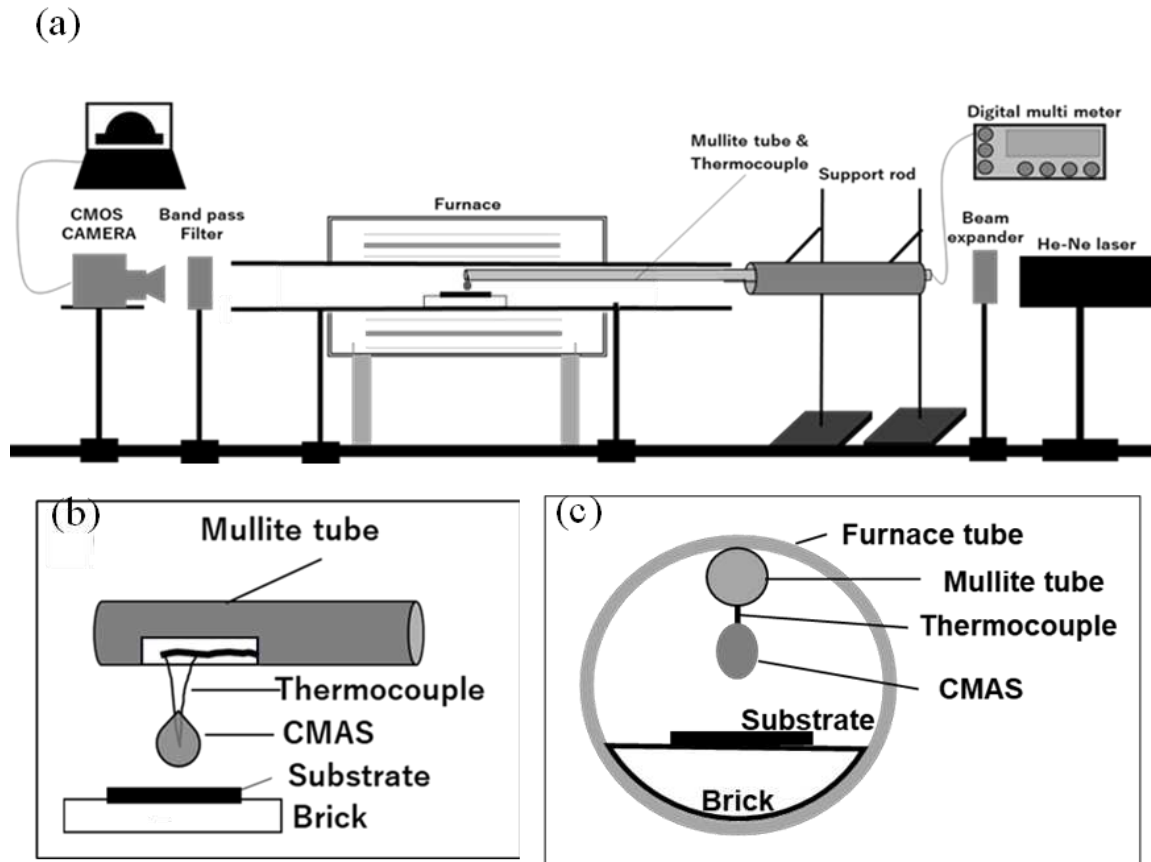


Fig. 1 Schematic diagram of the sessile drop apparatus, enlarged views of the area near the CMAS1 sample from the directions perpendicular and parallel to the longitudinal axis of the furnace tube

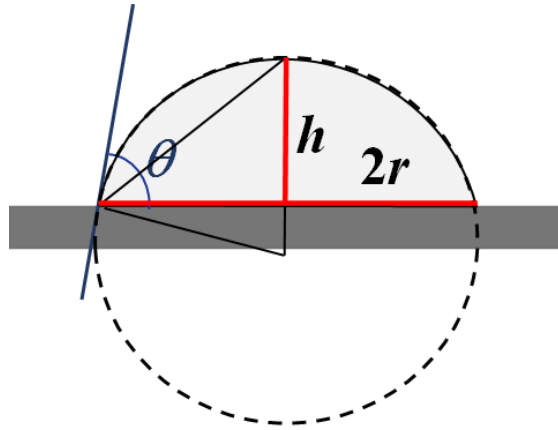


Fig. 2 Geometry of a sessile drop approximated by a spherical cap defined by the base radius r and height h above the basal plane

2.3 Interfacial reaction observation

One hour after the onset of the measurements, the substrate with a CMAS1 coating was removed from the furnace and air-cooled. The cross-sectional microstructures were observed using an electron probe microanalyzer (EPMA). For the Al_2O_3 substrate with CMAS1, backscattered electron (BE) and elemental mapping images were obtained using EPMA, and the crystalline phases formed at the interface were identified using micro-area X-ray diffraction.

The microstructural evolution during the early stage of the interfacial reaction and the compositional change in the vicinity of the interface between CMAS1 and single-crystal YSZ substrate were examined. Briefly, approximately 20 mg of CMAS1 glassy powder was uniformly spread on the surface of a single-crystal YSZ substrate at a coating density of 0.2 mg/mm^2 . The CMAS1-coated YSZ was heated at 1573 K in air for 10 min or 1 h. For the sample heated for 10 min, the cross-sectional area in the vicinity of the interface between CMAS1 and YSZ was observed using field-emission scanning electron microscope (FE-SEM). For the sample heated for 1 h, BE images and line profiles

of the constituent elements were obtained using EPMA.

2.4 Saturation solubility measurement of ZrO₂ in CMAS

Reagent-grade ZrO₂ powders (2 g) were uniaxially compacted at 40 MPa for 1 min to form a tablet with a diameter of 20 mm, which was then heated at 1400°C for 24 h in air. Four different CMAS glass powders were uniformly spread on the surface of the ZrO₂ tablets at a coating density of 0.95 mg/mm². The CMAS coated sample was heated at 1573 K in air for specific durations and air-cooled: CMAS1 for 12, 24 and 48 h, CMAS2 for 120 h, CMAS3 for 24, 48, 96 and 120 h, and CMAS4 for 72 h. The chemical composition of CMAS along the direction perpendicular to the CMAS/ZrO₂ interface was determined using quantitative EPMA by varying the vertical distance from the interface.

3. Results and Discussion

3.1 Wetting and spreading behavior of CMAS melts on YSZ substrate

Fig. 3 shows the typical wetting and spreading behavior of a CMAS droplet on a single-crystal YSZ substrate. **Fig. 4** shows the time-dependent contact angles of the CMAS melts on the polycrystalline YSZ, single-crystal YSZ and polycrystalline Al₂O₃ substrates. The contact angles of CMAS melts on polycrystalline and single-crystal YSZ substrates are approximately 5° and 20°, respectively, in 1200 s after the onset of the measurement, and continued to decrease even after 1200 s. In contrast, the contact angles of CMAS melts on Al₂O₃ substrates are 12° after 1200 s and remain stable thereafter. As reported by Krainer and Hirn, droplets can fill the cavities arising from surface roughness and infiltrate the porous substrate, thereby reducing the contact angle. [26] In this study, the CMAS melt exhibited a smaller contact angle on polycrystalline YSZ than on single-crystal YSZ because the droplet could penetrate the grain boundaries of the polycrystalline YSZ.

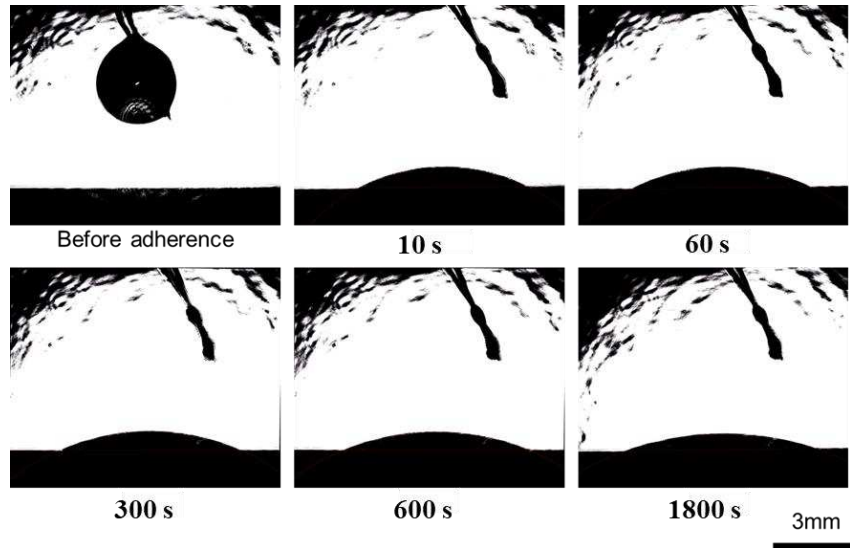


Fig. 3 Typical images showing the wetting and spreading behavior of a CMAS drop on a single-crystal YSZ substrate

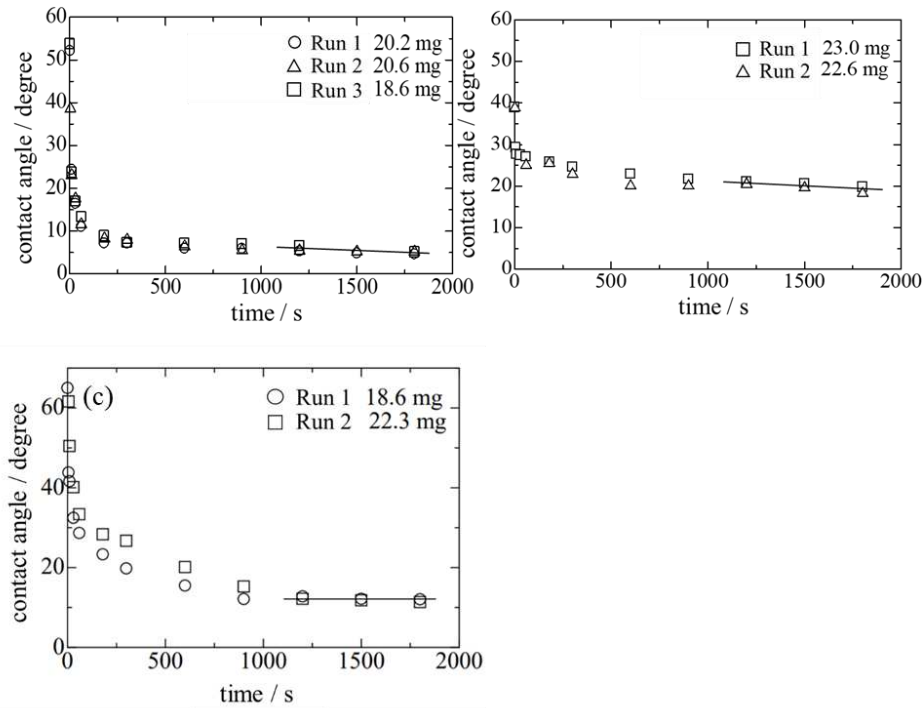


Fig. 4 Time-dependent contact angles of CMAS1 melts on (a) polycrystalline YSZ, (b) single-crystal YSZ, and (c) polycrystalline Al₂O₃ substrates

Fig. 5 shows the BE images of the cross-sectional areas in the vicinity of the interface between the

CMAS melts and the polycrystalline YSZ, single-crystal YSZ, and polycrystalline Al_2O_3 substrates after heating at 1573 K for 1800 s in the sessile drop apparatus. Spherical particles and mushy structures [19] were observed for the polycrystalline YSZ substrate, whereas spherical particles and cellular structures were observed for the single-crystal YSZ substrate. Interestingly, spherical particles were only present at the center of the droplet and not near the three-phase interface between the droplet, substrate, and gas phases. The decreases in contact angle and progressive spreading of the droplet over time imply that the contact time between the CMAS melt and the substrate is longer at the center of the droplet and shorter near the three-phase interface. Consequently, the cell structure (or mushy structure) formed first, followed by the spherical particles.

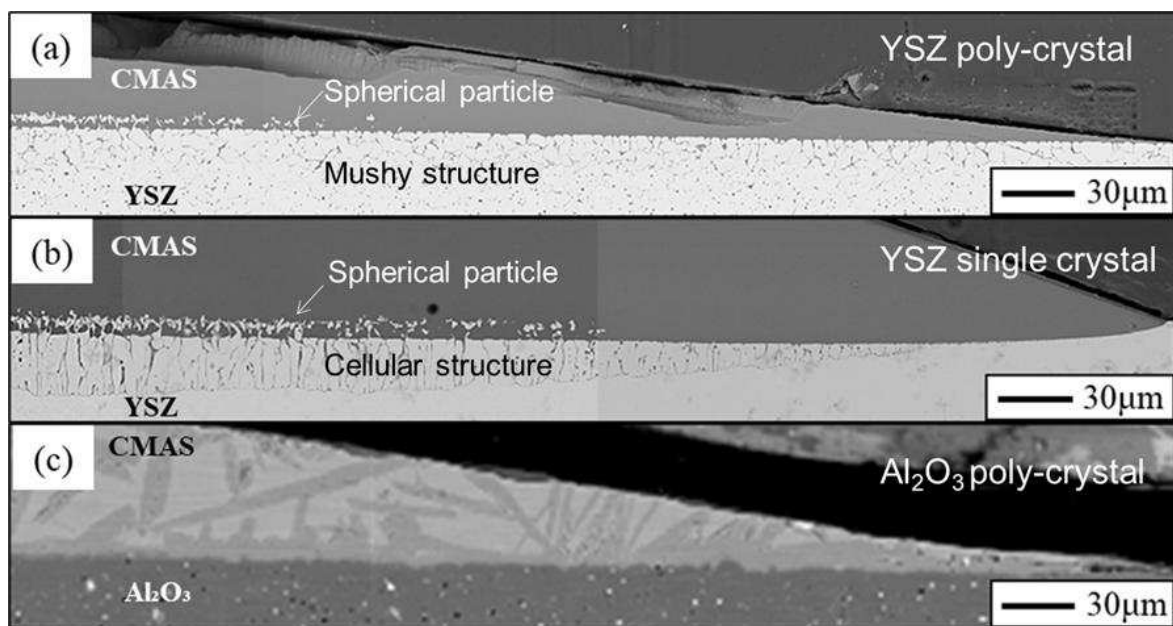


Fig. 5 Backscattered electron (BE) images of the interface between CMAS1 melts and (a) polycrystalline YSZ, (b) single-crystal YSZ, and (c) polycrystalline Al_2O_3 substrates after heating at 1573 K for 1800 s in the sessile drop apparatus

Fig. 6 shows the FE-SEM image of the cross-sectional area near the interface between CMAS and YSZ for the sample heated for 10 min, which reveals several particles near the concave interface of the YSZ substrate. According to the previous studies, these particles may be Y-depleted ZrO_2 reprecipitated from the CMAS melt, and may develop into a cell structure over time. [19]

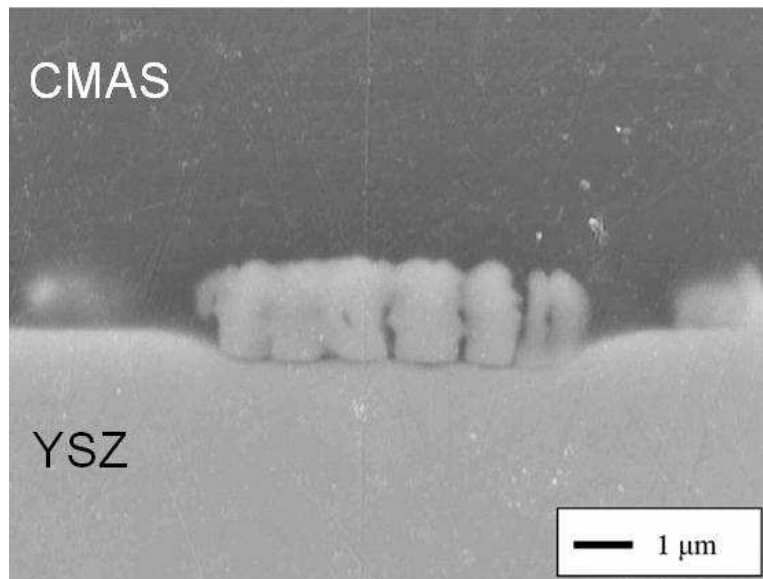


Fig. 6 FE-SEM image of the cross-sectional areas in the vicinity of the interface between CMAS1 and YSZ for the sample heated for 10 min

Fig. 7 shows a BE image of the cross-section and the line profiles of Zr, Y, Al, Si, Mg and Ca for the sample heated for 1 h. The line profiles revealed that the Zr, Mg and Ca concentrations in the cell structure were higher than those in the single-crystal YSZ, whereas the Y concentration was lower. These results indicated that the cell structure was composed of Y-depleted ZrO_2 with MgO and CaO. Aksay et al. have reported that when a reaction occurs between solid and liquid, the interfacial tension decreases, causing the liquid droplet to spread over the solid substrate. [12] Thus, the continuous decrease in the contact angles of the CMAS melts on the polycrystalline YSZ and single-crystal YSZ substrates shown in Figs. 4(a) and 4(b) is due to the interfacial reaction between CMAS and YSZ.

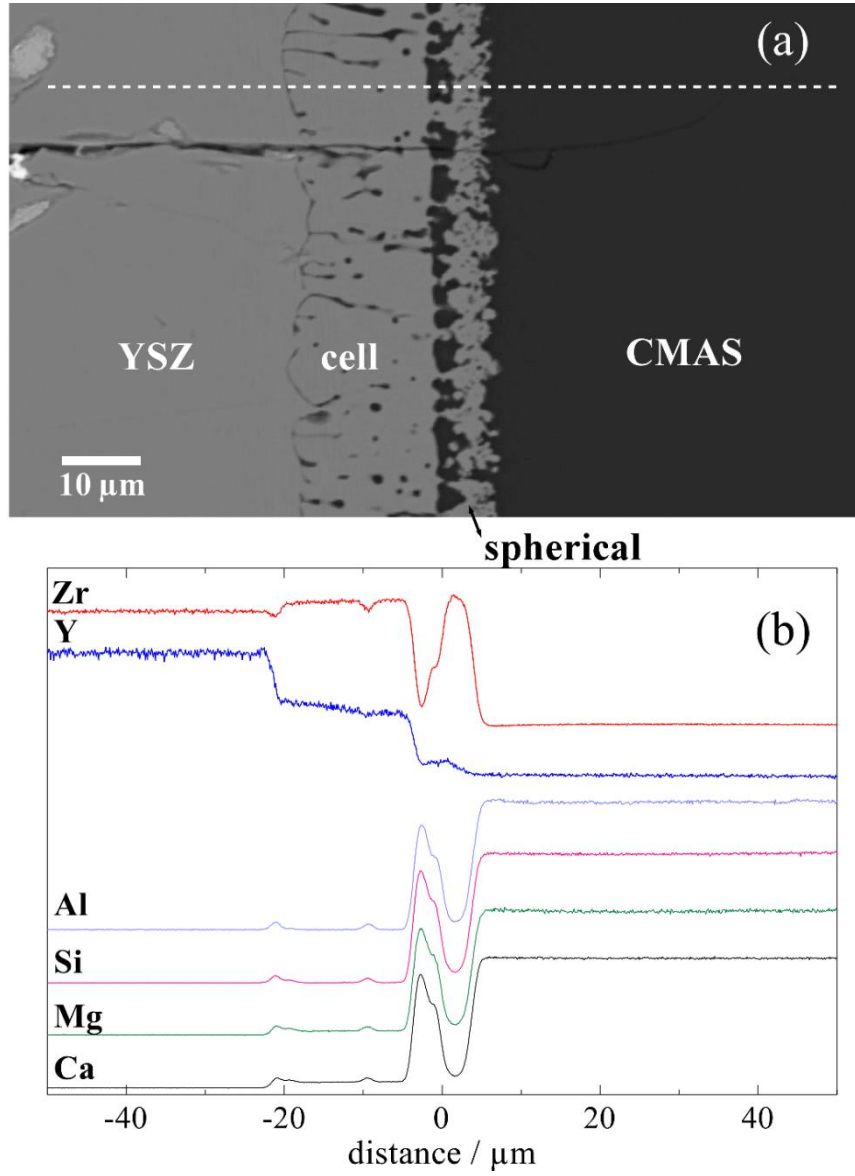


Fig. 7 (a) BE image of the cross-section and (b) line profiles of Zr, Y, Al, Si, Mg and Ca for the CMAS1-coated single-crystal YSZ after heating for 1 h

For the polycrystalline Al_2O_3 substrate, Fig. 5(c) shows that the crystalline layer covers the entire interface, and acicular crystals are produced in the CMAS melt. This observation is confirmed by **Fig. 8** (BE image and elemental mapping images in the vicinity of the interface between CMAS1 and the Al_2O_3 substrate after the sessile drop measurement) and **Fig. 9** (BE image with the position of the

micro-area X-ray diffraction analysis and the XRD profile). The acicular crystals precipitated from the CMAS melt were identified as anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), while spinel (MgAl_2O_4) particles were observed within the anorthite layer at the interface.

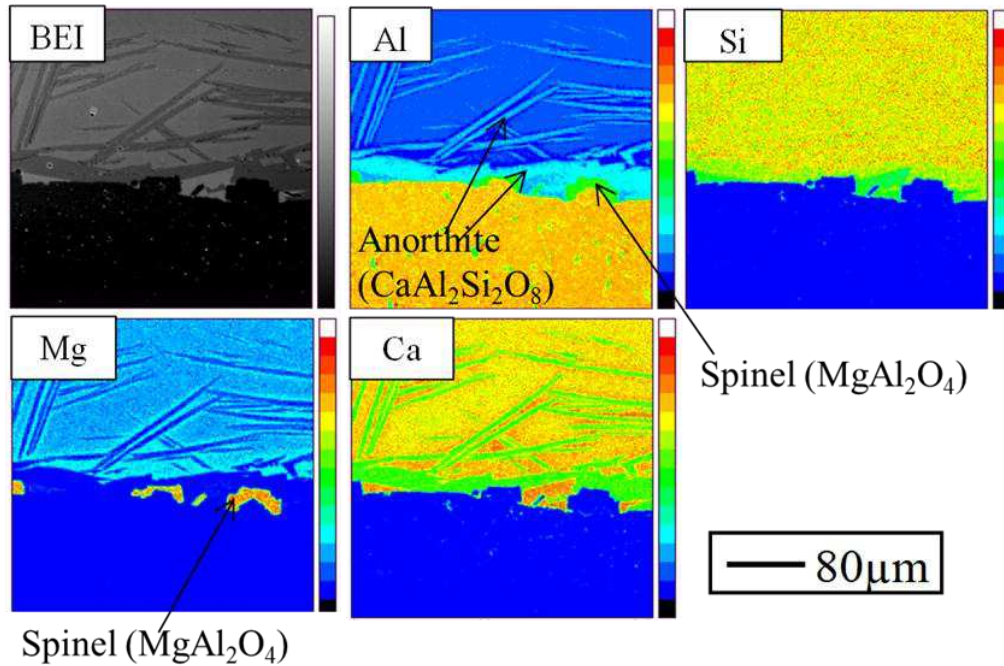


Fig. 8 BE image and elemental mapping images in the vicinity of the interface between CMAS1 and the Al_2O_3 substrate after sessile drop measurement

The chemical composition of CMAS1 falls in the primary phase region of pseudo-wollastonite (CaSiO_3) without considering the Mg content. When Al_2O_3 was dissolved in the CMAS1 melt from the substrate, the composition of the melt shifted to the primary phase region of anorthite. Thus, anorthite precipitates at the interface between CMAS1 and the Al_2O_3 substrate. The localized enrichment of Mg promoted the formation of spinel. [27] Spreading was not observed after 1200 s (Fig. 4) because the local equilibrium was reached at the interface and the interfacial reaction between CMAS and Al_2O_3 was suppressed by the formation of anorthite. The difference in the spreading behavior of CMAS melts on YSZ and Al_2O_3 substrates supports the conclusion that the spreading of CMAS melts on YSZ

substrates is driven by interfacial reactions.

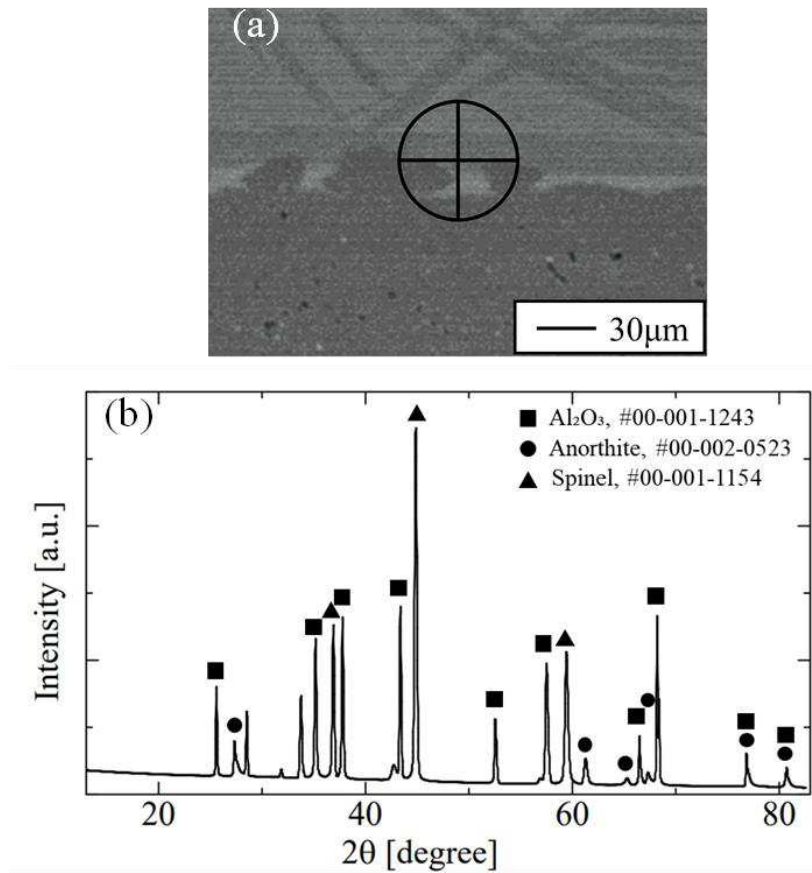


Fig. 9 (a) BE image with the position of the micro-area X-ray diffraction analysis and (b) XRD profile

3.2 Thermodynamical interpretation for reprecipitation of Y-depleted ZrO₂ from the CMAS melt

As shown in Fig. 5(b), spherical particles were only observed at the center of the droplet but not near the three-phase interface between the droplet, substrate, and gas phases. This difference can be attributed to the longer contact time between the droplet and the substrate at the center of the droplet compared with that near the three-phase interface. **Fig. 10** illustrates the formation process of the cell structure and spherical particles along with the BE images of the cross-sections at the different positions of the sample in Fig. 5(b) and at the center of the same sample.

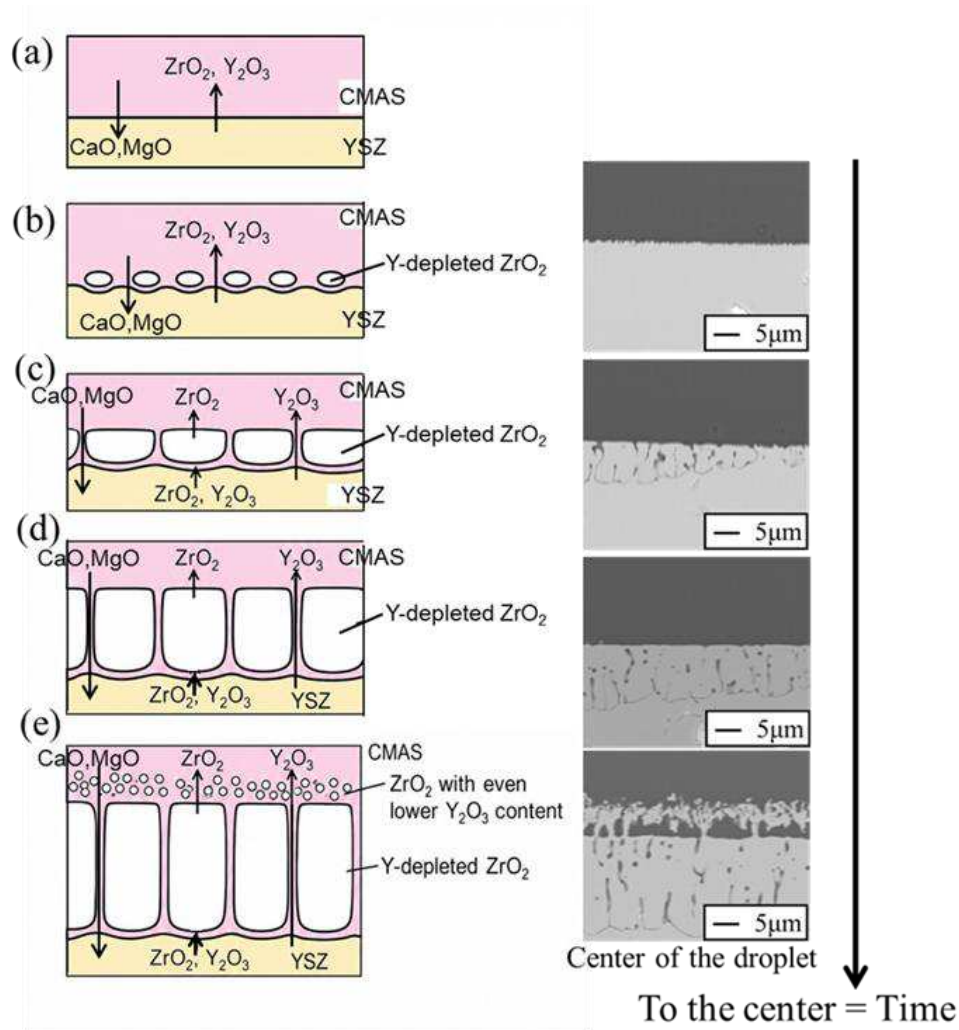


Fig. 10 (a-e) Illustration of the formation process of the cell structure and spherical particles and corresponding BE images of the cross-sections at the different positions of the sample in Fig. 5(b) and at the center of the same sample: (a) CaO and MgO diffuse into YSZ, and ZrO₂ and Y₂O₃ diffuse into CMAS; (b) Y-depleted ZrO₂ particles are formed; (c-d) Y-depleted ZrO₂ particles agglomerate, and grow to form a cell structure, while ZrO₂ of the cell structure dissolves into the CMAS melt, and (e) supersaturated ZrO₂ in the CMAS melt may precipitate as spherical particles

As shown in Fig. 10(a), CaO and MgO diffuse into YSZ, and ZrO₂ and Y₂O₃ diffuse into CMAS [19].

Assuming that the decrease in the CaO and MgO concentrations and/or the increase in the Y₂O₃

concentration in the CMAS melt can reduce the ZrO_2 saturation solubility of the CMAS melt, leading to the formation of Y-depleted ZrO_2 particles. [18,19] (Fig. 10(b)). Once the Y-depleted ZrO_2 particles agglomerate, they grow toward the CMAS/YSZ interface (downward in the figure), as CaO and MgO continue to diffuse from CMAS to YSZ, while ZrO_2 and Y_2O_3 diffuse from YSZ to CMAS, thereby forming a cell structure (Figs. 10(c) and 10(d)). As the cell structure grows, the ZrO_2 in the cell structure dissolves in the CMAS melt (Figs. 10(c) and 10(d)); subsequently, supersaturated ZrO_2 in the CMAS melt precipitates as spherical particles (Fig. 10(e)). To validate the aforementioned assumption, it is necessary to determine how the saturation solubility of ZrO_2 in CMAS containing ZrO_2 and Y_2O_3 changes with decreasing CaO and MgO concentrations (CMAS 1, 2, and 3), and increasing Y_2O_3 concentration (CMAS 1 and 4). **Fig. 11** shows the ZrO_2 concentration as a function of the vertical distance from the CMAS/ ZrO_2 interface for CMAS1, 2, and 4 (a) and CMAS3 (b). The CaO/MgO/ Al_2O_3 / SiO_2 ratio in all samples is nearly identical to the nominal compositions of the starting materials, regardless of the heating time and the distance. For CMAS1, the ZrO_2 concentration was independent of the heating time and distance from the interface, with an average value of 3.74 mol%. For CMAS2 and CMAS4, the ZrO_2 concentrations were also independent of distance, with average values of 2.94 mol% and 3.41 mol%, respectively. In contrast, for CMAS3, the ZrO_2 concentration decreased with increasing distance from the interface after 24 and 48 h of heating, because the high viscosity of CMAS3 could restrict diffusion- and convection-induced mass transfer at heating times shorter than 48 h. When the heating time was extended to 96 h and 120 h, the ZrO_2 concentration became independent of distance, with an average value of 1.97 mol%. Consequently, the saturation solubilities of ZrO_2 are 3.74, 2.94, 1.97 and 3.41 mol% for CMAS1, CMAS2, CMAS3 and CMAS4, respectively.

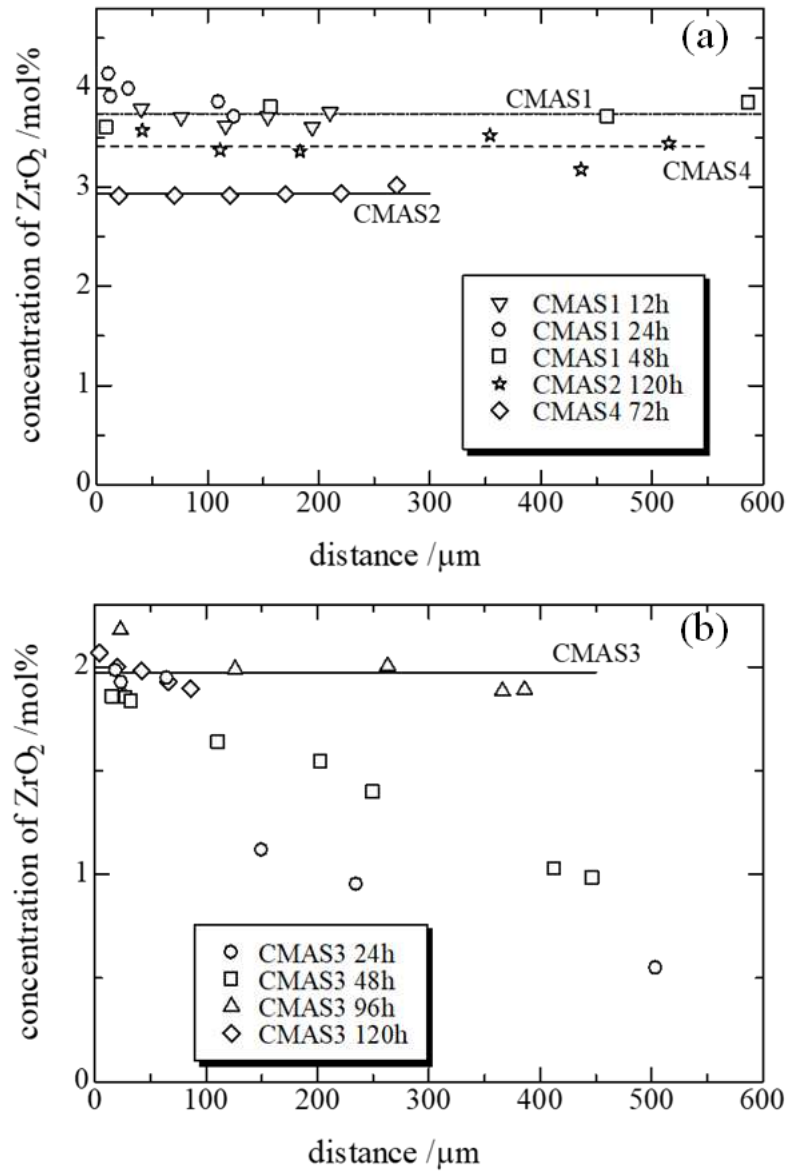


Fig. 11 ZrO_2 concentrations (mol%) as a function of the vertical distance from the interface between CMAS and ZrO_2 for (a) CMAS1, 2 and 4, and (b) CMAS3

Comparing the saturation solubilities of ZrO_2 in CMAS1, CMAS2, and CMAS3, a decrease in the CaO and MgO concentrations reduces the ZrO_2 solubility in the CMAS melt. In contrast, the difference in the ZrO_2 saturation solubilities of CMAS1 and CMAS4 indicates that an increase in the Y_2O_3 concentration also reduces the ZrO_2 solubility in the CMAS melt. The effect of CaO concentration on

the ZrO₂ solubility obtained in this study is consistent with that reported by Chang et al. [28] Consequently, the reprecipitation of Y-depleted ZrO₂ is attributed to the reduction in the saturation solubility of ZrO₂ in the CMAS melt near the interface. This reduction results from the interfacial reaction between CMAS and YSZ, which decreases the CaO and MgO concentrations and increases the Y₂O₃ concentration in CMAS melts.

The effects of CaO, MgO, and Y₂O₃ concentrations on the solubility of ZrO₂ in CMAS melts can be understood in terms of their roles in forming an aluminosilicates network structure. Specifically, CaO and MgO act as network modifiers: Ca²⁺ and Mg⁺ break the Si⁴⁺-O⁻ covalent bonds, resulting in the formation of ionic Ca²⁺-2O⁻ and Mg⁺-O⁻ bonds, respectively. In addition, some CaO and MgO work as charge compensators for Al₂O₃, i.e., Ca²⁺ and Mg⁺ located near Al³⁺ provide an electrical charge balance for Al³⁺, and as a result, Al₂O₃ can act as a network former. [29] In this study, Y₂O₃ was considered to be a network former with its charge-compensated by Ca²⁺ and Mg⁺ in the same manner as Al₂O₃ although Beniaiche et al. have reported that Y₂O₃ is an amphoteric oxide, and act as both a network former and a modifier. [30] The degree of depolymerization of the silicate network can be quantified by the ratio of the number of nonbridging oxygen atoms to the number of tetrahedrally coordinated atoms (NBO/T). [31] For CMAS containing Y₂O₃, the NBO/T ratio was calculated using Eq. (2).

$$\text{NBO/T} = \frac{2(x_{\text{CaO}} + x_{\text{MgO}} - x_{\text{Al}_2\text{O}_3} - x_{\text{Y}_2\text{O}_3})}{x_{\text{SiO}_2} + 2(x_{\text{Al}_2\text{O}_3} + x_{\text{Y}_2\text{O}_3})} \quad (2)$$

where x denotes the molar fraction. **Fig. 12** shows the saturation concentrations of ZrO₂ as a function of the NBO/T ratio. The saturation concentrations of ZrO₂ in the CMAS melt increased with the NBO/T ratio, implying that ZrO₂ is more readily dissolved in silicate melts with a higher degree of depolymerization. The behavior also suggests that ZrO₂ acts as a network former in accordance with the results of previous studies. [32,33] Therefore, Y-depleted ZrO₂ may not recrystallize in highly

basic CMAS melts because of its high saturation concentration.

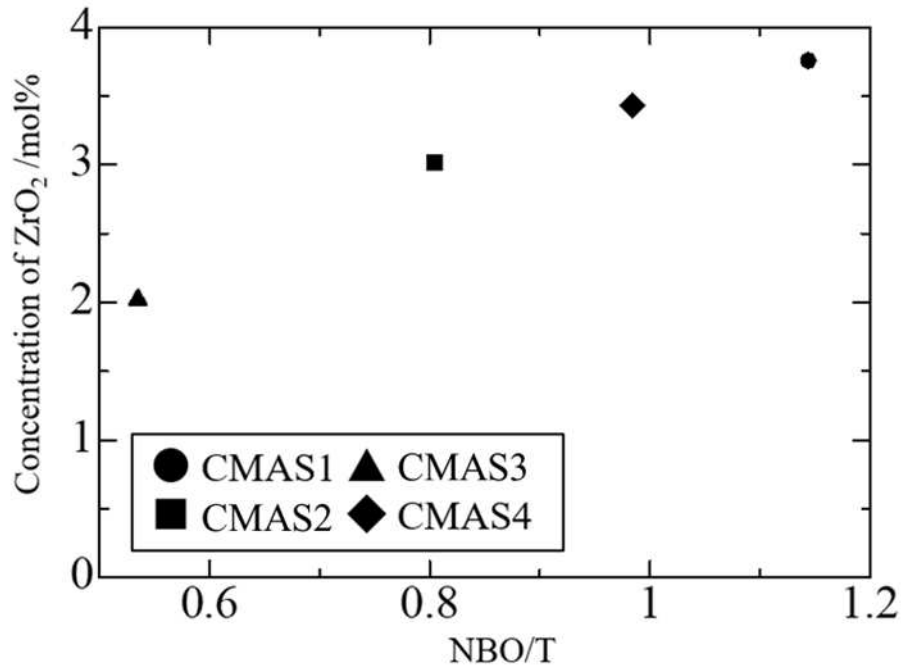


Fig. 12 Saturation concentrations of ZrO_2 as a function of NBO/T ratio.

4. Conclusions

- The sessile drop measurements and EPMA observations revealed that the contact angles of CMAS melts on polycrystalline and single-crystal YSZ substrates were approximately 5° and 20° , respectively, 1200 s after the onset of the measurement, and continuously decreased even after 1200 s owing to the progress of the reaction, leading to the formation of Y-depleted ZrO_2 . On the other hand, the contact angles of the CMAS melts on the Al_2O_3 substrates remained constant at 12° after 1200 s because of the formation of anorthite on the entire interface.
- The interfacial reactions between the CMAS melts and ZrO_2 tablets revealed that a decrease in the CaO and MgO concentrations reduces the ZrO_2 solubility in the CMAS melt, and that an increase in the Y_2O_3 concentration also reduces the ZrO_2 solubility in the CMAS melt. Thus, the reprecipitation of

Y-depleted ZrO_2 is attributed to the reduction in the saturation solubility of ZrO_2 in the CMAS melt near the interface, resulting from the interfacial reaction between CMAS and YSZ, which decreases the CaO and MgO concentrations and increases the Y_2O_3 concentration in CMAS melts.

Statements and Declarations

The authors declare no conflicts of interest regarding this manuscript.

All authors contributed to the conception and design of this study. Material preparation, data collection and analyses were performed by Genki Sano, Kazuki Tsukamoto, Takashi Watanabe and Rie Endo.

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