Corrosion behavior of volcanic ash and calcium magnesium aluminosilicate on Yb$_2$SiO$_5$ environmental barrier coatings

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High-temperature corrosion behavior of volcanic ash and artificial calcium-magnesium-aluminosilicate (CMAS) on sintered ytterbium monosilicate (Yb$_2$SiO$_3$), and the corrosion resistance of Yb$_2$SiO$_5$ as an environmental barrier coating, are investigated. Dense sintered Yb$_2$SiO$_5$ specimens were prepared using the spark plasma sintering method at 1400°C for 10 min. These specimens were subjected to a hot corrosive environment of molten Iceland volcanic ash and CMAS at 1400°C for 2, 12, and 48 h.

Different corrosion phenomena, i.e., continuous reaction with CMAS and weak reaction with the volcanic ash, were observed. From the results of in-situ high temperature X-ray diffraction measurement and scanning electron microscope-energy dispersive X-ray spectrometry studies, Yb$_2$SiO$_5$ exhibits excellent resistance to volcanic ash but lacks resistance to CMAS attack.

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1. Introduction

Developments in gas turbine engine technology have created a need for increased fuel efficiency and carbon emission reduction. This largely depends on the development of advanced materials, including high-temperature structural materials, and correlative protective ceramic coating materials. Although superalloys currently occupy the dominant position in high-temperature structural material use for gas turbines, there is a limit on their temperature capabilities. Non-oxide silicon-based ceramics, such as silicon nitride (Si$_3$N$_4$), silicon carbide (SiC), and SiC/ SiC composites are of interest as materials that could replace metallic materials under ultra-high temperature conditions. However, the disadvantages of using SiC/SiC composites in gas turbines are their vulnerability to corrosion and performance degradation in combustion environments due to volatilization of the protective silica (SiO$_2$) scales, which leads to a high recession rate. In order to solve this problem, a protective layer, an environmental barrier coatings (EBCs), is necessary. To qualify as EBCs candidate material, some fundamental chemical properties are required, such as high melting point, low thermal conductivity, low oxygen diffusion, favorable chemical stability, and thermodynamic compatibility with the substrate. In addition, the EBCs requires a highly dense microstructure that ensures all the pathways between the substrate and oxygen/steam are blocked. Therefore, the appropriate coefficient of thermal expansion seems the most critical property for EBCs candidate materials. Based on the above demands, Yb$_2$SiO$_5$ has attracted the most interest as a commercial protective layer for non-oxide silicon-based ceramics.

Generally, research on the degradation of EBCs has focused on corrosion behavior and resistance to high-temperature water vapor and oxygen. However, since 2010 when the Icelandic volcano Eyjafjallajökull erupted and caused economic losses of more than 2 billion US dollars, investigators have discovered that a serious threat to the stability of EBCs comes from sand, volcanic ash, and other siliceous matter. One of the reasons for this is that sand and volcanic ash can be seen as a kind of FOD (foreign object debris) impacting on the EBCs. A particle that enters a combustion gas stream at a velocity of 600 m/s can attack the coating during operation of the turbine machinery, which may cause radial cracks and damage to the EBCs. However, another report discussed the phenomenon of volcanic ash attached to aircraft engines for the first time and indicated that, compared with mechanical damage, more serious degradation of EBCs comes from chemical corrosion. Investigation into the corrosion behavior between TBCs degradation and Middle-East dust found, for the first time, that the main composition of the attachment is CMAS.

The main composition of sand and volcanic ash is defined as CMAS, and is relatively easy to obtain and analyze under laboratory conditions. In most of the research, CMAS takes the place of natural sand and volcanic ash as the corrosive for EBCs. However, scientists using real volcanic ash to attack TBCs,
indicated that iron (Fe), sodium (Na), and manganese (Mn), elements not included in CMAS, also penetrated the substrate. In order to further completely investigate, in this study, not only CMAS, but also the volcanic ash has been adopted as the corrosive for EBCs. As one potential EBCs candidate material, Yb$_2$SiO$_5$ offers excellent resistance to combustion environment.$^{45}$ However, the reaction of Yb$_2$SiO$_5$ with CMAS and volcanic ash has not been investigated. In this work, two kinds of corrosives, natural volcanic ash and artificial CMAS, are employed. The purpose of this study is to investigate the differences in corrosion behavior of volcanic ash and CMAS on the sintered Yb$_2$SiO$_5$. We explain how volcanic ash and CMAS attack Yb$_2$SiO$_5$ ceramics and predict the corrosion resistance of Yb$_2$SiO$_5$ EBCs to volcanic ash and CMAS.

2. Experimental procedures

In this study, two types of corrosion media, natural Icelandic volcanic ash and artificial CMAS, were adopted. The composition of volcanic ash varies geographically and for use in this experiment, it was necessary to characterize its basic properties, such as composition, phase, and melting temperature. The composition, including elements and oxides, was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES; ICP-8100, Shimadzu, Japan), and phase relation and crystallinity were measured using X-ray diffraction (XRD; D/MAX-2200 and SmartLab, Rigaku, Japan). In addition, the melting point was measured using thermo-gravimetric analysis and differential scanning calorimetry (TG-DSC, STA-PT1600, Linseis Inc., Germany).

CMAS having 33CaO·9MgO·13AlO$_3$·4SiO$_2$ mol % composition, was synthesized by Al$_2$O$_3$ (Kento Chemical, Japan), CaO (Wako pure chemical industries, Japan), MgO (Wako pure chemical industries, Japan), and SiO$_2$ (Kento Chemical, Japan). For making a homogeneous mixture, ball-mill method with ZrO$_2$ balls and ethanol was used and employed at room temperature for 2 h. After the ball-milling process, the suspension was dried at room temperature, and then a two-step heat treatment was carried out using an Al$_2$O$_3$ crucible; at 80°C for 10 h and 1200°C for 24 h to synthesize CMAS. The synthesized CMAS was ground to a fine powder before use.

In order to obtain highly dense sintered Yb$_2$SiO$_5$, spark plasma sintering (SPS) equipment was used. The Yb$_2$SiO$_5$ powder was synthesized by solid-state reaction with Yb$_2$O$_3$ (Kento Chemical, Japan) and SiO$_2$ (Kento Chemical, Japan) powders. The mass fractions of two powders were determined as 1:1 in molar ratio, after ball-milling process, the Yb$_2$O$_3$·SiO$_2$ mixed powder was heated at 1400°C for 20 h for synthesis. The synthesized Yb$_2$SiO$_5$ powders were then put into a graphite mold having 30 mm diameter. The mold was placed in the spark plasma apparatus (Synetx, Inc., Japan) and the temperature raised to 1400°C in a vacuum of 10$^{-2}$Pa. Sintering was conducted under 60 MPa pressure. The phases of the Yb$_2$SiO$_5$ powder and SPS sintered body were determined using XRD (D/MAX-2200, Rigaku, Japan) with Cu K$_\alpha$ radiation ($\lambda = 1.54184$ Å) at a scan rate of 2$^\circ$/min over the 2$\theta$ range of 10–70$^\circ$.

The sintered Yb$_2$SiO$_5$ was cut with a diamond saw into 10 × 5 mm specimens, each about 3 mm thick. After ultrasonic cleaning of the samples with acetone and then ethanol, the volcanic ash and CMAS were attached to the polished surface of each specimen using paste at a concentration of 40 mg/cm$^2$. High temperature corrosion tests were then carried out in a muffle furnace (KBF314N, Koyo Thermo Systems, Japan). The corrosive temperature was selected at 1400°C with various duration hours; 2, 12, and 48 h. The heating rate was set as 5°C/min, and after high-temperature corrosion, the specimens were cooled naturally to room temperature. The corrosive phenomenon of each specimen was investigated using a scanning electron microscope (SEM) (SEM, JSM-7001F, JEOL Co., Japan). Energy dispersive X-ray spectroscopy (EDS) was employed to determine the penetration elements, distribution, and content.

The reaction temperatures of volcanic ash and Yb$_2$SiO$_5$ was measured using TG-DSC. The volcanic ash and Yb$_2$SiO$_5$ mixed powders (1:1 wt % ratio) were evenly stirred. The heating profile in this experiment was set from room temperature (around 25°C) to 1400°C, accompanied by a heating rate of 10°C/min. The chamber held 80% atmospheric air and 20% protective argon gas. Phase evolution of volcanic ash and Yb$_2$SiO$_5$, mixed powders (1:1 wt % ratio) up to 1400°C was observed using high-temperature X-ray diffractometer (HT-XRD, SmartLab, Rigaku, Japan) with Cu K$_\alpha_1$ radiation ($\lambda = 1.54056$ Å) under air. Each of target temperatures for HT-XRD measurement was chosen from the peaks positions of TG-DSC results.

3. Results & discussion

3.1 Characterization of Icelandic volcanic ash and Yb$_2$SiO$_5$ sintered body

Chemical components of Icelandic volcanic ash, including element and oxide mass percentages, were measured using ICP-OES as shown in Table 1.$^{19}$ It contains a huge mass amount of Si together with Al, Fe, Na, Ca, Mg, K, and traces of Ti, Mn, and P. As oxide basis it showed SiO$_2$, Al$_2$O$_3$, FeO$_2$, Na$_2$O, CaO, and MgO. The result is similar as Sakurajima volcanic ash.$^{20}$ The XRD pattern of the volcanic ash is shown in Fig. 1.$^{19}$ It can be seen that the volcanic ash was well crystallized, and the major phase components are Sodian-anorthite (Ca,Na)(Al,Si)$_2$Si$_2$O$_8$, Aluminian-augite (Mg,Fe,Al)(Si,Al)$_2$O$_6$, Analcime NaAlSi$_2$O$_6$/H$_2$O, and Albite Na(Si$_3$Al)O$_8$. Figure 2 shows the XRD results of both the synthetic Yb$_2$SiO$_5$ powder and the sintered specimen. According to the XRD patterns of synthetic Yb$_2$SiO$_5$ powder in Fig. 2(a), where only the diffraction peaks corresponding to

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**Table 1. Chemical composition of Iceland volcanic ash was measured by ICP-OES**

| Element | Si | Al | Fe | Na | Ca | Mg | K | Ti | Mn | P |
|---------|---|----|---|---|---|---|---|---|---|---|
| Mass %  | 27.1| 7.9| 6.8| 3.9| 3.8| 2.1| 1.7| 0.9| 0.2| 0.1|
| Oxides  | SiO$_2$| Al$_2$O$_3$| FeO$_2$| Na$_2$O| CaO| MgO| K$_2$O| TiO$_2$| MnO| P$_2$O$_5$|
| Mass %  | 58.1| 14.9| 9.7| 5.3| 3.4| 3.5| 2.1| 1.5| 0.2| 0.3|

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**Fig. 1. XRD pattern of Iceland volcanic ash.**

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Yb₂SiO₅ are present, pure Yb₂SiO₅ powder was successfully synthesized by the solid-state reaction at 1400°C for 24 h. As shown in Fig. 2(b), the XRD pattern of the sintered Yb₂SiO₅ was shown as pure phase.

3.2 Corrosion behavior of sintered Yb₂SiO₅ by volcanic ash

Figure 3 shows a back-scattered electron (BSE) image of the corrosion morphology of the sintered Yb₂SiO₅ which was reacted with Iceland volcanic ash after high-temperature corrosion at 1400°C, with durations of (a), (b) 2 h; (c), (d) 12 h; and (e), (f) 48 h. As shown in the low-magnification Figs. 3(a), 3(c), and 3(e), the corrosion morphologies show striking similarities, and the thickness of the reaction layer does not change very much, even with long durations of high-temperature corrosion at 1400°C, and is difficult to observe. In other words, the reaction of sintered Yb₂SiO₅ with volcanic ash is very small; this implies that sintered Yb₂SiO₅ exhibits good corrosion resistance to molten volcanic ash attack. In addition, Figs. 3(b), 3(d), and 3(f) reveal magnified BSE images of the black box in Figs. 3(a), 3(c), and 3(e), which show that after heat treatment at 1400°C, the pores of sintered Yb₂SiO₅ reduce with time. Moreover, under high magnification, the average reaction layers can be clearly seen at the interface between sintered Yb₂SiO₅ and molten volcanic ash in Figs. 3(b), 3(d), and 3(f). As mentioned in more detail later, the thickness of the reaction layer grew slowly; therefore, the stable reaction layer can be seen as a kind of protective layer, blocking the penetration of volcanic ash.

Figure 4 is the BES image of sintered Yb₂SiO₅ reacted with
Iceland volcanic ash after heat treatment at 1400°C for 12 h. As mentioned above, this reaction is very weak. The EDS mapping images were enumerated around the SEM image, and according to the results, a clear-cut boundary can be drawn between molten volcanic ash and sintered Yb$_2$SiO$_5$. The elements which only occur in the volcanic ash such as Ca, Fe, Al, and Mg exist only in the molten volcanic ash layer, and Yb occurs mainly in the sintered substrate. These results show that no obvious element penetration occurred even for Fe and Ca, which are usually considered as the main invasive elements present in molten volcanic ash layer, suggesting that even after high-temperature corrosion for 12 h, the sintered Yb$_2$SiO$_5$ still showed excellent resistance to volcanic ash attack. The details of the reaction layer, after high temperature corrosion at 1400°C, are shown in the BSE images as follows: Fig. 5(a) the overall view; Fig. 5(b) a magnified view of the black box in Fig. 5(a). The thin and wavy reaction layer covered the sintered Yb$_2$SiO$_5$ substrate. As mentioned in Fig. 3, the sintered Yb$_2$SiO$_5$ substrate seemed to re-sinter at 1400°C as the pores reduced due to the heat treatment, and a transverse crack occurred, probably caused by a mismatch in thermal expansion coefficients between the sintered Yb$_2$SiO$_5$ substrate and molten volcanic ash. Although the crack may not exist at high temperature a lot, however it also could be considered as a kind of transmission path for invasive elements in probability, fortunately, this path was blocked by an enough dense reaction layer, as shown in the black circle in Fig. 5(b). In order to evaluate the composition of the reaction layer, an EDS point analysis was carried out. One point, in the range of molten volcanic ash layer, was selected as point A; another, in the middle of reaction layer, was chosen as point B; and point C was located in sintered Yb$_2$SiO$_5$ substrate, see Fig. 5(b). The results of the chemical composition of point A, including all the volcanic ash elements such as Na, Mg, Al, Si, Ca, and Fe, but not the substrate Yb, are shown in Table 2. On the other hand, the chemical composition of the reaction layer (point B) and sintered Yb$_2$SiO$_5$ substrate (point C) shows big differences. Considering the measurement error range of EDS point analysis, the lack of Na, Mg, Al, Ca, and Fe in the reaction layer implies that almost of the volcanic ash elements did not penetrate the reaction layer (point B). The reaction layer can be defined as ytterbium disilicate (Yb$_2$Si$_2$O$_7$) due to the equal atomic percentages of Yb and Si. Moreover, according to the results at point C, no volcanic ash element penetration was observed in the sintered Yb$_2$SiO$_5$ substrate, where the main elements were O, Si, and Yb.

Iceland volcanic ash after heat treatment at 1400°C for 12 h. As mentioned above, this reaction is very weak. The EDS mapping images were enumerated around the SEM image, and according to the results, a clear-cut boundary can be drawn between molten volcanic ash and sintered Yb$_2$SiO$_5$. The elements which only occur in the volcanic ash such as Ca, Fe, Al, and Mg exist only in the molten volcanic ash layer, and Yb occurs mainly in the sintered substrate. These results show that no obvious element penetration occurred even for Fe and Ca, which are usually considered as the main invasive elements present in molten volcanic ash layer, suggesting that even after high-temperature corrosion for 12 h, the sintered Yb$_2$SiO$_5$ still showed excellent resistance to volcanic ash attack. The details of the reaction layer, after high temperature corrosion at 1400°C, are shown in the BSE images as follows: Fig. 5(a) the overall view; Fig. 5(b) a magnified view of the black box in Fig. 5(a). The thin and wavy reaction layer covered the sintered Yb$_2$SiO$_5$ substrate. As mentioned in Fig. 3, the sintered Yb$_2$SiO$_5$ substrate seemed to re-sinter at 1400°C as the pores reduced due to the heat treatment, and a transverse crack occurred, probably caused by a mismatch in thermal expansion coefficients between the sintered Yb$_2$SiO$_5$ substrate and molten volcanic ash. Although the crack may not exist at high temperature a lot, however it also could be considered as a kind of transmission path for invasive elements in probability, fortunately, this path was blocked by an enough dense reaction layer, as shown in the black circle in Fig. 5(b). In order to evaluate the composition of the reaction layer, an EDS point analysis was carried out. One point, in the range of molten volcanic ash layer, was selected as point A; another, in the middle of reaction layer, was chosen as point B; and point C was located in sintered Yb$_2$SiO$_5$ substrate, see Fig. 5(b). The results of the chemical composition of point A, including all the volcanic ash elements such as Na, Mg, Al, Si, Ca, and Fe, but not the substrate Yb, are shown in Table 2. On the other hand, the chemical composition of the reaction layer (point B) and sintered Yb$_2$SiO$_5$ substrate (point C) shows big differences. Considering the measurement error range of EDS point analysis, the lack of Na, Mg, Al, Ca, and Fe in the reaction layer implies that almost of the volcanic ash elements did not penetrate the reaction layer (point B). The reaction layer can be defined as ytterbium disilicate (Yb$_2$Si$_2$O$_7$) due to the equal atomic percentages of Yb and Si. Moreover, according to the results at point C, no volcanic ash element penetration was observed in the sintered Yb$_2$SiO$_5$ substrate, where the main elements were O, Si, and Yb.

The reaction temperature of Yb$_2$SiO$_5$ and volcanic ash mixed powder was measured using TG-DSC as shown in Fig. 6. In order to clearly determine phase relations, pure Yb$_2$SiO$_5$ powder and 100% volcanic ash powder were also measured as references. The result showing no endothermic peak or exothermic peaks suggests that Yb$_2$SiO$_5$ exhibits good thermodynamic properties as a high temperature material (Fig. 6). On the other hand, a sharp endothermic trough for volcanic ash, occurring around 1180°C, was found in Fig. 6. This temperature could be considered the melting point of volcanic ash. In case of the mixed powders, one sharp endothermic peak at 1180°C and a further one, just below at 1300°C were observed. This suggests that the first endothermic peak is the first stage of volcanic ash melting, and the second is the reaction temperature of volcanic ash and Yb$_2$SiO$_5$.

According to the results of TG-DSC, the mixed powder was studied by in-situ HT-XRD. Generally, the temperatures at the peak and trough points have attracted most attention, because some kind of phase change or reaction always occurs around that temperature. According to the literature, the temperature at peak or trough points can always be selected as target temper-
atures for sample heat treatment. To evaluate the phase of the reactant, ex-situ room temperature-XRD was performed on these samples. However, it is highly possible that phase change occurs during the cooling process, even under rapid cooling. To avoid this phase inversion, in-situ HT-XRD, which can directly perform phase evaluations at target temperatures, was introduced into this study. More importantly, the most of previous works\textsuperscript{20–23} indicates that volcanic ash does not possess any corrosive ability until it melts, then silicous matter infiltrates and degrades porous coatings. Therefore, investigation of the dynamic reaction process of molten volcanic ash with sintered Yb\textsubscript{2}SiO\textsubscript{5} is necessary and can only be observed using HT-XRD. Due to the melting temperature (1180°C) and the reaction temperature (just below at 1300°C) of the mixed powder, the HT-XRD measurement temperatures were selected at 1100, 1200, and 1300°C, to investigate the dynamic phase relations. Subsequently, further continuous heating to 1400°C was carried out to produce an adequate reaction. The phase relations on dynamic cooling process were also investigated, down to room temperature (30°C). The HT-XRD patterns did not change up to 1200°C. [Figs. 7(a)–7(c)] It suggests that the mixture did not react with each other up to the temperature. The strong signal from crystalline Yb\textsubscript{2}SiO\textsubscript{5} powder hides the relatively weak signal from the volcanic ash and, as a result, only Yb\textsubscript{2}SiO\textsubscript{5} peaks are observed. Moreover, as shown in Fig. 7(d), when the temperature elevates to 1300°C, all the peaks changed drastically, and they were defined as Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}. The behavior is matched with the results of EDS point analysis, point B in Table 2, and can be considered as further experimental evidence that the reaction product is Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}. The Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} phase may be reacted results between Yb\textsubscript{2}SiO\textsubscript{5} and silicates in volcanic ash. In fact, Liu et al. suggests, when rare-earth monosilicates are exposed to the silica in silicous matter they react, and transform to rare-earth disilicates.\textsuperscript{13} According to other research works,\textsuperscript{23} this can be attributed to the differences in Yb\textsubscript{2}O\textsubscript{3} thermodynamic activity in Yb\textsubscript{2}SiO\textsubscript{5} and Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}. Yb\textsubscript{2}SiO\textsubscript{3} shows higher Yb\textsubscript{2}O\textsubscript{3} activity, more than three orders of magnitude above Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7},\textsuperscript{23} and this causes it to react more with the silica from the silicous matter. In the other words, from the thermodynamic point of view, the reaction between Yb\textsubscript{2}SiO\textsubscript{3} and volcanic ash is intense, however, the thin and dense reaction product, Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}, plays a critical role as a protective layer for resistance to attack by molten volcanic ash.

### 3.3 Corrosion behavior of sintered Yb\textsubscript{2}SiO\textsubscript{5} by CMAS

When sintered Yb\textsubscript{2}SiO\textsubscript{3} reacts with the frequently-used CMAS, entirely different phenomena are exhibited. Figure 8 shows the corrosion morphology of CMAS reacted with sintered Yb\textsubscript{2}SiO\textsubscript{3} at 1400°C for 2, 12, and 48 h. From the comparison of the corrosive results between volcanic ash and CMAS, the most distinctive difference of CMAS corrosion is the thickness of the reaction layer. A visible reaction layer can be observed even after an exposure time as short as 2 h. Moreover, as shown in Figs. 3(b), 3(d), and 3(f), the CMAS was significantly reacted to the Yb\textsubscript{2}SiO\textsubscript{3} layer.

Figure 9 shows the BSE image of sintered Yb\textsubscript{2}SiO\textsubscript{3} reacted with CMAS after heat treatment at 1400°C for 12 h. The reaction layer was a loose form, and it was formed by apatite-type phase Ca\textsubscript{2}Yb\textsubscript{2}(SiO\textsubscript{4})\textsubscript{6}O\textsubscript{2}.\textsuperscript{23} The EDS mapping images were enumerated around the BSE image, and the result shows that the typical apatite structures are saturated with Yb, Al, O, and Ca. In addition, no penetration layer was detected between the interface of reaction layer and substrate. In order to evaluate the composition of the corrosive layer, an EDS point analysis was carried out. One point, in the molten CMAS layer, was selected as point D; another, in the center of the reaction layer, was point E; and point F was in the substrate. According to the results in Table 3, the chemical composition of point D shows only Ca, Mg, Al, and Si, and no Yb is detected. The chemical composition of point F only exhibits Yb, Si, and O, and implies that no CMAS penetrated the substrate. Moreover, the chemical composition of point E shows O, Al, Si, Ca, and Yb. This oxide, which possess apatite structure, can be defined as Ca\textsubscript{2}Yb\textsubscript{2}(SiO\textsubscript{4})\textsubscript{6}O\textsubscript{2}.\textsuperscript{23} Thickness of the reaction layer grew significantly following the heat treatment hours at 1400°C (Fig. 10). As previously discussed, the sintered Yb\textsubscript{2}SiO\textsubscript{3} exhibits excellent resistance to attack by molten volcanic ash, therefore, it is embodied in the nearly level line in Fig. 10. The thicknesses of the reaction layer after heating for 2, 12, and 48 h with volcanic ash were estimated approximately 3.3, 4.6, and 8.1 μm, respectively. In other words, the reaction layer grew 2.5 times from 2 to 48 h. However, when the sintered

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**Fig. 7.** HT-XRD patterns of volcanic ash and Yb\textsubscript{2}SiO\textsubscript{5} mixed powders.

**Fig. 8.** Corrosion morphology of sintered Yb\textsubscript{2}SiO\textsubscript{3} was reacted with CMAS after heat treatment at 1400°C with duration of (a) for 2 h, (b) for 12 h, and (c) for 48 h.
Yb$_2$SiO$_5$ reacted with artificial CMAS, the thickness of reaction layer became almost exponential. After heat treatment for 2, 12, and 48 h with CMAS, the thickness was calculated as approximately 12.2, 41.5, and 121.7 μm, respectively, implying that the sintered Yb$_2$SiO$_5$ had been rigorously consumed by CMAS attack.

In summary, different corrosion phenomena were observed in CMAS and volcanic ash. As mentioned in the previous works, the behavior of CMAS attack on Yb$_2$SiO$_5$ is very intense. On the other hand, in the case of volcanic ash attack, Yb$_2$SiO$_5$ exhibits excellent resistance. This can be attributed to the generation of a thin and dense reaction layer, which may act as a protective layer, blocking the penetration paths of volcanic ash. In addition, another plausible reason for the different corrosion phenomena, is the difference in concentration of the main corrosion elements in volcanic ash and CMAS. In spite of more elements occurring in natural volcanic ash, a higher concentration of corrosive elements, in terms of Ca, occur in CMAS. In other words, CMAS having higher Ca concentration will react with Yb$_2$SiO$_5$, more easily and vigorously, resulting in fast growth of the apatite-type Ca$_3$Yb$_2$(SiO$_4$)$_6$O$_2$ reactant.

4. Conclusion

In this study, fully dense sintered Yb$_2$SiO$_5$ was fabricated by the SPS process at 1400°C for 10 min under a pressure of 60 MPa, and its high-temperature corrosion performance evaluated, using natural Icelandic volcanic ash and man-made CMAS at 1400°C with different durations at 2, 12, and 48 h, respectively. According to the XRD result, the major phase components of the Icelandic volcanic ash are Sodian-anorthite (Ca,Na)(Al,Si)$_2$Si$_2$O$_8$, Aluminian-augite Ca(Mg,Fe,Al)(Si,Al)$_2$O$_6$, Albite Na(Si$_3$Al)O$_8$, and Analcime NaAlSi$_2$O$_6$/$\text{H}_2\text{O}$. The high-temperature corrosion of sintered Yb$_2$SiO$_5$ and volcanic ash was carried out at 1400°C for 2, 12, and 48 h. The thickness of the reaction layer was almost the same from 2 to 48 h, implying the excellent resistance of Yb$_2$SiO$_5$ to molten volcanic ash attack. According to the HT-XRD results, before heat treatment the relatively weak volcanic ash signal is hidden, i.e., only Yb$_2$SiO$_5$ peaks are observed. When the temperature increases to the reaction temperature of 1300°C, all of the peaks can be defined as Yb$_2$Si$_2$O$_7$. This can be attributed to the differences in thermodynamic activity between Yb$_2$O$_3$ and Yb$_2$SiO$_5$. Higher activity of Yb$_2$SiO$_5$ leads to more reactions with the silica that comes from siliceous matter. However, when the sintered Yb$_2$SiO$_5$ reacted with frequently-used CMAS, it exhibited entirely different phenomena. Due to a higher concentration of corrosive elements, which can be defined here in terms of Ca, CMAS with a higher Ca concentration reacted more easily and vigorously with Yb$_2$SiO$_5$, resulting in fast growth of the apatite structure Ca$_3$Yb$_2$(SiO$_4$)$_6$O$_2$ reactant. Therefore, the corrosion behavior of CMAS attack on sintered Yb$_2$SiO$_5$ can be seen as the continuous subduction of Yb$_2$SiO$_5$.

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