Hot corrosion of Al$_2$O$_3$ and SiC ceramics by KCl–NaCl molten salt

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1. Introduction

Thermal storage technology using molten salts has received considerable attention with respect to the effective use of waste thermal energy from factories and solar thermal energy.¹ The molten salt is expected to serve as a thermal storage material in the mid-to-high-temperature region because of its stability at high temperatures combined with its large latent heat. However, since molten salt has strong corrosive properties, the tanks and heat exchangers for molten salt need to be corrosion-resistant. Ceramics are expected to be used for the tank and the piping of the heat exchangers because of their superior chemical stability and mechanical properties at high temperatures. These ceramics must feature corrosion resistance to molten salt (in the state of liquid and vapor). Therefore, basic data characterizing the molten-salt corrosion of these ceramics are required.

Mixed KCl–NaCl is a common molten salt. Its eutectic point is at 645°C,² and it is widely used as salt-bath material for steel at 700–900°C. In addition, this mixed salt is non-flammable, nontoxic, and inexpensive. Therefore, KCl–NaCl mixed salt is expected to be used as thermal storage material at mid-to-high temperatures. However, there has not been much research on the corrosion of ceramics parts used for thermal energy storage against KCl–NaCl molten salt. On the other hand, there has been much research on the corrosion behavior of ceramics under the effects of molten salt in which NaCl is involved. For example, the influence of Na$_2$SO$_4$ molten salt on the corrosion behavior of ceramics used in turbines was studied.⁵–¹⁵ Na$_2$SO$_4$ is generated from NaCl contained in seawater and S contained in fuel.¹⁴ The corrosion of such turbine components occurs upon exposure to small amounts of Na$_2$SO$_4$ molten salt, which adheres to the surface of the components.⁴–⁶,⁸,¹¹ Compared with the corrosion of turbine components, in the case of the corrosion of the tanks and thermal exchangers used for thermal energy storage, the inner walls are exposed to large amounts of KCl–NaCl molten salt for prolonged periods.

In this research, hot corrosion tests of the typical structural ceramics Al$_2$O$_3$ and SiC under the effects of KCl–NaCl molten salt were performed at high temperatures and for long times. The ceramic samples were tested by being immersed in molten salt and under salt vapor. Based on these measurements, basic corrosion data, such as the corrosion product, surface conditions, and 4-point bending strength, were acquired.

2. Experimental procedure

KCl–NaCl equimolar mixed powder (SSQKN, Osaka Chem. Co. Ltd.) was used as the corrosive agent. Commercial high-purity Al$_2$O$_3$ (99.5% purity, 3.89 g/cm³) and SiC ceramics (3.17 g/cm³) were used as sample materials, and boron and carbon were employed as sintering additives for the SiC ceramics. The samples were machined to obtain test pieces of suitable size (3 × 50 mm). One of the 4 × 50 mm facets was polished to a mirror finish by using diamond paste.

The hot corrosion tests were conducted in lidded Al$_2$O$_3$ crucibles (SSA-S grade purity: >99.5%, Nikkato Co.). The temperatures of the lidded Al$_2$O$_3$ crucibles were raised at a rate of 10°C/min to the test temperature (700 and 800°C) for soak times of 100–400 h in air. The samples underwent corrosion in the molten salt (referred to as immersed samples) and under salt vapor (referred to as exposed samples) were then washed with water after the corrosion test.

The crystalline phase of the sample surfaces was examined using X-ray diffraction (XRD). Roughness profiles of the samples were established by a surface-roughness tester. The microstructure of the sample surfaces was observed with scanning electron microscopy (SEM). The polished surfaces of the samples...
were used for these evaluations. The bending strength of the samples was determined by the 4-point bending test with an inner span length of 10 mm and an outer span length of 20 mm and a crosshead speed of 0.5 mm/min. For each condition, there were five samples.

3. Results and discussion

3.1 Hot corrosion of $\text{Al}_2\text{O}_3$ ceramics

Figure 1 shows the XRD patterns of the samples before and after the corrosion test. The $\text{Al}_2\text{O}_3$ sample in this study is composed of only $\alpha$-$\text{Al}_2\text{O}_3$, as shown in Fig. 1(a). Likewise, only $\alpha$-$\text{Al}_2\text{O}_3$ peaks were detected in the samples after the corrosion test. No corrosion product was detected. Figure 2 shows the surface-roughness curves of the samples before and after the corrosion test. In the case of the sample before the corrosion test, the roughness curve was straight, and only a few peaks of less than 1 μm in depth (considered to be pores or defects) were observed, as shown in Fig. 2(a). On the other hand, in the case of the immersed samples, some peaks of more than 2 μm in depth were observed, though the entire roughness curve was almost straight. For the exposed sample, an almost straight curve with a few shallow peaks was observed. No upward peaks considered to arise from corrosion products were detected. Figure 3 shows the SEM photographs of the polished surfaces of the samples before and after the corrosion test. Some defects were observed, though the overall surface of the sample before the corrosion test was flat and smooth. The surface of the sample immersed at 800°C for 400 h was also flat and smooth; however, a slight roughness appeared at the surfaces of the $\text{Al}_2\text{O}_3$ particles, as shown in Fig. 3(b). In the case of the sample exposed at 800°C for 400 h, a flat and smooth surface was observed, as was the case for the sample before the test, as shown in Fig. 3(c). Neither significant roughness nor any corrosion product was observed in these corroded samples. Figure 4 shows the average bending strength of the samples before and after the corrosion test. The average bending strength of the $\text{Al}_2\text{O}_3$ ceramic used in this study was 241 MPa. The average bending strength of the samples immersed at 700°C was 221–238 MPa. No decrease in bending strength with increasing corrosion time could be detected. In the cases of the sample exposed at 700°C for 400 h and the samples immersed and exposed at 800°C, the average bending strengths were decreased slightly. However, no significant decrease in...
bending strength occurred since almost all samples had bending strengths exceeding 200 MPa after the corrosion test. After the corrosion test, neither corrosion products nor significant roughness of the particle surfaces was observed, as can be seen in Figs. 1–3. Furthermore, no significant decrease in the bending strengths of the corroded samples occurred. These results revealed that the Al₂O₃ ceramic has high corrosion resistance to KCl–NaCl molten salt. Therefore, Al₂O₃ is expected to be used as the material for tanks and piping for molten salts. However, some peaks with depths of 1–2 μm, which are considered to be defects, appeared in the surface roughness curves. This result indicates that the Al₂O₃ grain boundaries were attacked by corrosion, and then particles were peeled off from the sample surface. These defects might influence the reliability of the container, but this effect could not be quantitatively characterized in the present study.

3.2 Hot corrosion of SiC ceramics

Figure 5 shows the XRD patterns of the SiC samples before and after the corrosion test. The SiC sample used for this study is composed of only SiC, as shown in Fig. 5(a). Regarding the samples after the test, both SiC and SiO₂ were detected, as shown in Figs. 5(b)–5(g). Figure 6 shows the surface roughness curves of the samples before and after the corrosion test. In the case of the sample before the test, the roughness curve was almost straight, as shown in Fig. 6(a). On the other hand, the surface roughness of the immersed samples was significant. The roughness on the surface became more pronounced with increasing corrosion temperature and time, as shown in Figs. 6(b)–6(e). The sample immersed at 800°C for 400 h exhibited some peaks with heights above 10 μm. On the other hand, no significant peaks were observed for the exposed samples, as shown in Figs. 6(f) and 6(g). Figure 7 shows the SEM photographs of the samples before and after the corrosion test. Before the test, the samples had flat and smooth surfaces. On the other hand, in the case of the sample immersed at 800°C for 400 h, many corrosion products of hemispherical shape were observed on the rough surface, as shown in Fig. 7(b). Some holes through which gas jetted out could be identified at the surface of these corrosion products. Furthermore, such a rough surface is considered as the signature of peeled-off corrosion products. In contrast, in the case of the sample exposed at 800°C for 400 h, the surface of the sample was coated with corrosion products containing many cracks, as shown in Fig. 7(c). Figure 8 shows the average 4-point bending strength of the samples both before and after the corrosion test. The average bending strength of the SiC sample used in this study was 423 MPa. However, the data varied widely. In the case of the samples immersed at 700°C, the average strength was in the range 381–482 MPa. However, a clearly decreasing tendency in the bending strength for extended corrosion times could not be established. Furthermore, no significant decrease in strength was observed, though the average strength of the samples exposed at 700°C and immersed and exposed at 800°C was not more than 410–450 MPa.

Na₂SO₄ attacks the SiC ceramic, and water-soluble sodium silicate is generated as a corrosion product. Furthermore, these molten salts generate SiO₂ as another corrosion product. SiO₂ is soluble only in HF. In this study, SiO₂ was detected on the surfaces of the corroded samples, as shown in Fig. 5. This result indicates that the KCl–NaCl molten salt attacked the SiC ceramic, and SiO₂ was generated as the corrosion product. The SiO₂–Na₂O–K₂O phase diagram indicates that the corrosion products have melting points of 540°C or more and, accordingly, SiO₂.
Na$_2$SiO$_3$, K$_2$SiO$_3$, and other compounds can be generated.\textsuperscript{15) Since mixed KCl–NaCl was used as molten salt in this study, there is a possibility that water-soluble sodium silicate and potassium silicate were formed. However, because the samples were washed with water after the corrosion test, these silicates were not detected. Therefore, the composition and distribution of these silicates remain unclear.

SiC oxidizes as follows:

\begin{equation}
\text{SiC} + 3/2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}^7) \tag{1}
\end{equation}

This oxidation process progresses in the presence of molten salts, such as Na$_2$SO$_4$, under an oxygen atmosphere. Since SiO$_2$ was detected on the surface of the corroded samples, as shown in Fig. 5, it is clear that SiC was oxidized during the corrosion by KCl–NaCl molten salt. SiO and CO are generated under a low partial pressure of oxygen, and SiO$_2$ does not act as a protective film in that case, thereby leading to corrosion of the sample until the sample disappears.\textsuperscript{16,17) As a result, the immersed sample exhibits a rough surface, hemispherical corrosion products, and ejection holes, as shown in Fig. 7(b). The SiC particles of the immersed samples will continue being corroded.

No significant decrease in bending strength was observed in the corroded samples though the reason for the spread of the data remains unclear. However, in the case of the immersed samples, corrosion continues until the sample disappears. Therefore, predicting the lifetime of the material is important if SiC is intended to be used as a container material for molten salt. Forming a SiC coating by chemical vapor deposition or by preliminary oxidation are both effective means for the control of corrosion by molten salts, such as Na$_2$SO$_4$.\textsuperscript{11,12) The sample coated by either of these techniques is expected to have sufficient corrosion resistance against KCl–NaCl molten salt.

4. Conclusions

Hot corrosion tests of Al$_2$O$_3$ and SiC ceramics under the effects of KCl–NaCl molten salt were performed at high temperatures (700 and 800°C) and for long times (100–400 h) in order to develop a suitable container material for thermal energy storage. The samples were tested in molten salt and under salt vapor. Basic corrosion data, such as the corrosion product, surface conditions, and 4-point bending strength, were acquired. In particular, the following results were obtained:

1) In the case of the Al$_2$O$_3$ ceramics, neither corrosion products nor a significant roughness of the Al$_2$O$_3$ particles was observed after the corrosion tests. Furthermore, no significant strength decrease could be detected. Therefore, the Al$_2$O$_3$ ceramics are believed to represent a suitable container material for molten salts.

2) In the case of the SiC ceramics, SiO$_2$ emerged as a corrosion product, and a significant roughness was observed at the surface of the immersed sample. The roughness at the surface became more pronounced as the corrosion temperature and time increased. On the other hand, the SiO$_2$ thin film was present on the surface of the exposed sample. Like in the case of Al$_2$O$_3$, no significant strength decrease was observed. Prediction of the lifetime of the material is necessary if SiC ceramics are to be used for components being exposed to molten salts.

References