Journal of the European Ceramic Society **18** (1998) 1121–1129
© 1998 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00007-7
0955-2219/98/$19.00 + 0.00

Hot Corrosion of Cordierite Ceramics by Na- and K-salts

Junichi Takahashi,* Yoshie Kawai and Shiro Shimada

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Kita-13 Nishi-8, Kita-ku, Sapporo 060, Japan

(Received 1 July 1997; accepted 19 December 1997)

Abstract

The corrosion behavior of cordierite ceramics by Na-salts (NaCl and Na_2SO_4*) and K-salts (KCl and* K_2SO_4*) was studied at high temperatures between 700 and 1200°C. In case of the corrosion by Na-salts at 1000°C, small idiomorphic crystals were formed on the surface of the sample. They were identified with MgO and* Mg_2SiO_4 *in the corrosion by NaCl and* Na_2SO_4*, respectively. EPMA analysis showed the Mg concentration in the corrosion layer abruptly changed from a high level on the surface to nearly null in the successive corroded region where nepheline and cristobalite were produced. Some gaseous Mg-species might be responsible for the characteristic features observed in the hot corrosion by Na-salts. On the other hand, K-salts reacted with cordierite ceramics at higher temperatures to form kaliophilite and forsterite (1100°C), or leucite, forsterite and spinel (1200°C). The surface layer corroded by K-salts had many cracks and was partially removed from the sample.* © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

In advanced coal-fueled power generation systems, solid particles are emitted during combustion or gasification process. They must be efficiently cut off with filter elements to avoid failure of rotating turbines by erosion. The severe environment of the hot gas streams in the systems requires filter elements to have excellent properties in thermal shock resistance, mechanical strength and chemical stability under working conditions (800∼1000°C). Porous ceramic materials have been assessed in terms of material strength during filter operation.[1,2] Among the candidate materials for high temperature filtration applications, cordierite ceramics are considered to be the best material, mainly because of its superior thermal shock resistance property.[3] However, examinations of particulate removal from hot gas streams for synthetic cordierite filters have shown that some difficulties remained to be overcome regarding a long-term filter operation.

Additionally, corrosive chemical species such as alkali metals, chlorine and sulfur are released from the combustor or gasifier. Such corrosive species also dominate the lifetime of a filter element seriously. Hence it is very important to make clear the corrosion behavior of the filter material to be used. In spite of the increasing demand of cordierite ceramics for practical filtration applications, there are few studies on the hot corrosion of cordierite ceramics. This is probably due to the lack of long-term structural durability for synthesized cordierite filters. In burner rig tests of the fuel containing large amounts of impurities, Brooks *et al.*[4] reported that the corrosion of cordierite samples occurred very slightly at 1100°C but was extensively enhanced at 1400°C. Bianco *et al.*[5] examined the corrosion of cordierite bodies in Na_2SO_4 at 1000°C and showed the production of $NaAlSiO_4$ and Mg_2SiO_4 in furnace tests. Chlorine and sulfur present in coal are considered to be released as corrosive alkali chlorides and sulfates.[2] In the present study, therefore, to elucidate the fundamental corrosion behavior of cordierite ceramics, hot corrosion in a concentrated NaCl, KCl, Na_2SO_4 or K_2SO_4 atmosphere was performed in the temperature range from 700 to 1200°C. The hot corrosion processes by each corrosive species were examined by the identification of the corrosion products and observation of X-ray elemental distributions in the corroded region.

---

*To whom correspondence should be addressed.

2 Experimental Procedure

2.1 Preparation of cordierite ceramics

Sols of alumina and silica (Nissan Kagaku) and magnesium hydroxide powder (99·9%, Kojundo Kagaku) were used as starting materials. At first, fixed amounts of both sols were mixed by stirring. A $Mg(OH)_2$ powder suspended in distilled water was then poured into the mixed sol. They were thoroughly mixed with the addition of an appropriate amount of distilled water to form a viscous slurry, which was followed by microwave drying. The dried powder was calcined at 1300°C for 10 h in air and ball-milled in ethyl alcohol to prepare cordierite powder for sintering. Green compacts formed by uniaxial pressing (50 MPa) and subsequent cold isostatic pressing (100 Mpa) were heated at 1450°C for 10 h to produce highly densified cordierite ceramics (relative density~97%).

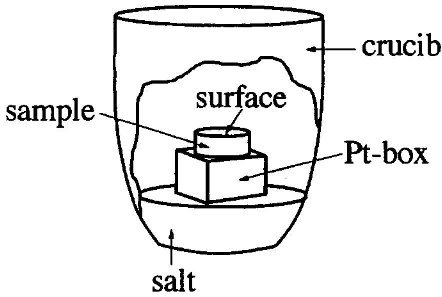

Fig. 1. A cordierite sample in a crucible.

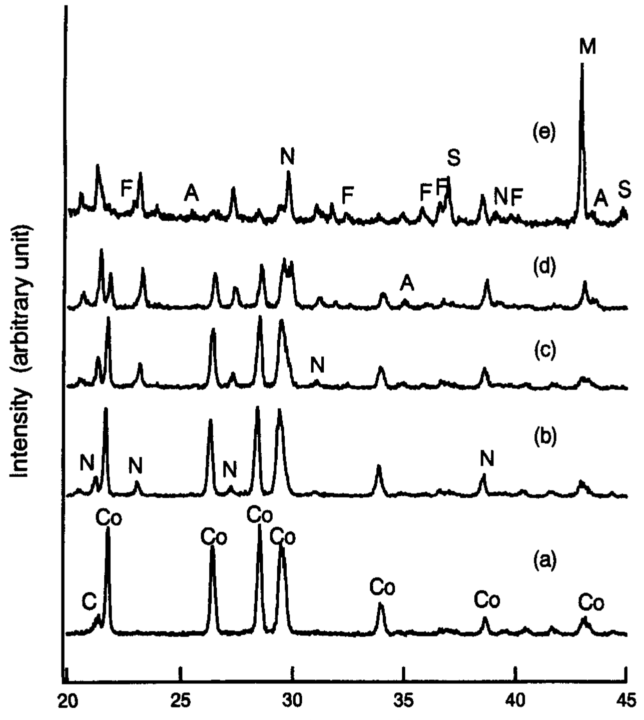

Fig. 2. XRD patterns of cordierite ceramics attacked by NaCl for 4 h at (a) 700°C, (b) 800°C, (c) 900°C, (d) 1000°C and (e) 1100°C. Co: cordierite ($Mg_2Al_4Si_5O_{18}$); N: nepheline ($NaAlSiO_4$); F: forsterite (Mg_2SiO_4); A: α-alumina (α-Al_2O_3); S: spinel ($MgAl_2O_4$); C: cristobalite (SiO_2); M: MgO.

2.2 Hot corrosion

NaCl (m.p. 801°C), Na_2SO_4 (m.p. 884°C), KCl (m.p. 770°C) and K_2SO_4 (m.p. 1067°C) were used as sources of corrosive species of alkali, chlorine and sulfur. A sintered cordierite sample was placed on a Pt-box around which a given amount of a powder of each corrosive chemical reagent was packed in an alumina crucible (Fig. 1). A covered crucible were set in an electric furnace and heated at 700~1200°C for 1~24 h. After each run, most of the surface of as-corroded samples was covered with a water-soluble solid powder. No difference in the corrosion products between as-corroded and washed samples could be detected except the water-soluble solid phase of each raw powder. Therefore, the compounds formed on the surface after hot corrosion were identified by X-ray diffractometry (XRD) of washed samples. The surface morphology of a corroded sample was observed by scanning electron microscopy (SEM). For X-ray elemental analysis, a corroded sample was mounted in a resin, cut into two pieces and polished with diamond paste. The cross-sectional distributions of specified elements in a corroded region were measured with a wavelength dispersive X-ray microprobe analyzer (WDX).

3 Results

3.1 Corrosion products and element distributions in cordierite ceramics attacked by NaCl

Figure 2 shows XRD patterns of surfaces of samples corroded at 700~1100°C for 4 h. At 700°C, a small and broadened peak could be identified with cristobalite (indicated by ‘C’ in the figure). Clear peaks of nepheline ($NaAlSiO_4$, letters ‘N’ in Fig. 2) can be seen in the sample heated at 800°C, indicating the definite occurrence of corrosion by NaCl. The intensities of the nepheline peaks increase as an increase in heating temperature. MgO and α-Al_2O_3 (‘A’ in Fig. 2) are formed at 1000°C. For the sample corroded at 1100°C, the formation of new solid phases can be recognized in addition to a remarkable increase in relative intensity of the MgO peak. They are forsterite (Mg_2SiO_4, ‘F’) and spinel ($MgAl_2O_4$, ‘S’). The disappearance of appreciable peaks of cordierite implies that the hot corrosion of cordierite ceramics by NaCl substantially proceeded.

An SEM image of the sample corroded at 1000°C for 24 h is shown in Fig. 3(a). Surfaces of the corroded samples were covered with characteristically shaped particles. Element analysis [Fig. 3(b)] showed that they were MgO particles. The size of the MgO particles increased as heating temperature were raised.

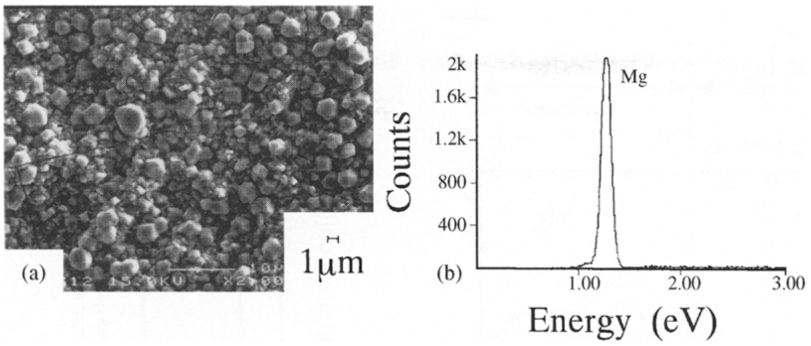

Fig. 3. Scanning electron microphotograph of cordierite ceramics corroded by NaCl at 1000°C for 24 h showing (a) MgO particles on the surface with (b) the associated EDX result.

By the cross-sectional WDX analysis from the surface to interior of the corroded samples, a Mg-enriched region was proved to exist on the surface, which corresponded to MgO particles observed by SEM (Fig. 4). Interestingly, the Mg-enriched region is followed by Mg-missing part where corrosive Na penetrates. In order to obtain detailed information on the element distribution toward an inner part of the specimen, the intensity changes of specified elements were measured by WDX along several lines from surface to interior. A typical result of the line analysis can be seen in Fig. 5 for a sample heated for 24 h. The Mg-enriched part lasts over about 5 μm depth from the surface, where there is no other elements. After this part, Na-existing region appears and extends to a distance of

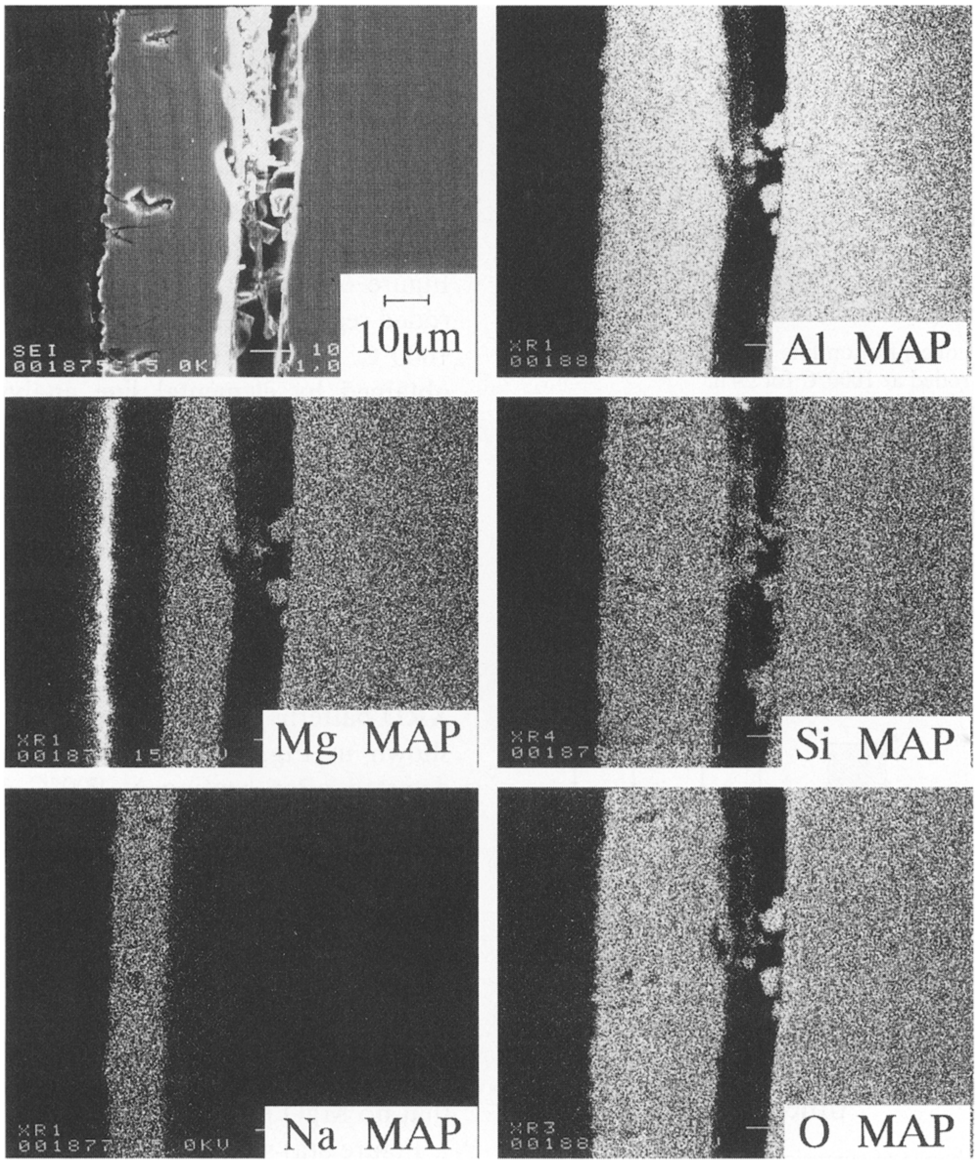

Fig. 4. Polished cross-section and associated X-ray elemental dot maps of a sample corroded at 1000°C for 24 h.

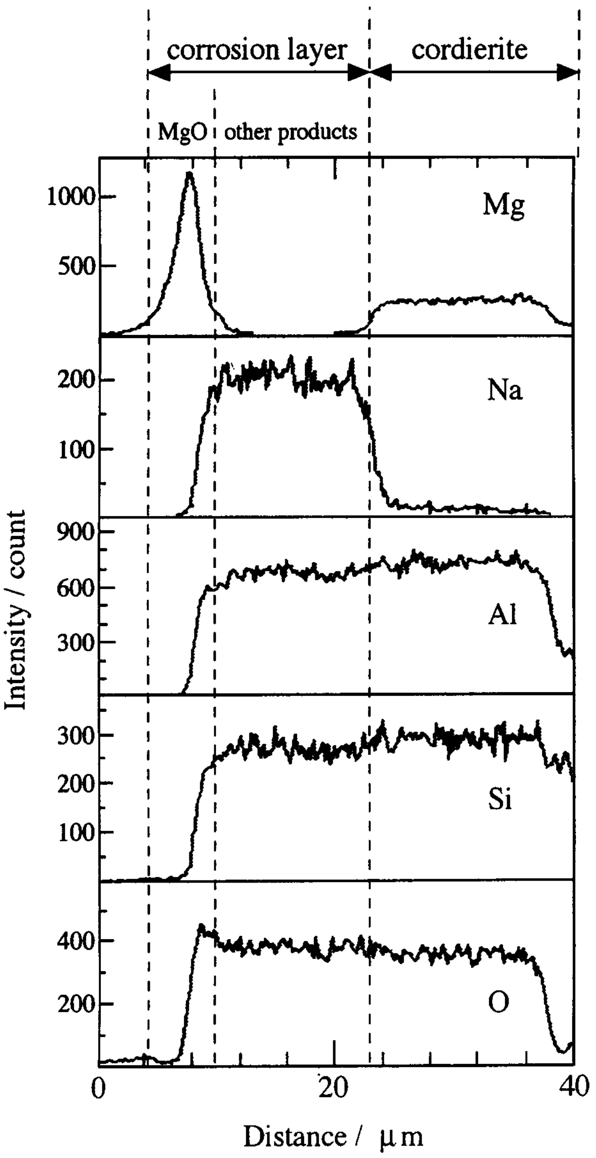

Fig. 5. Elemental concentration line profiles of a sample corroded at 1000°C for 24 h.

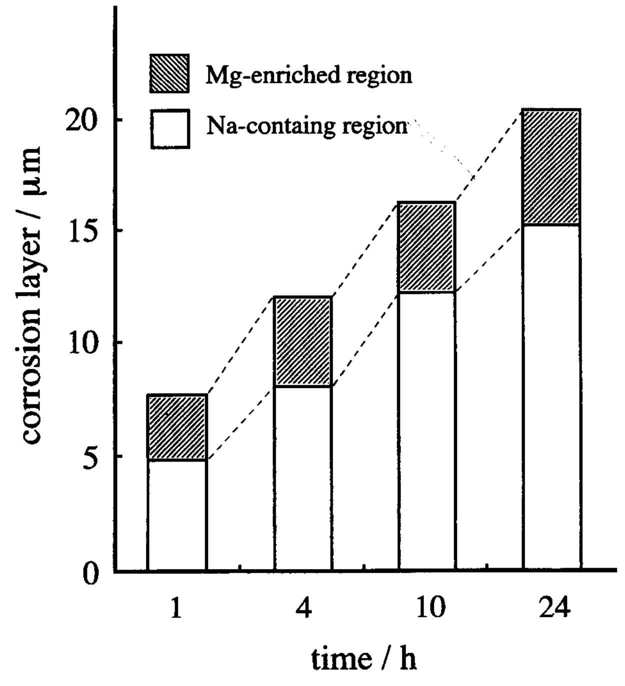

Fig. 6. Thickness change of corrosion layer with reaction time for samples corroded at 1000°C.

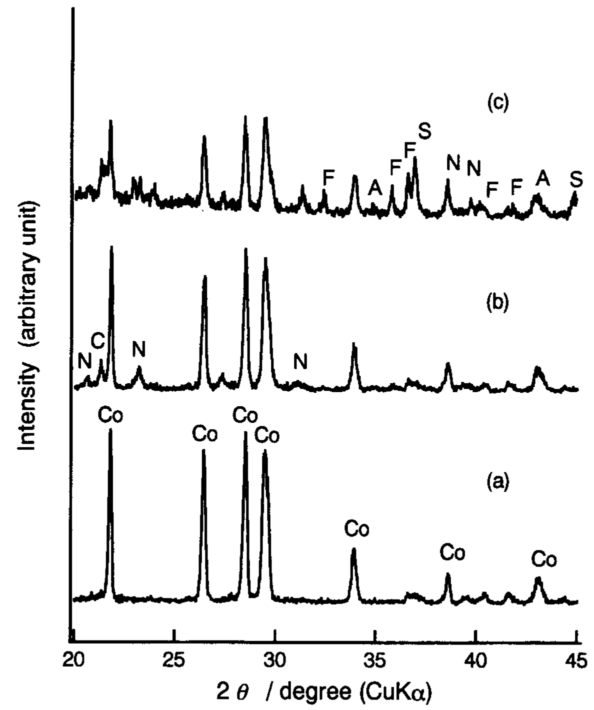

Fig. 7. XRD patterns of cordierite ceramics corroded by Na_2SO_4 for 4 h at (a) 900°C, (b) 1000°C and (c) 1100°C. Co: cordierite ($Mg_2Al_4Si_5O_{18}$); N: nepheline ($NaAlSiO_4$); F: forsterite (Mg_2SiO_4); A: α-alumina (α-Al_2O_3); S: spinel ($MgAl_2O_4$); C: cristobalite (SiO_2).

about 20 μm length from the surface. This region consisted of Al and Si but no Mg. Besides there are little chlorine detectable through the measured region. From this result, the corroded region could be estimated to be about 20 μm from the surface. Figure 6 shows the thickness change of the corroded region with an increasing heating duration at 1000°C. Each values were estimated from results obtained by elemental line analysis with WDX. From this qualitative presentation, both the Mg-enriched and Na-containing regions corresponding to MgO and $NaAlSiO_4$, respectively, were found to gradually increase as corrosion time increased, finally being about 20 μm after corrosion at 1000°C for 24 h.

3.2 Attack by Na_2SO_4

XRD patterns of samples corroded by Na_2SO_4 are shown in Fig. 7. No additional compound was detected after heating at 900°C and lower temperatures. However, hot corrosion at 1000°C resulted in the formation of cristobalite and nepheline. The XRD peak intensities of those compounds increase as the increasing corrosion temperature up to 1100°C. At 1100°C, α-Al_2O_3, forsterite and spinel were additionally formed. Comparing with the result obtained for NaCl, the corrosion products were nearly the same except that no MgO peaks appeared.

Figure 8(a) shows a SEM image of the surface of the cordierite body heated at 1000°C for 24 h.

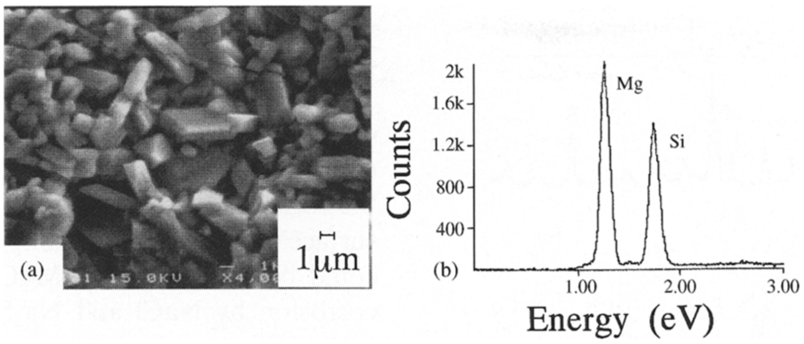

Fig. 8. Scanning electron microphotograph of cordierite ceramics corroded by Na_2SO_4 at 1000°C for 24 h, showing (a) forsterite particles on the surface with (b) the associated EDX result.

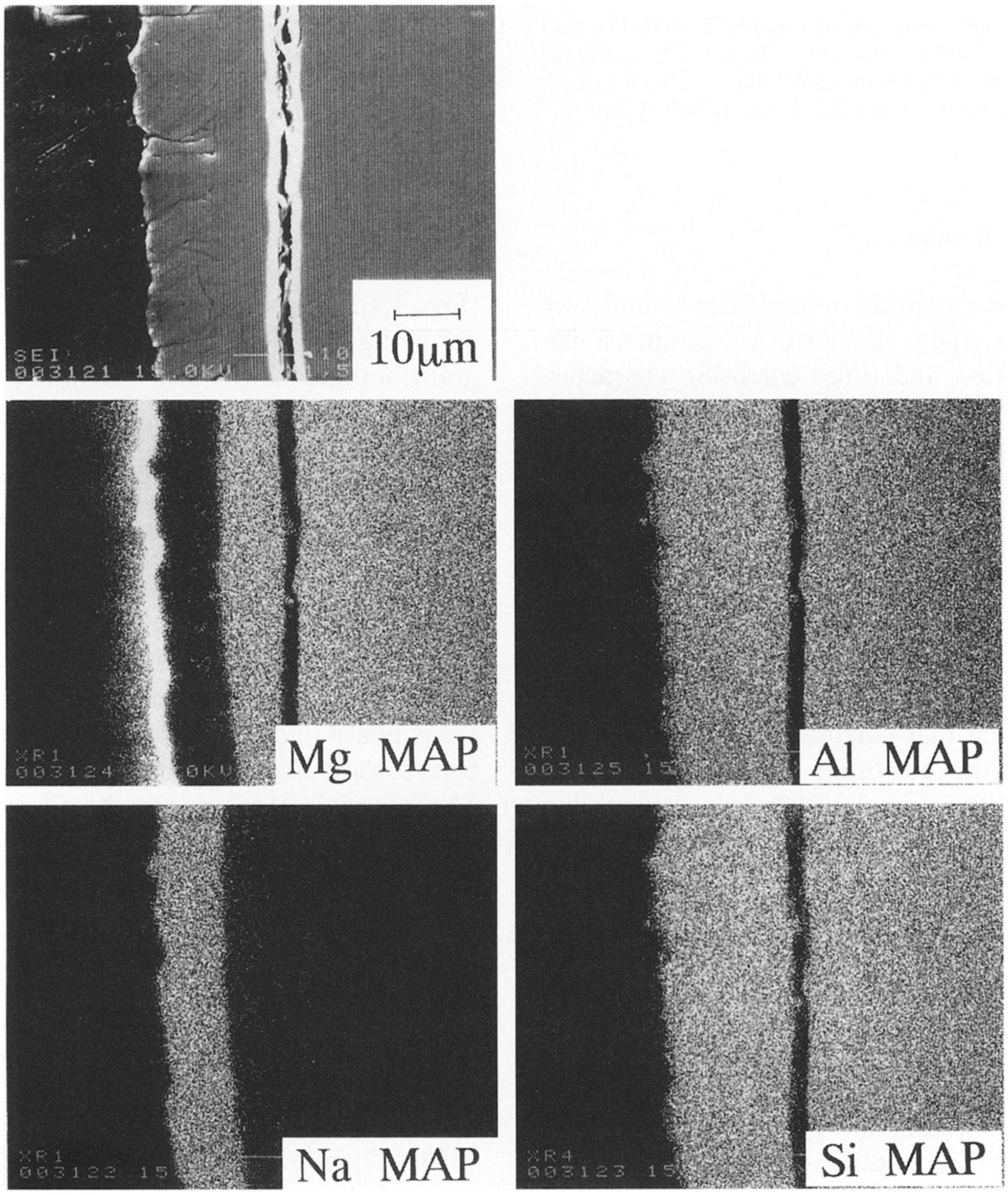

Fig. 9. Polished cross-section and associated X-ray elemental dot maps of a sample corroded at 1000°C for 24 h.

Plate-like particles observed in the SEM image could be identified as forsterite [Fig. 8(b)]. The formation of the forsterite phase was good agreement with the result obtained by Bianco *et al.*[4] X-ray elemental maps of Mg, Al, Na and Si are given in Fig. 9. Mg is highly concentrated in the surface region. This region is followed by Mg-missing one where the homogeneous distribution of Na can be recognized. Consequently, the Mg-enriched surface layer and subsequent Mg-missing but Na-concentrated region are the characteristics of the corrosion behavior of cordierite ceramics attacked by Na-salts. In both cases, no chlorine and sulfur could be detected.

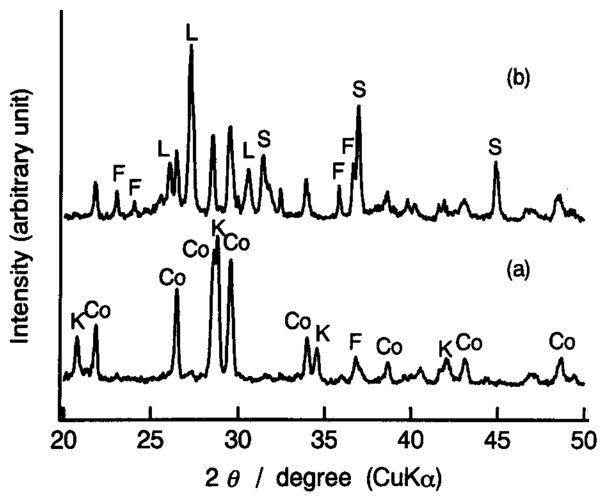

Fig. 10. XRD patterns of cordierite ceramics corroded by KCl for 24 h at (a) 1100°C and (b) 1200°C. Co: cordierite ($Mg_2Al_4Si_5O_{18}$); K: kaliophilite ($KAlSiO_4$); L: leucite ($KAlSi_2O_6$); F: forsterite (Mg_2SiO_4); S: spinel ($MgAl_2O_4$).

3.3 Attack by K-salts

Concerning the corrosion of cordierite ceramics by K-salts in this study, the corrosion products, element distribution and other corrosion characteristics are the same between KCl and K_2SO_4. Hence in most cases the results which will be shown in this section are those obtained in the corrosion by KCl.

Figure 10 shows XRD patterns of the cordierite ceramics heated at various temperatures with the presence of KCl. Below 1000°C no corrosion reaction took place. Heating at 1100 and 1200°C caused the considerable corrosion of cordierite. It can be also seen that corrosion products strongly depended on the corrosion temperature. Major product at 1100°C and 1200°C is kaliophilite ($KAlSiO_4$; 'K' in Fig. 10) and leucite ($KAlSi_2O_6$; 'L'), respectively. In addition to the compounds, spinel and forsterite could be also produced. The surface morphologies of the samples corroded at 1100°C are given in Fig. 11. There are few definitely-shaped particles on the surface. This is very different from those observed for the sample corroded by Na-salts. (Figs 3 and 8) Besides, the occurrence of cracking and partial removal of the corrosion layer can be seen in the corroded surface. As clearly shown in the element maps of Fig. 12, the distribution of corrosive K extends with very high concentration up to about 7 μm in depth, which was estimated to be the corrosion layer, and further penetrates into an inner part of the sample body. For the Mg map, no highly concentrated nor low-level region could be detected. The major difference between the hot corrosion by Na-salts and K-salts was found to be the distribution of Mg in each corrosion layer.

4 Discussion

4.1 Corrosion reaction with Na-salts

The outstanding features in the hot corrosion of cordierite ceramics by Na-salts are (1) the specified distribution of Mg in the corrosion layer and (2) the formation of small idiomorphic crystals on the surface of the corroded sample. The crystals grown could be identified with MgO and Mg_2SiO_4 in the corrosion by NaCl and Na_2SO_4, respectively. The surface Mg-enriched region resulting from the formation of those crystals were followed by the Mg-missing part where $NaAlSiO_4$ and SiO_2 (cristobalite) could be detected. This result suggested following possible corrosion reactions between cordierite and Na-salts at 1000°C in a crucible (Fig. 13).

4.1.1 NaCl

Molten NaCl deposited on the surface of a cordierite sample penetrated into the inner part of the sample along grain boundaries and through open pores, while attacking the boundary regions. [Fig. 13(a)] Then the reaction (eqn (1)) between cordierite and NaCl occurred at pore surfaces and grain boundaries to form $NaAlSiO_4$ and SiO_2 as initial corrosion product.

$$Mg_2Al_4Si_5O_{18}(s)+4NaCl(l) \rightarrow 4NaAlSiO_4(s) + SiO_2(s) + 2MgCl_2(g) \tag{1}$$

$MgCl_2$ which should be simultaneously formed according to the above equation probably becomes a gas phase under the present conditions and diffuses towards the surface of the sample. [Fig. 13(b)]. The formation of the gaseous $MgCl_2$ species seemed to be supported by the fact that $MgCl_2$ melts at 714°C in air and also by the experimental result that the Mg distribution in the corrosion layer abruptly changed from a very high concentration level at the surface to a nearly zero level in the inner part. The gaseous $MgCl_2$ species react with oxygen in air on the surface of the sample [eqn (2)], resulting in the growth of MgO crystals there [Fig. 13(c)].

$$2MgCl_2(g) + O_2(g) \rightarrow 2MgO(s) + 2Cl_2(g); \quad \Delta G^\circ = -23{\cdot}2\,\text{kcal mol}^{-1} \tag{2}$$

4.1.2 Na_2SO_4

The cordierite ceramics were attacked by Na_2SO_4 at 1000°C according to:

$$Mg_2Al_4Si_5O_{18}(s)+2Na_2SO_4(l) \rightarrow 4NaAlSiO_4(s) + SiO_2(s) + 2MgSO_4(g) \tag{3}$$

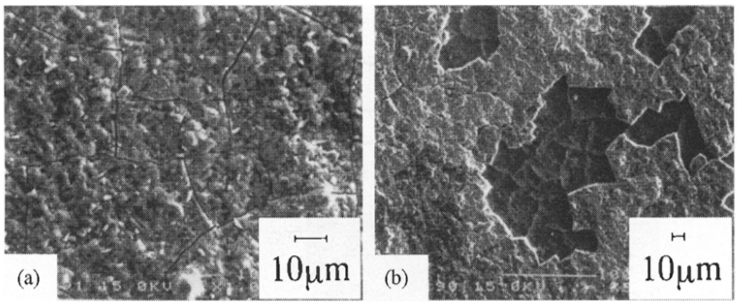

Fig. 11. Surface morphologies of samples corroded by (a) KCl and (b) K_2SO_4 at 1100°C for 24 h.

In this corrosion, the presence of a gas phase ($MgSO_4$) could be assumed, because the Mg distribution in the corrosion layer and the growth of idiomorphic crystals were very similar to those obtained in the corrosion by NaCl. $MgSO_4$ itself melts at 1185°C which was higher than the corrosion temperature (1000°C). However, as can be clearly seen from the phase diagram of the Na_2SO_4–$MgSO_4$ system (Fig. 14), $MgSO_4$ can melt at substantially lower temperatures with the presence of Na_2SO_4 (below 800°C at Na_2SO_4: $MgSO_4 = 1{:}1$). Because the similar chemical environment would be easily established under the present corrosion conditions, the gaseous $MgSO_4$ species might be produced [Fig. 13(e)]. The gaseous $MgSO_4$ which can diffuse to the surface of the sample might

$$MgSO_4(g) + \rightarrow MgO(s) + SO_2(g) \tag{4}$$

or reaction with SiO_2

$$2MgSO_4(g) + SiO_2(s) \rightarrow Mg_2SiO_4(s) + 2SO_2(g) \tag{5}$$

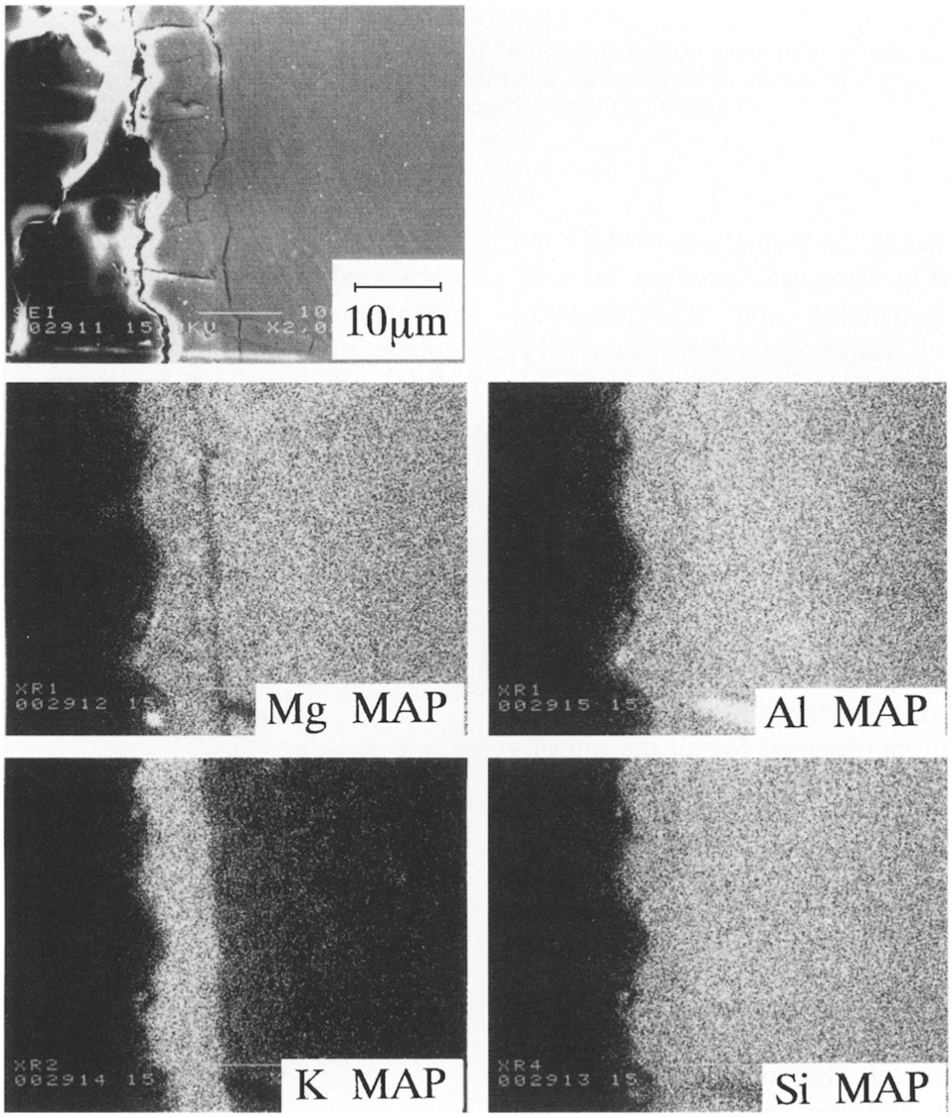

Fig. 12. Polished cross-section and associated X-ray elemental dot maps of a sample corroded by KCl at 1100°C for 24 h.

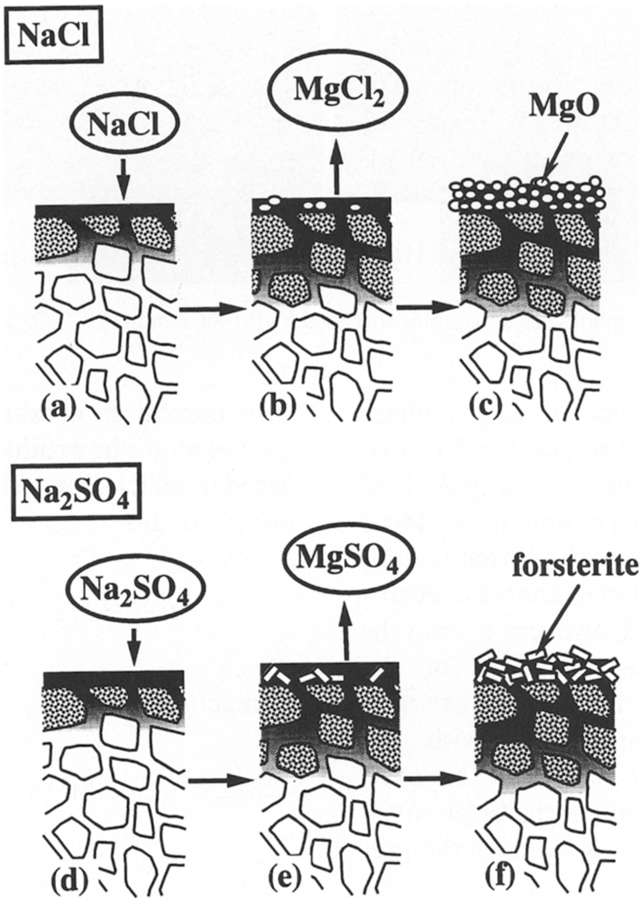

Fig. 13. Schematic presentation of possible sequential reactions in corrosion (i) by NaCl: (a) step-1: deposition of NaCl; (b) step-2: diffusion of $MgCl_2$; (c) step-3: formation of MgO crystals, and (ii) by Na_2SO_4; (d) step-1: deposition of Na_2SO_4; (e) step-2: diffusion of $MgSO_4$; (f) step-3: formation of Mg_2SiO_4 crystals.

Free energy changes in the formation of MgO and Mg_2SiO_4 at 1000°C were calculated to be $\Delta G°$ (MgO) = +6·1 kcal mol^{-1} and $\Delta G°(Mg_2SiO_4)$ = −11·7 kcal mol^{-1}, respectively. Obviously, Mg_2SiO_4 could be favorably formed according to eqn (5) [Fig. 13(f)]. The source of SiO_2 might be a corrosion product indicated by eqn (3) and/or that in a glassy boundary phase of the sintered sample. The glassy phase could be formed during sintering because of the local composition heterogeneity in the starting powder.

In the hot corrosion of cordierite ceramics by Na-salts, no corrosion layer was taken away from its surface. Instead, at further inner region a large lateral crack could be observed for all the samples examined. (Figs 4 and 9) This might be formed in cooling process after heating or in polishing process prior to microscopic observation. Whichever it might be, large strain would be stored at that region. There is substantial difference in the thermal expansion coefficient between the cordierite ceramics ($\alpha = 1{\cdot}4 \times 10^{-6}$/°C) and a major corrosion product $NaAlSiO_4$, ($\alpha = 14{\cdot}5 \times 10^{-6}$/°C). This fact predicted that a crack should be formed at the interface between the corrosion layer and the uncorroded cordierite ceramics. However, the experimental result indicated that a crack could be observed at further inner part from the interface. Probably corrosion layer consisted of a mixed phase of nepheline and glassy and/or crystalline SiO_2, resulting in a small stress at the interface. Instead, a large stress might be produced at the corrosion tip in the host cordierite ceramics where Na could penetrate beyond the interface.

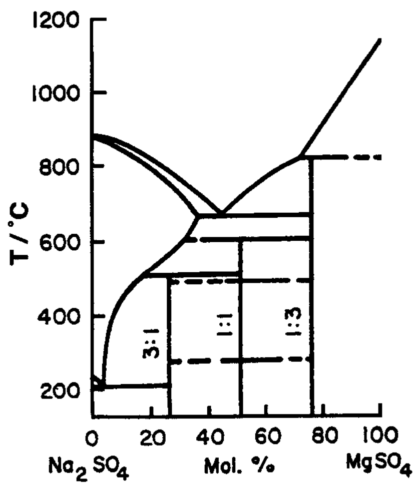

Fig. 14. Phase diagram of the system Na_2SO_4–$MgSO_4$.[6]

4.2 Hot corrosion by K-salts

Compared with the hot corrosion by Na-salts, some essential differences could be recognized in the corrosion by K-salts. Those are (1) a constant Mg distribution both in the corrosion layer and in the successive host ceramics (Fig. 12), and (2) the formation of many vertical and lateral cracks and the partial removal of the surface corrosion layer (Fig. 11). The results suggested that the corrosion reaction between host cordierite ceramics and K-salts was substantially different from that with Na-salts. Although KCl melts at 770°C which is lower than the melting temperature of NaCl, no corrosion reaction was detected even at 1000°C. This result together with those mentioned above indicated that each corrosive chemical species (KCl and K_2SO_4) deposited on the sample surface directly reacted with the host cordierite to form kaliophilite and forsterite at 1100°C, and leucite, forsterite and spinel at 1200°C. These corrosion products were breakable mainly due to their different thermal properties. This might cause the crack formation and removal of the corrosion layer.

5 Conclusion

The hot corrosion of cordierite ceramics by Na-salts was found to take place above 800°C and was examined in detail at 1000°C. Characteristic features of the hot corrosion were (1) the formation of small idiomorphic crystals on the surface of corroded samples and (2) the peculiar distribution of Mg atom across the corrosion layer. The small crystals could be identified with MgO and Mg_2SiO_4 in the corrosion by NaCl and Na_2SO_4, respectively. The X-ray Mg map was characterized by an abrupt change in concentration from a high level on the surface of the corroded sample to nearly null in the successive inner region where nepheline ($NaAlSiO_4$) and cristobalite (SiO_2) were formed. These results suggested that the gaseous Mg species ($MgCl_2$ or $MgSO_4$) might be formed during the hot corrosion, leading to the production of idiomorphic crystals on the surface.

In the hot corrosion by K-salts, on the contrary, no corrosion product was detected below 1000°C. At 1100°C, kaliophilite and forsterite were produced and the products were changed to leucite, forsterite and spinel at 1200°C. The corrosion layers consisting of these products had many cracks and were partially removed from the surface of the sample. The Mg-distribution was found to be constant through the corrosion layer.

References

1. Zievers, J. F., Eggerstedt, P. and Zievers, E. C., Porous ceramics for gas filtration. *Am. Ceram. Soc. Bull.*, 1991, **70**(1), 108–111.
2. Alvin, M. A., Lippert, T. E. and Lane, J. E., Assessment of porous ceramic materials for hot gas filtration applications. *Am. Ceram. Soc. Bull.*, 1991, **70**(9), 1491–1498.
3. Higashi, K. and Maeno, H., The latest status of the development of the advanced ceramic tube filter. *Reports Res. Lab. Asahi Glass Co., Ltd*, 1992, **42**(1), 81–95.
4. Brooks, S. and Morrell, R., *Environmental Degradation of High Temperature Materials*, Vol. 2. Institute of Metallurgists, London, 1980, pp. 3/21–3/25.
5. Bianco, R. and Jacobson, N., Corrosion of cordierite ceramics by sodium sulfate at 1000°C. *J. Mater. Sci.*, 1989, **24**, 2903–2910.
6. Ginsberg, A. S., *Z. Anorg. Chem.*, 1909, **61**, 126–128.