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Corrosion Behavior of Sialon Ceramics in Supercritical Water

Masahiro Nagae,[†] Yasunori Koyama,[‡] Seita Yasutake,[§] and Tetsuo Yoshio

Graduate School of Environmental Science, Okayama University, Okayama 700-8530, Japan

Kohei Oda

Department of Materials Science, Yonago National College of Technology, Yonago 683-8502, Japan

The corrosion behavior of sialon ceramics was investigated in supercritical water at 450°C under 45 MPa for 2–50 h. α-sialon exhibited better corrosion resistance than β-sialon and α/β-sialon. Pitting corrosion with the formation of corrosion products was observed in the case of β-sialon and α/β-sialon. By contrast, the corrosion behavior of α-sialon was characterized by uniform corrosion with the formation of corrosion products. The degree of strength deterioration was strongly dependent on the corrosion morphology. The bending strength of α-sialon after corrosion for 30 h was about 90% of its initial strength, while the strength of β-sialon decreased to 65% of its original strength.

I. Introduction

Supercritical water oxidation (SCWO) is a promising method for decomposing dioxin, PCB, and other materials, which cannot be easily decomposed by conventional processes, as well as for chemical recycling of waste plastic products.[1,2] Ni-based super alloys, such as Inconel and Hastelloy, have been considered as reactor materials. However, to date, no acceptable reactor materials have been developed that can withstand the severe supercritical water (SCW) conditions containing the corrosive HCl and HF generated by decomposition reactions. In the middle of the 1990s, ceramics began to be considered as candidates for SCWO reactors instead of Ni-based super alloys.[3,4] Hara and Sugimoto[5] carried out a screening test of 18 kinds of ceramics and demonstrated that oxide ceramics had better corrosion resistance than non-oxide ceramics in an SCW environment. However, the details of the corrosion mechanism of each ceramic in an SCW environment were not fully clarified.

We have conducted a series of fundamental studies on the corrosion behavior of various ceramics in a high-temperature water environment under equilibrium vapor pressure, simulating a light-water reactor, to investigate the influence of sintering methods and sintering aids on corrosion behavior.[6–9] Our recent study on the corrosion behavior of representative structural ceramics, such as Si_3N_4, SiC, and Al_2O_3, in an SCW environment has revealed that the presence of grain boundary phases was detrimental to the corrosion resistance of these ceramics.[10]

In this paper, we report the corrosion behavior of sialon ceramics in an SCW environment. Sialon[11] has two different crystal structures, α- and β-sialon, which have the same structure as α- and β-Si_3N_4, respectively. Grain boundary phases, such as $Y_3Al_5O_{12}$, remain in β-sialon after sintering, whereas it is theoretically possible to form an interstitial solid solution of α-sialon and sintering aids without any remaining grain boundary phase. The aim of this study is to investigate the influence of the presence of the grain boundary phase in sialon ceramics on the corrosion behavior and the degree of strength deterioration.

II. Experimental Procedure

Three kinds of sialon, α-, α/β-, and β-sialon, were used in this study. The chemical compositions of the specimens are listed in Table I. α-sialon is an interstitial solid solution with Y_2O_3 and does not have a grain boundary phase. α/β-sialon is a composite of the α- and β-phases. β-sialon contains 5 wt% Y_2O_3 as a sintering aid. The specimens were prepared for bending tests in accordance with JIS R1601.[12] Rectangular specimens ($7.5^L \times 4^W \times 3^T$ mm) were cut out from the sialon, ultrasonicated in acetone, and dried in a desiccator before weight measurement. The corrosion tests were performed in a chamber made of Hastelloy C-22 (TAS-01, Taiatsu Techno Corporation, Tokyo, Japan) at 450°C under 45 MPa for 2–50 h. The eluate was redistilled water (pH = 5.6 as measured with a pH meter). The filling ratio of redistilled water was 34.33% to attain the pressure of 45 MPa at 450°C on the basis of the relationship between temperature and pressure by Kennedy.[13] The V/A ratio was set at 52 cm (V, volume of the chamber; A, geometrical surface area of the test specimen). After corrosion testing, the specimens were dried at 110°C and then cooled naturally in a desiccator. Once the specimens cooled down to ambient temperature, their weight change and dimensional change were measured. X-ray diffraction (XRD; Rigaku RINT 2000, Tokyo, Japan) was performed with Cu$K\alpha$ radiation for phase identification. Corrosion behavior was examined by scanning electron microscopy (SEM; JEOL JSM-6330F, Tokyo, Japan). In order to evaluate the degree of strength deterioration, three-point bending tests were performed at room temperature at a crosshead speed of 0.5 mm/min. The span of the jig was 30 mm.

III. Results and Discussion

Figure 1 shows the time dependence of the weight loss after corrosion in SCW. The weight loss of all the specimens tended to saturate with increasing corrosion time. As can be seen, the weight loss of α-sialon, which has no grain boundary phase, was lower than those of α/β- and β-sialon. A similar trend was observed in the case of high-temperature high-pressure water at 300°C under 8.6 MPa.[14] This suggests that the corrosion resistance of sialon is strongly affected by the presence of the grain boundary phase.

Figure 2 shows an SEM image of the surface of β-sialon after corrosion for 30 h. The specimen surface was covered with crystalline corrosion products. Similar corrosion products were identified on the surface of α- and α/β-sialon. In order to analyze the corrosion products, fracture surfaces of specimens after corrosion were examined with an energy dispersive X-ray

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[†] Author to whom correspondence should be addressed. e-mail: nagae@cc.okayama-u.ac.jp

[‡] Present address: Mate Co. Ltd., 526-3 Saeki, Saeki-cho, Wake 709-0514, Japan.

[§] Present address: Sanyo Special Steel Co. Ltd., Hyogo 672-8677, Japan.

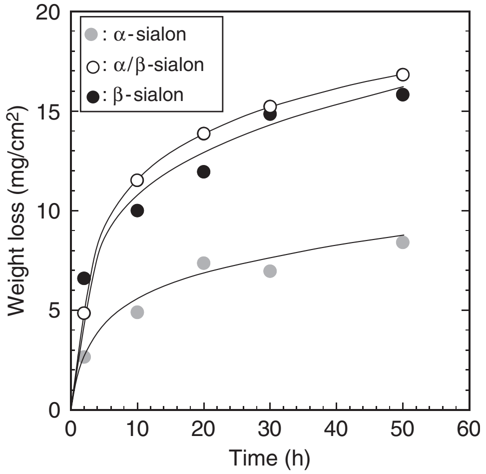

Fig. 1. Time evolution of the weight loss after corrosion in supercritical water.

(EDX) spectrometer. Figure 3 shows a SEM image and EDX line analysis profiles of the fracture surface of β-sialon after corrosion for 30 h. The thickness of the corroded layer increased with corrosion time, showing a diminishing rate of growth. Similar results were obtained for α- and α/β-sialon. Thus, the corroded layer provided a certain degree of protection against corrosion of the sialon substrate by SCW. EDX line analysis showed that the concentration of Si and N in the corroded layer was lowered, whereas O and Al were enriched. A similar trend was observed for α- and α/β-sialon. Although XRD results showed no evidence of any compounds other than sialon, on the basis of the composition of sialon, the crystalline corrosion products were identified as hydrates of the SiO_2–Al_2O_3 system, such as kaolinite ($Al_2Si_2O_5(OH)_4$). (The possibility of the existence of a small amount of amorphous compounds should not be ruled out, although no harrow-like pattern was observed.)

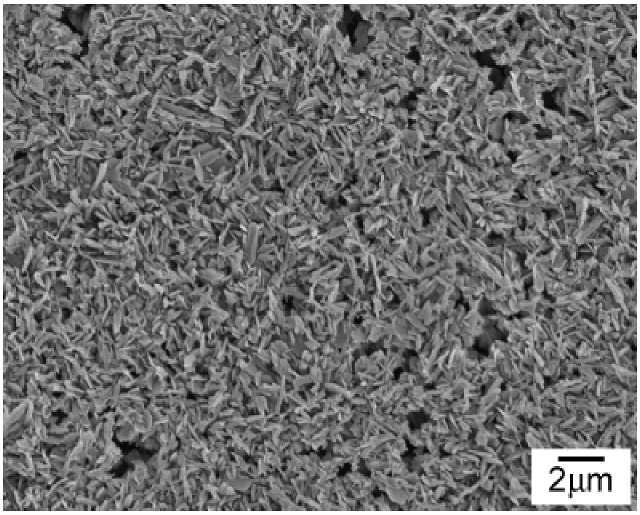

Fig. 2. Scanning electron microscopy image of the surface of β-sialon after corrosion for 30 h.

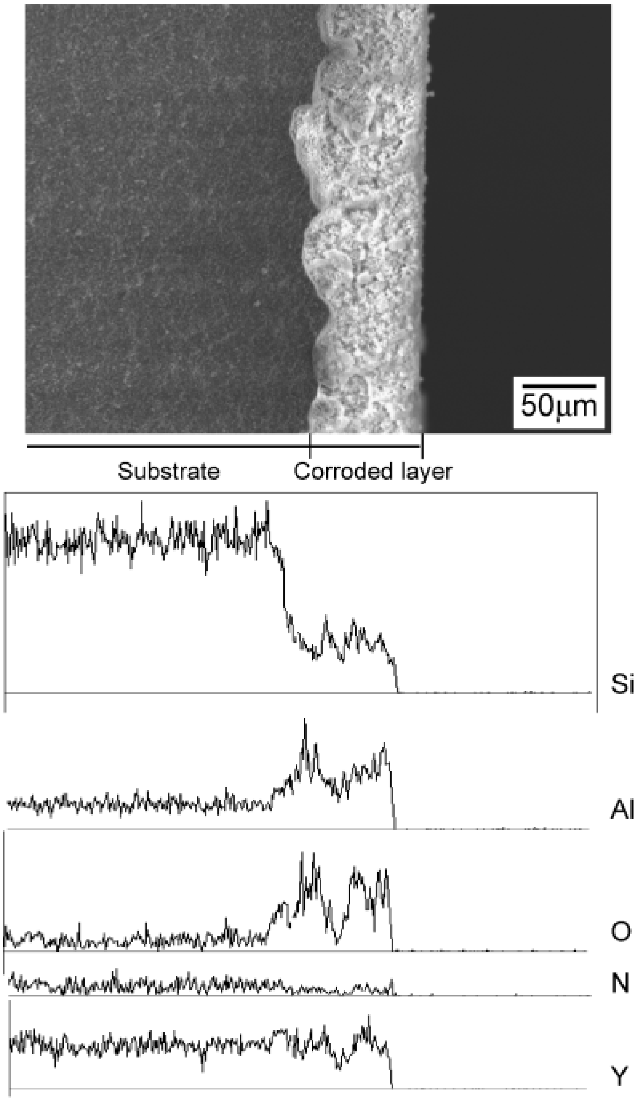

Fig. 3. Scanning electron microscopy image and energy dispersive X-ray line analysis profiles of the fracture surface of β-sialon after corrosion for 30 h.

Figure 4 shows SEM images of the surface of α-sialon (a), α/β-sialon (b), and β-sialon (c) after removal of surface corrosion products by ultrasonication in redistilled water. The corrosion time was 30 h. As observed previously[10] for Si_3N_4 containing Y_2O_3 and Al_2O_3 as sintering aids, a number of corrosion pits were clearly observed in the case of α/β- and β-sialon. The diameter and number of the pits depended on the corrosion time. Thus, the corrosion morphology of α/β- and β-sialon was characterized by pitting corrosion. The unevenness of the interface between the corroded layer and β-sialon substrate (see Fig. 3) resulted from the pitting corrosion. By contrast, the surface of the substrate of α-sialon was smooth, and no corrosion pits were observed. This means that α-sialon itself corroded uniformly in SCW. It is known that Si_3N_4 corrodes in high-temperature high-pressure water by the following reaction[15,16]:

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3 \tag{1}$$

$$SiO_2 + OH^- \rightarrow HSiO_3^- \tag{2}$$

Sialon is basically corroded by a similar reaction in SCW. In the case of α/β- and β-sialon, corrosion pits are formed by leaching of the grain boundary phase. Corrosion of sialon in the pits presumably increases the pH locally, resulting in the accelerative dissolution of SiO_2 by reaction (2). The weight loss of α/β- and β-sialon was larger than that of α-sialon because of such local corrosion.

In order to investigate the influence of the difference in corrosion morphology on the degree of strength deterioration, three-point bending tests were performed at room temperature. Figure 5 shows the average flexural strength S after corrosion in SCW for 30 h. The ratio of S to the initial strength S_0 was also shown in the figure. The initial strength increased in the order

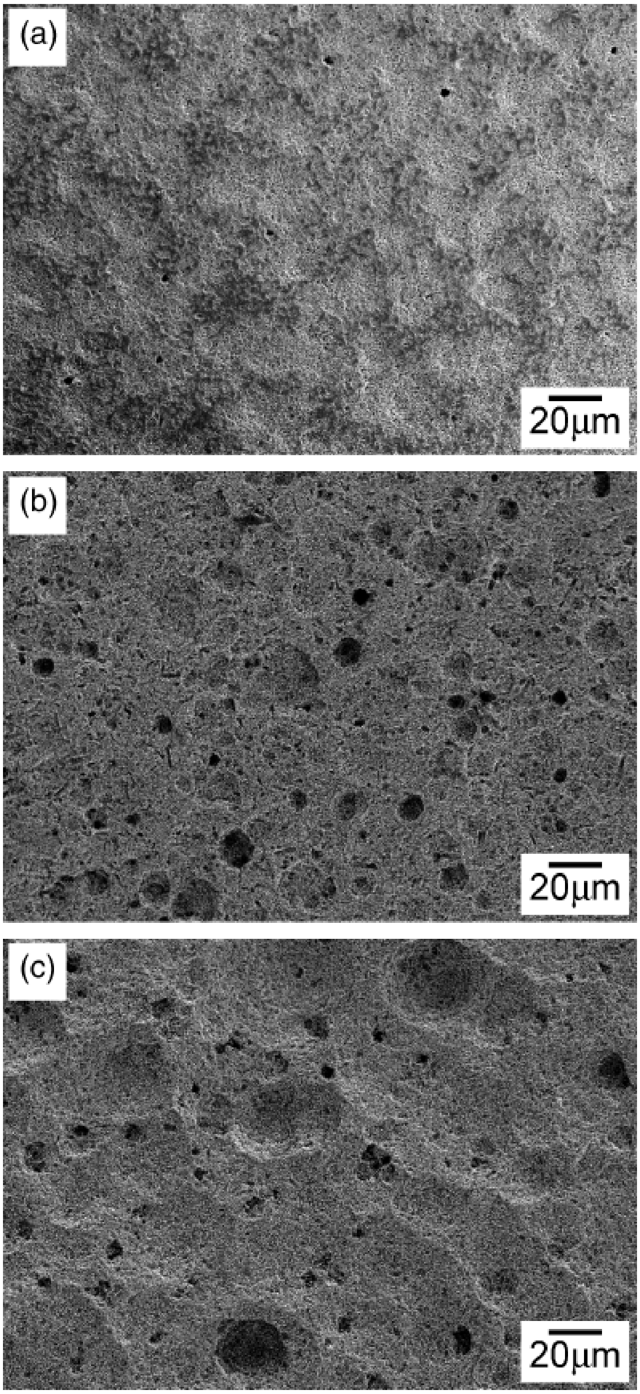

Fig. 4. Scanning electron microscopy images of the surface of α-sialon (a), α/β-sialon (b), and β-sialon (c) after corrosion for 30 h. The corrosion products were removed by ultrasonication in redistilled water.

α-sialon < β-sialon < α/β-sialon as shown in Table I, whereas the strength of α-sialon after corrosion was higher than that of β-sialon after corrosion. The strength deterioration of β-sialon (35%) was the largest among the three sialons. Fractography using SEM showed that the origin of fracture was a corrosion pit. These results indicate that corrosion pits generated by corrosion of β-sialon are fatal defects that cause large strength deterioration. The strength deterioration of α-sialon, which corroded uniformly, was small because no new defects were formed as corrosion proceeded. As the dimples due to pitting corrosion were smaller for α/β-sialon than for β-sialon (see Fig. 4), α/β-sialon showed intermediate strength deterioration during corrosion, between α- and β-sialon. However, if the corrosion pits grow as a result of extended corrosion, the strength deterioration of α/β-sialon will increase. The initial strength of α/β- and β-sialon, which consist of columnar crystals, is higher than that of α-sialon, which consists of equiaxed crystals. However, the strength deterioration due to pitting corrosion and the variation in the strength of α/β- and β-sialon make their life prediction difficult. Thus, it is concluded that α-sialon, in which pitting corrosion due to grain boundary phases does not occur, is more advantageous in SCW environment.

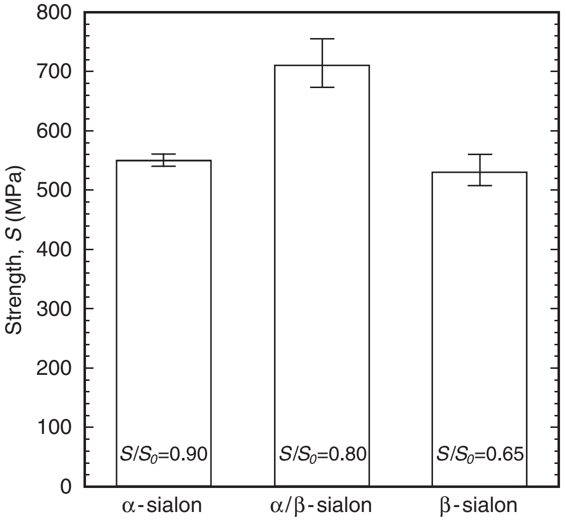

Fig. 5. Average flexural strength of α-, α/β-, and β-sialon after corrosion for 30 h.

IV. Conclusion

The corrosion behavior of sialon ceramics in supercritical water (450°C, 45 MPa) was studied. The results can be summarized as follows:

(1) α-sialon showed lower weight loss compared with α/β- and β-sialon.

(2) All three sialons were covered with a corroded layer consisting of crystalline SiO_2–Al_2O_3 system compounds.

(3) α-sialon, which has no grain boundary phases, was corroded uniformly without generating new defects on the substrate surface.

(4) In the case of α/β- and β-sialon, corrosion pits that caused serious strength deterioration were formed by leaching of the grain boundary phase.

(5) On the basis of these results, it is concluded that α-sialon is preferable to the other sialons as, in the case of α-sialon, supercritical water corrosion forms no corrosion pits, which act as sources of fracture.

Table I. Chemical Composition and Initial Strength of the Specimens Used in This Study

Specimen	α-sialon	α/β-sialon	β-sialon[†]
Composition	$Y_X\ (Si_{12-4.5X},\ Al_{4.5X})(O_{1.5X},\ N_{16-1.5X})$ $X = 0.5$	$X = 0.2$	$Si_{6-Z}Al_ZO_ZN_{8-Z}$ $Z = 0.5$
Initial strength,[‡] S_0 (MPa)	617	902	794

[†] Doped with 5 wt% Y_2O_3. [‡] At room temperature.

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