CORROSION OF HOT-PRESSED SILICON NITRIDE IN ALKALI CARBONATE MELTS

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ABSTRACT

The corrosion behavior of hot-pressed Si₃N₄ in alkali carbonate melts was investigated under air, N₂, and CO₂ environments. The rate of corrosion could be shown by weight loss per unit surface area of Si₃N₄. From the experiments at 800-1000°C, the apparent activation energies of the reactions in Li₂CO₃, Na₂CO₃, and K₂CO₃ were 163, 138, and 153 kJ/mol, respectively. The rate of corrosion in Li₂CO₃ was about twenty times faster than that in Na₂CO₃ and about two-hundred times faster than that in K₂CO₃. The rates of corrosion in Li₂CO₃-Na₂CO₃ or Li₂CO₃-K₂CO₃ mixtures were in the middle of the rates in each pure carbonate. The rate became faster with the increase in the mole fraction of Li₂CO₃. From the above results and SEM observations, the corrosion mechanism was discussed. Under CO₂ environment, the rate of corrosion was slower than that under atmosphere. Thus, it was suggested that the basic oxide concentration in molten carbonate had an effect on the rate of corrosion.

INTRODUCTION

Non-oxide ceramics, such as Si₃N₄ and SiC, are being considered as structural materials to be used in corrosive environments at high temperature. This consideration also includes the applicability of such ceramics to structural materials in the molten carbonate fuel cell. However, relatively little work has been done on the corrosion of such ceramics in molten salts.[1-3] Moreover, quantitative analysis of the reaction rate is very limited.[4] Therefore, for the first step of the study on the reaction of ceramics with molten salts, we selected hot-pressed Si₃N₄ as a non-oxide ceramics and the alkali carbonates as molten salts. We investigated the effects of parameters such as temperature, kinds of alkali carbonates, and environment, on the corrosion behavior of this material in alkali carbonate melts.
EXPERIMENTAL

Ceramic samples were prepared as commercial hot-pressed Si$_3$N$_4$ (Toshiba Co. Ltd., 7% (Y$_2$O$_3$-Al$_2$O$_3$), 3.25 g/cm$^3$) cut into 5.2 x 4.4 x 1.8 mm$^3$ sizes by a diamond cutter. The carbonates used were analytical grade (Wako Chemical Co.).

Figure 1 shows a schematic diagram of the reaction apparatus. About 0.1 mole of specified carbonate, pure or mixed, in a Pt crucible was heated by an electric furnace. After the temperature of the carbonate reached a fixed value, a Si$_3$N$_4$ sample, which was weighed and measured precisely, was put into the crucible. After heat treatment, the crucible was taken out and quenched in air. The sample was washed in water and HCl solution, rinsed, dried, weighed, and measured.

The corrosion experiments in N$_2$ or CO$_2$ environments were the same as that mentioned above only with 250 ml/min. of gas flow from the gas inlet.

Scanning Electron Microscopy (SEM) was carried out with an Akashi Alpha-10.

RESULTS AND DISCUSSION

(1) Reaction Kinetics

As an example, the weight loss of a Si$_3$N$_4$ specimen in Li$_2$CO$_3$ melt is shown in figure 2. By measuring of dimensional change of the specimen, this reaction was considered to proceed isotropically. Therefore, the relation between the reaction time and the weight loss of the specimen per unit surface area was plotted. The plots of the reaction in Li$_2$CO$_3$ and of that in Na$_2$CO$_3$ are shown in figures 3 and 4, respectively. The relations were approximately linear. Consequently, the reaction could be regarded as being controlled by surface reaction. Then, the factor of the rate of corrosion, $k$, would be defined as a unit of the speed of weight loss per unit area. The $k$ value would be used in subsequent analyses.

(2) The Effects of Reaction Temperature

As shown in figures 2-4, the rates of corrosion varied significantly with changes in the temperature. Figure 5 shows the Arrhenius plots of these reaction rates. From these plots, apparent activation energies of the hot-pressed Si$_3$N$_4$ with molten Li$_2$CO$_3$, Na$_2$CO$_3$, and K$_2$CO$_3$ were obtained as 163, 138, and 153 kJ/mol, respectively. It has been reported that the value of the corrosion of Si$_3$N$_4$ in K$_2$SO$_4$ melt was 724 kJ/mol. Comparing these values, it could be postulated that the apparent activation energy was strongly affected by the kind of anion constituting each melt.

(3) The Effects of the Kinds of Carbonate

Figure 5 also shows the effects of the kind of alkali carbonate on the rate of corrosion. As shown in figure 5, at the same temper-
ature, the rate of corrosion in Li$_2$CO$_3$ was about twenty times faster than that in Na$_2$CO$_3$, and about two-hundred times faster than that in K$_2$CO$_3$. It seemed that the smaller the radius of the alkali ion, the faster the rate of corrosion.

When binary mixtures, Li$_2$CO$_3$-Na$_2$CO$_3$ or Li$_2$CO$_3$-K$_2$CO$_3$, were used as the melts, the relations between the composition of carbonate and the rate of the corrosion are given in figure 6. The values of the rate of corrosion in the mixture are in the middle of that in each pure carbonate. The logarithm of the value of the rate of corrosion had a linear relation with the mole fraction of Li$_2$CO$_3$ on the Li$_2$CO$_3$-Na$_2$CO$_3$ system.

(4) SEM Observations

The microstructures of the surface and the section of the Si$_3$N$_4$ samples, both original and corroded, are shown in figure 7. Because of corrosion, the surface of the sample became rough with the appearance of Si$_3$N$_4$ grains. This means that the grain boundary of the sample was eroded faster than the Si$_3$N$_4$ grains in the sample.

The microstructure of the section of the corroded sample indicates that the region, where structural change by the corrosion occurred, is limited only near the surface.

From these observations, it could be supposed that the reaction of the Si$_3$N$_4$ samples with carbonate melts was not completed on the surface of the samples, but proceeded by the mechanism that Si$_3$N$_4$ grains in the samples were eliminated with the erosion of the grain boundary.

If this assumption was accepted, the difference of the rate of corrosion of the Si$_3$N$_4$ sample by the kinds of carbonates could be explained partly as the difference of the diffusivities of alkali ions into the grain boundary of the Si$_3$N$_4$ sample by the difference of the ion radius. However, the determination of the reaction rate of pure Si$_3$N$_4$ with carbonate melt, the composition analysis of the carbonate in the reacting crucible, and other factors are needed in order to verify this assumption.

(5) The Effects of Environment

Some of the results of the experiments, which were carried out under N$_2$ or CO$_2$ environment, are also shown in figures 2-4. The rate of corrosion in carbonate under N$_2$ environment was fast, and that under CO$_2$ environment was slow, compared with that under air environment.

The following explanation has been reported [2,4] on the corrosion behavior in each environment. Under an air environment, SiO$_2$ film is formed on the surface of the Si$_3$N$_4$, and the film supresses the reaction. But under an N$_2$ environment, SiO$_2$ film is not formed; therefore, the reaction proceeds rapidly.

It seems that the results of the experiments under a CO$_2$ environment suggests that the basic oxide concentration in the carbonate melt affects the rate of corrosion of the Si$_3$N$_4$ sample. Under an air environment, some of the carbonate would decompose to
basic oxide. But under a CO$_2$ environment, the decomposition would be suppressed. It might be considered that the higher the basic oxide concentration in the carbonate melt, the faster the rate of corrosion. This also was suggested from the result that the corrosion of the sample occurred faster when the amount of carbonate initially in the crucible was decreased. However, more precise experiments under a controlled environment are needed to assure the above suggestion.

SUMMARY

The corrosion behavior of hot-pressed Si$_3$N$_4$ in alkali carbonates melts was investigated, and the following results were obtained:

a) The corrosion was apparently controlled by surface reaction.
b) Apparent activation energies were obtained. These energies did not vary greatly for different alkali carbonates.
c) The differences in the rates of corrosion among the alkali carbonates were large and increased in the order Li$_2$CO$_3$ > Na$_2$CO$_3$ > K$_2$CO$_3$.
d) The rate of corrosion of the hot-pressed Si$_3$N$_4$ in carbonates under an N$_2$ environment was fast, while that under a CO$_2$ environment was slow, compared to the rate under an air environment.

REFERENCES

1. R. E. Tressler, M. D. Meiser and T. Yonushonis, J. Am. Ceram. Soc., 59, 278 (1976).
2. D. W. Mackee and D. Chatterji, J. Am. Ceram. Soc., 59, 441 (1976).
3. N. Nassif and S. B. Hanna, Thermochim. Acta, 79, 305 (1984).
4. T. Sato, Y. Kanno, T. Endo and M. Shimada, Yogyou-Kyokai-Shi, 94, 123 (1986). (in Japanese)
1 gas inlet
2 quartz tube
3 PR thermocouple
4 electric furnace
5 Pt crucible
6 carbonate melt
7 Si₃N₄ sample

Figure 1. Schematic Diagram of the Reaction Apparatus.

Figure 2. Weight Loss of Si₃N₄ Samples in Li₂CO₃ Melt under Air Environment. (except • at 900°C, under CO₂ environment)

Figure 3. Plots of the Reaction time vs. Weight Loss per Unit Area for the Reaction in Li₂CO₃ under Air Environment. (except •)

Figure 4. Plots same as Figure 3 for the Reaction in Na₂CO₃.
Figure 5. Arrhenius Plots for the Reaction

Figure 6. Effects of the Composition of Carbonate Melt to the Reaction Rate.

Figure 7. Microstructure of the Si$_3$N$_4$ sample.
(a) the Surface of the Original Sample. (b) the Surface after Corroded. (c) the Section of Original Sample. (d) the Section after Corroded.