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Accelerated Corrosion of Stainless Steels with the Presence of Molten Carbonates below 923 K

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The high-temperature corrosion of stainless steels (SUS316L and SUS310S) in the presence of lithium-potassium eutectic carbonate and lithium-sodium eutectic carbonate has been studied by thermogravimetry and the metal consumption method under a carbon dioxide–oxygen atmosphere in the temperature range of 773–1123 K. Although the corrosion of SUS310S obeyed the parabolic rate law for all reaction conditions, the corrosion of SUS316L significantly depended on the reaction conditions. At or above 923 K, the corrosion of SUS316L obeyed the parabolic rate law, even with a carbonate coating. The corrosion rates were accelerated during the initial period of corrosion tests below 923 K, especially around 823 K with a lithium-sodium carbonates coating. The initial accelerated corrosion was a local corrosion, which produced through holes in the metal specimens, and occurred more clearly at higher carbon dioxide partial pressures with the lithium-sodium carbonate coating than with the lithium-potassium carbonate coating.

Generally, energy conversion processes utilizing a molten salt have many advantages, such as a high reaction rate and high conversion efficiency, due to the high operating temperature and the wide potential window. However, processes of molten salts always have material problems with respect to commercialization. Molten carbonate fuel cells (MCFCs) are typical molten salt processes for energy conversion, and are expected to be promising power generation systems for the future due to their high conversion efficiency, excellent environmental characteristics and ability to utilize a wide variety of fuels. For the practical use of MCFCs, a long life of over 40,000 hours, as well as high performance, are required. Although 40,000 hours of operation were performed using a small size single cell,[1] there still remain material problems, especially for high-pressure operations. The degradation of the MCFCs was analyzed. Further, the material deficiencies should be improved, especially concerning the nickel oxide cathode and the stainless-steel components, e.g., the current collector and the separator.[2] The nickel short circuit is caused by a dissolution of the NiO cathode and the electrolyte loss is caused by a corrosion of the stainless-steel components.

The basicity control by optimization of the molten carbonate composition is an important method to stabilize the nickel oxide cathode. The lithium-sodium eutectic carbonate melt is more suitable than the lithium-potassium eutectic carbonate from the viewpoint of nickel oxide solubility.[3] Since lithium-sodium eutectic carbonate has a lower oxygen solubility than lithium-potassium eutectic carbonate, lithium-sodium eutectic carbonate might have a higher cathode reaction polarization, but with a higher ionic conductivity.[4] A small-cell operation showed that the cell voltage with the lithium-sodium carbonate electrolyte is better than that with the lithium-potassium carbonate electrolyte, especially at a high operating pressure.[5]

During the operations of MCFCs using lithium-sodium carbonate, severe corrosion of the separators was found. Stainless steels, such as SUS316L and SUS310S, are used as a separator material because of their cost and productivity. Normally, the corrosion scale of stainless steels has two layers. The outer layer is $LiFeO_2$, which acts as a protection layer from the carbonate attack that causes liquid chromate formation, since $LiFeO_2$ is very stable in carbonate melts. The inner layer is a chromium-rich oxide. Because metallic diffusion through the chromium-rich layer is very slow, the corrosion of stainless steels is controlled by the stability of this layer.[6] Although SUS310S has a higher corrosion resistance than SUS316L, SUS316L shows a smaller increase in the electronic resistance and small electrolyte loss for use in a MCFC.[7]

Although SUS316L stainless steel is widely used as a separator material for MCFC, its corrosion with the lithium-sodium eutectic carbonate melt was found to be accelerated during the heating process.[8]

In the present work, high-temperature corrosions of stainless steels (SUS316L and SUS310S) in the presence of lithium-potassium eutectic carbonate and lithium-sodium eutectic carbonate were kinetically studied by thermogravimetry and the metal consumption method under a carbon dioxide–oxygen atmosphere in order to prevent an accelerated corrosion of the stainless steels at lower temperatures.

Experimental

Commercially available stainless steels (SUS316L and SUS310S) were used as specimens for corrosion tests. Table 1 shows impurity analyses of the specimens. The specimens were 0.5 mm thick metal sheets that were cut to into a rectangular size of 6 × 12 mm. Corrosion tests were carried out in the presence of a carbonate melt film up to 57.3 mg cm^{-2}. The carbonates were coated on the surface of the specimen by dispersion of the carbonate powder-ethanol mixture; the mixture was dried in air at 423 K.

Table 1. The Impurity Analyses of the Specimens (%)

	C	Si	Mn	P	S	Cr	Ni	Mo	Fe
SUS316L	≦ 0.013	≦ 0.57	≦ 0.78	≦ 0.28	≦ 0.001	18	12	2	Bal.
SUS310S	≦ 0.08	≦ 1.50	≦ 2.00	≦ 0.04	≦ 0.03	20	25	—	Bal.

The amount of the carbonate on the metal was determined by the weight change before and after the coating process. The corrosion tests were conducted in the temperature range from 773 to 1123 K under a carbon dioxide-oxygen atmosphere with $(Li_{0.62}K_{0.38})_2CO_3$ [Li/K carbonate] or $(Li_{0.52}Na_{0.48})_2CO_3$ [Li/Na carbonate]. The total pressure was atmospheric pressure. A thermogravimetric analysis (TGA) was used for continuous monitoring of the weight gain of the specimens using a Shimazu TGA-51. The heating rate of the TGA from room temperature was 40 K min^{-1}. The oxide scale of the specimens was removed by etching, and the metal consumption due to the corrosion reactions was determined.

Results and Discussion

The weight gains of the stainless steels during the corrosion test with the lithium-potassium carbonate coating are shown in Fig. 1. The coating amount of carbonate, atmosphere, and temperature were 40 mg cm^{-2}, 33% O_2–67% CO_2, and 923 K, respectively. Under this condition, the corrosion rates were not very different between SUS316L and SUS310S. For SUS316L, although the weight gain curve included swings from 10 to 30 hours, the swings would be affected by cracks of the corrosion scale. These weight-gain curves show that the corrosion reaction follows a parabolic rate law, where the rate-determining step is diffusion of the reactant through the corrosion layer. The parabolic rate law is usually observed for the high temperature corrosion of stainless steels in air.

The weight gain of the stainless steels during the corrosion test with the lithium-sodium carbonate coating is shown in Fig. 2. The coating amount of carbonate, atmosphere, corrosion, and temperature were 30 mg cm^{-2}, 33% O_2–67% CO_2, and 923 K, respectively. The corrosion of SUS310S obeyed the parabolic rate law with both the lithium-potassium and lithium-sodium carbonate coatings. The parabolic rate constant with the lithium-sodium coating is greater than that with the lithium-potassium carbonate coating, although the difference is very small. However, the corrosion of SUS316L with the lithium-sodium carbonate coating was very different from that with the lithium-potassium carbonate coating. A large weight gain was observed during the initial period, and then a weight loss occurred.

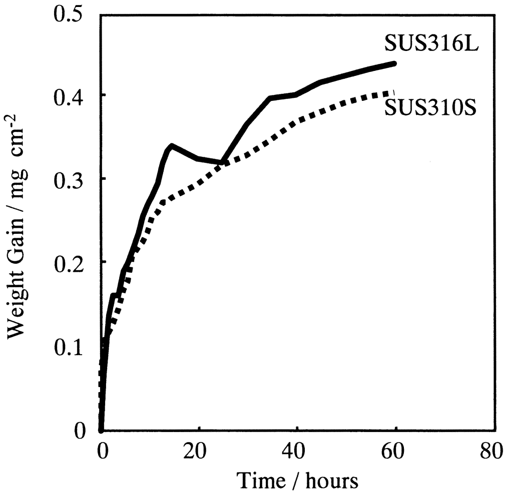

Fig. 1. Weight gain for stainless steels with 40 mg cm^{-2} Li/K = 62/38 carbonate under 33% O_2–67% CO_2 at 923 K.

The weight gain and metal loss plots for the SUS316L stainless steel with 30 mg cm^{-2} Li/K = 62/38 carbonate at 923 K under 33% O_2–67% CO_2 are shown in Fig. 3. Although there was some dispersion for the weight gains, other samples that were not measured for metal loss indicated a similar tendency. Not only the weight gain, but also the metal loss, shows that

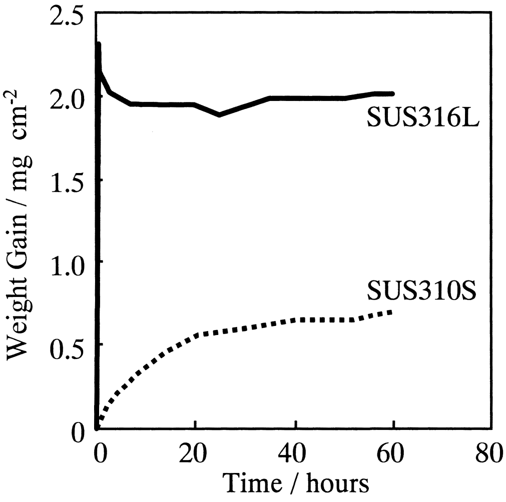

Fig. 2. Weight gain for stainless steels with 30 mg cm^{-2} Li/Na = 52/48 carbonate under 33% O_2–67% CO_2 at 923 K.

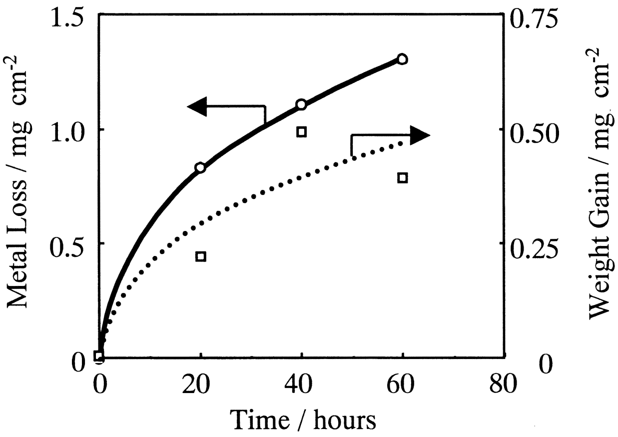

Fig. 3. Weight gain and metal loss plots for SUS316L stainless steel with 30 mg cm^{-2} Li/K = 62/38 carbonate under 33% O_2–67% CO_2 at 923 K.

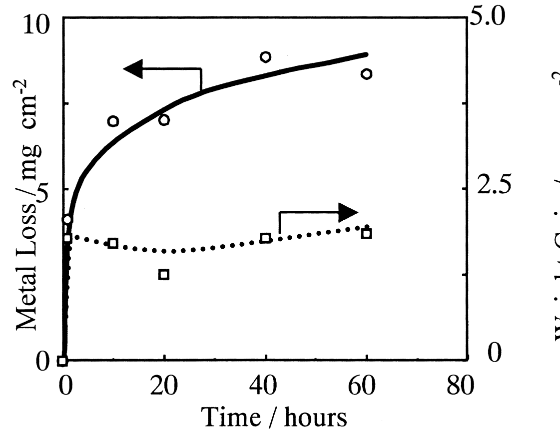

Fig. 4. Weight gain and metal loss plots for SUS316L stainless steel with 30 mg cm^{-2} Li/Na = 52/48 carbonate under 33% O_2–67% CO_2 at 923 K.

the corrosion reaction follows a parabolic rate law. The weight gain is almost proportional to the metal loss.

The weight gain and metal loss plots for the SUS316L stainless steel with 30 mg cm^{-2} Li/Na = 52/48 carbonate under 33% O_2–67% CO_2 at 923 K are shown in Fig. 4. The trend is quite different from that in Fig. 3. The weight rapidly increased at the beginning of the reaction. After the initial period, a small weight loss took place, and then the weight gradually increased again. On the other hand, the metal loss continuously increased even if a weight loss took place. The weight decrease might be caused by CO_2 liberation due to a reaction of the oxide and carbonate.

$$Fe_2O_3 + Li_2CO_3 \rightarrow 2\,LiFeO_2 + CO_2\uparrow$$

When the initial accelerated corrosion occurred, several through holes were observed in the metal specimens after the corrosion scale was removed. These through holes might be formed during the initial drastic weight gain.

The corrosion of SUS316L significantly depends on the reaction conditions. The weight gains of SUS316L during a corrosion test with the 30 mg cm^{-2} lithium-potassium carbonates coating at various temperatures are shown in Fig. 5. The weight gains at 923 K and 823 K followed a parabolic rate law, but at 773 K, the weight significantly increased during the initial period.

The weight gains of SUS316L during a corrosion test with 30 mg cm^{-2} lithium-sodium carbonates coating at various temperatures are shown in Fig. 6. The weight gains above 973 K followed a parabolic rate law, but a significant gain was observed during the initial period below 923 K. After the initial significant weight gain, a weight loss always took place. The accelerated corrosion significantly depended on temperature. The initial accelerated corrosion was observed at higher temperatures with the lithium-sodium carbonate than that with lithium-potassium carbonate.

The weight gain for the corrosion of SUS316L with various amounts of the lithium-sodium carbonate coating in the 33% oxygen–67% carbon dioxide atmosphere at 873 K is shown in Fig. 7. Under these conditions, most of the weight gain took

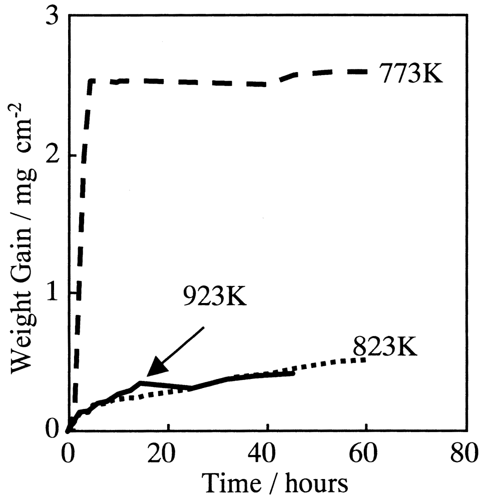

Fig. 5. Weight gain for the corrosion of SUS316L with 30 mg cm^{-2} Li/K = 62/38 carbonate melt under 33% O_2–67% CO_2.

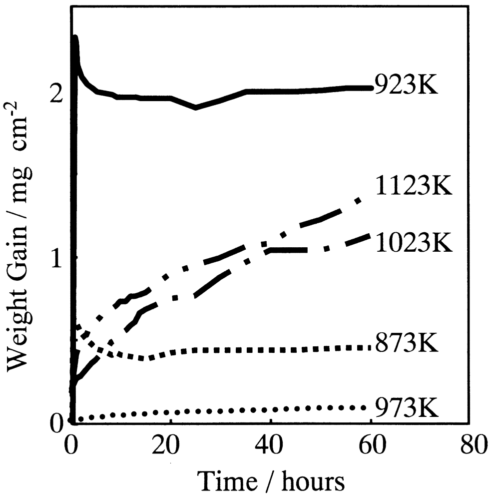

Fig. 6. Weight gain for the corrosion of SUS316L with 30 mg cm^{-2} Li/Na = 52/48 carbonate melt under 33% O_2–67% CO_2.

place during the initial period and the weight gain depended on the amount of the carbonate coating. Figure 8 shows the weight gain of the SUS316L after a 60 hour corrosion test as a function of the coating amount. The initial accelerated corrosion was observed in the carbonate coating range of 10 to 30 mg cm^{-2}. With a small amount of carbonate coating, the accelerated corrosion did not take place. This might be due to the formation of a stable oxide scale. The stable oxide scale might be formed in the presence of the carbonate melt. When a large amount of the carbonate was coated, accelerated corrosion did not take place. The oxygen diffusion might be limited through the thick carbonate film in this case.

The weight gains for the corrosion of SUS316L with the 30 mg cm^{-2} lithium-sodium carbonate melt and the 40 mg cm^{-2} lithium-potassium carbonate melt at 923 K under 10% O_2–CO_2 (–Ar balance) are shown in Figs. 9 and 10. These conditions were in the severe corrosion range. The large weight gain at

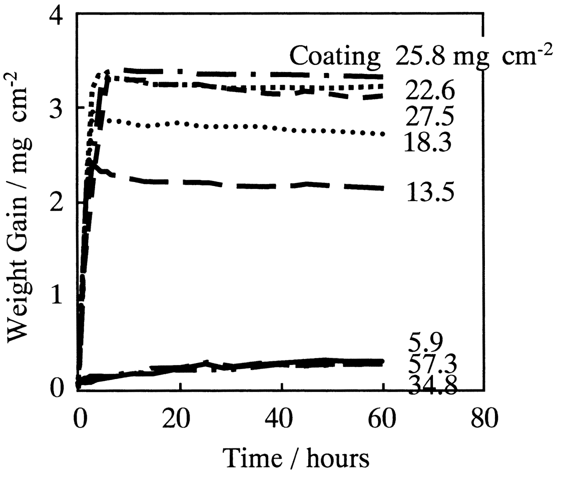

Fig. 7. Weight gain for the corrosion of SUS316L with various amount of the Li-Na eutectic carbonate coating at 873 K under 33% O_2–67% CO_2.

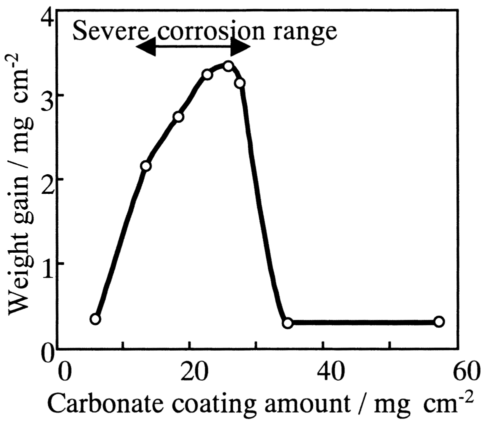

Fig. 8. Weight gain of SUS316L after 60 hours corrosion test at 873 K under 33% O_2–67% CO_2 as a function of coating amount of Li-Na eutectic carbonate melt.

the beginning and the weight decrease thereafter became greater at higher CO_2 pressures. This means that the initial weight increase might be related to CO_2 as well as O_2. The weight gain of SUS316L as a function of the carbon dioxide partial pressure after 50 hours corrosion at 923 K under argon balanced with 10% oxygen–carbon dioxide from Fig. 9 and 10 is shown in Fig. 11. These weight gains mainly took place during the initial portion of the reaction. The weight gains increased with the carbon dioxide partial pressure. The dependence of the weight gain on the carbon dioxide partial pressure with the lithium-potassium carbonate is greater than that with the lithium-sodium carbonate. When the CO_2 pressure was below 0.5 atm, the initial corrosion with the lithium-sodium carbonate coating was much greater than with the lithium-potassium coating. This result might be important for the MCFC.

Since a carbonate melt becomes acidic under high CO_2 pressures, the initial accelerated corrosion might be related to the stability of the oxide scale that dissolves into the carbonate melt by the acid dissolution mechanism.

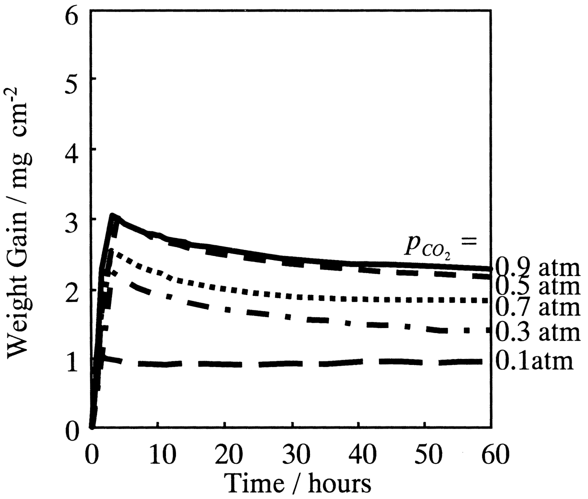

Fig. 9. Weight gain for the corrosion of SUS316L with 30 mg cm^{-2} Li/Na = 52/48 carbonate melt at 923 K under 10% O_2–CO_2 (–Ar balance).

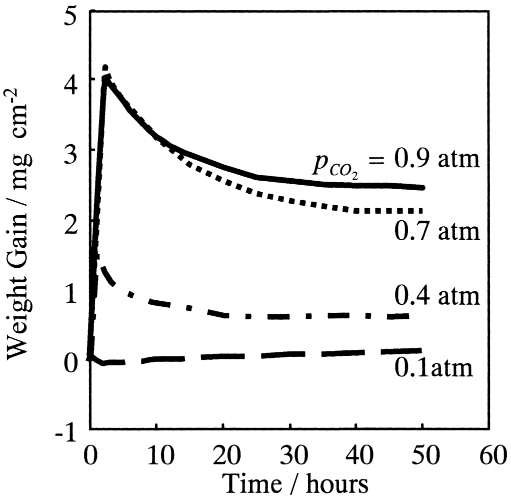

Fig. 10. Weight gain for the corrosion of SUS316L with 40 mg cm^{-2} Li/K = 62/38 carbonate melt at 923 K under 10% O_2–CO_2 (–Ar balance).

Conclusion

The high-temperature corrosion of stainless steels (SUS316L and SUS310S) in the presence of lithium-potassium eutectic carbonate and lithium-sodium eutectic carbonate was studied by thermogravimetry and the metal consumption method under a carbon dioxide-oxygen atmosphere. The corrosion of SUS316L significantly depends on the reaction conditions. There were two types of accelerated corrosions. With the carbonate coating, the corrosion rates were accelerated during the initial period of the corrosion tests below 923 K. The initial accelerated corrosion was a local corrosion, which was produced through holes in the metal specimens and occurred more clearly at higher carbon dioxide partial pressures. This corrosion could be an important concern when considering the start-up conditions of the MCFCs. Although the details of the corrosion mechanism are not clear, the higher

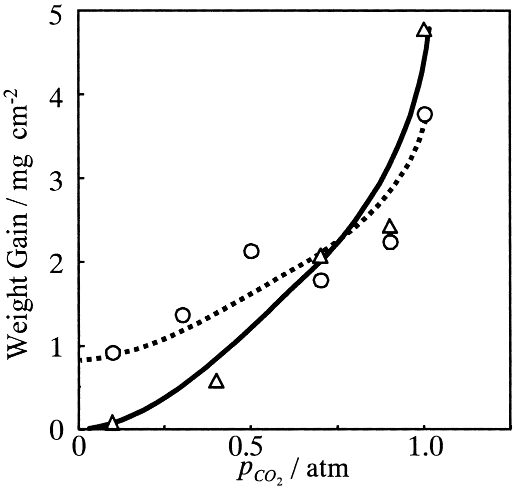

Fig. 11. Weight gain of SUS316L as a function of carbon dioxide partial pressure for 50 hours corrosion at 923 K under 10% O_2–CO_2–Ar balance.
- - ○- -: Li/Na = 52/48, 30 mg cm^{-2},
—△—: Li/K = 62/38, 40 mg cm^{-2}.

oxygen and lower carbon dioxide partial pressures for the initial corrosion are important in order to avoid accelerated corrosion.

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