HIGH TEMPERATURE CORROSION OF NICKEL COATED WITH MOLTEN ALKALI CARBONATES

Ken-ichiro Ota, Baek-un Kim, Hideaki Yoshitake and Nobuyuki Kamiya
Department of Energy Engineering, Yokohama National University
156 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

ABSTRACT
The materials durability should be improved in order to develop the molten carbonate fuel cell. The corrosion of Ni alkaline carbonate coating were measured in CO\textsubscript{2}/O\textsubscript{2} atmosphere at 873 K–1173 K. The corrosion of Ni with carbonate coating usually obeyed the parabolic rate law in CO\textsubscript{2}/O\textsubscript{2} atmosphere. The parabolic rate constant decreased with the increase of the temperature with (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3} coating. At 1073 K the hot corrosion was observed several times with (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3} coating under low CO\textsubscript{2} pressure. The hot corrosion might take place by the dissolution/reprecipitation mechanism of the NiO scale owing to the solubility gradient in the carbonate film.

INTRODUCTION
The molten carbonate fuel cell (MCFC) is favored by the fact that wide variety of fuels, such as hydrogen, hydrocarbons, carbon monoxide, and their mixtures (coal gas) can be used. The exhaust heat of the MCFC is more valuable than that of the phosphoric acid fuel cell (PAFC), since the operating temperature of the MCFC is high. The MCFC can serve as a cogeneration system. However, the durabilities of the components of the MCFC cause big problems for long time operation (1). The corrosion of the metallic materials caused by the molten carbonate is one of them. Metals are easily attacked by molten salts at high temperature and the catastrophic corrosion occasionally occurs with the presence of the thin film of molten salt on the metal that is called "hot corrosion". The hot corrosion is mostly studied with the presence of Na\textsubscript{2}SO\textsubscript{4} melt (2). The fluxing model is the predominant theory for the hot corrosion, where the solubility of the metal oxide that is formed by the corrosion reaction and the dissolution mechanism of the oxide are the important factors (2). Although the hot corrosion have been reported with the presence of molten carbonate (3–6), no paper discussed in relation to the solubility of the corrosion product that is the key factor to realize the effect of molten salt. In this study Ni was selected to the metallic material since Ni is an important component for high temperature alloys and also used as the electrode and the separator material for MCFC. The corrosion of Ni with the presence of molten...
melt under 67%CO2-33%O2 atmosphere. The corrosion reaction obeyed the parabolic rate law and the parabolic rate constants were very close to that obtained in air by Gulbransen(11). Since the results were very close to that obtained without CO2 and the corrosion rate of Ni in 100%CO2 atmosphere was so small that the weight gain could not be measured at these temperatures, the major oxidant in gas is O2 and CO2 gas does not directly affected the corrosion reaction without the presence of the carbonate melt.

1. Corrosion with Li2CO3 coating
   With the presence of carbonate film, the corrosion reaction proceeded faster. Figure 2 shows the parabolic plots of the corrosion of Ni with Li2CO3 melt coating under 67%CO2-33%O2 atmosphere at 1073 K. Except the initial period the reaction obeyed the parabolic law. The parabolic rate constants depended on the amount of coating.

   Figure 3 shows the relation between the parabolic rate constant kp and the coated amount of carbonate melt at 1073 K. The reaction rate kp increased with the small amount of the carbonate melt coating and gave a maximum of 0.12 mg2cm-4h-1 at 4 mgcm-2 coating. The reaction rate did not depend on the coating amount if the amount was larger than 10 mgcm-2.

   Figure 4 shows the parabolic plot of the weight gain of the corrosion of Ni with Li2CO3 coating of 30 mgcm-2 at the temperature range from 1023 K to 1173 K. Clearly the corrosion reaction obeyed the parabolic law from the initial period of the reaction at 1023 ~ 1123 K. At 1173 K the parabolic law was observed after 10 h.

   Figure 5 shows the cross section of the specimen after corrosion for 100 h at 1073 K. The corrosion scale had double layer and the outer layer was relatively porous.

2. Corrosion with (Li0.62K0.38)2CO3 coating
   Figure 6 shows the parabolic plot of the corrosion of Ni with (Li0.62K0.38)2CO3 coating. Other reaction conditions were same as those of Fig.2. During the initial several hours the reaction did not obey the parabolic law. During this period the amount of corrosion was 2 or 3 times larger than that with Li2CO3 coating. This might be caused by the difference of the solubilities of NiO in the carbonate melts. At this condition the solubilities of NiO are 4x10-6(mole fraction) in Li2CO3 melt and 13x10-6 in (Li0.62K0.38)2CO3 melt(10). Since the solubility of the oxide scale is higher in (Li0.62K0.38)2CO3 melt, the oxide scale that was formed during the corrosion was unstable and the corrosion reaction proceeded faster. After 60 h
carbonate was reported in few papers(7~9). Ting reported that the corrosion of Ni was accelerated with the molten carbonate coating and in O\textsubscript{2} atmosphere(8). He also reported that the molten carbonate penetrated through the oxide scale and reached the metal/oxide interface(7,8). Their results were obtained only at 923 K. In order to elucidate the hot corrosion mechanism of Ni with carbonate coating, more wide reaction conditions, such as temperature, amount of melt, gaseous compositions, etc. should be studied. In this paper the corrosion of Ni with molten carbonate coating has been studied in CO\textsubscript{2}/O\textsubscript{2} atmosphere. The results were compared with the solubility of NiO(10).

**EXPERIMENTAL**

Ni specimens 6x12 mm were cut from sheet Ni (1 mm thickness, 99.7% purity. Impurities are given in Table 1) and were polished successively with #600 - #1500 SiC abrasive papers, followed by degreasing with a neutral detergent, washing with ethanol, and drying and weighing before test.

The Ni specimens were coated with 0~60 mg/cm\textsuperscript{2} of (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3} or Li\textsubscript{2}CO\textsubscript{3} by dipping the carbonate-ethanol mixture on the metal and drying. The amount of carbonate on the metal was obtained by the weight change of Ni specimen before and after the carbonate coating. The coated specimen was placed in a reaction vessel. Before starting the corrosion test, the specimen was held at 463 K for 20 min in order to remove the remaining moisture. The weight gain of the specimen was measured and monitored continuously by TGA(Shimazu DT-40). The atmosphere was normally 67%CO\textsubscript{2}-33%O\textsubscript{2} gas mixture with the flow rate of 75 cm\textsuperscript{3}/min. To see the effect of gaseous composition, CO\textsubscript{2} pressure was changed from 10\textsuperscript{-5} to 0.85 atm and O\textsubscript{2} pressure was changed from 0.1 to 0.3 atm. The reaction temperature was from 873 to 1173 K. The reaction time was normally 100 h. After the weight measurement, the specimens were analyzed by SEM and EPMA.

**RESULTS AND DISCUSSION**

Before the corrosion study, the vaporization and the weight loss of the carbonate melt was checked. 0.238 g of (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3} was placed in a test cell and the weight change was measured for 100 h under 67%CO\textsubscript{2}-33%O\textsubscript{2} at 1073 K. The observed weight loss was less than 0.1 mg. Since the vapor pressure of Li\textsubscript{2}CO\textsubscript{3} is smaller than (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3}, the vaporization loss of Li\textsubscript{2}CO\textsubscript{3} was estimated to be also smaller than that of (Li\textsubscript{0.62}K\textsubscript{0.38})\textsubscript{2}CO\textsubscript{3}. Since the weight loss could not be detected below this temperature, the weight loss owing to the vaporization of the carbonate was neglected in this study.

Figure 1 shows the parabolic plots of the weight gain of Ni without carbonate coating...
the corrosion reaction obeyed the parabolic law.

Figure 7 shows the dependence of the parabolic rate constant on the amount of the carbonate on the specimen. The maximum reaction rate was 0.12 \( \text{mg}^2\text{cm}^{-4}\text{h}^{-1} \) at 5 \( \text{mgcm}^{-2} \) coating. Although this maximum reaction rate with (Li\text{0.62}K\text{0.38})\text{2CO3} coating is higher than that with Li\text{2CO3} coating, the difference was very small compared to the difference during the initial period. Since the corrosion reaction obeyed the parabolic law, the reaction was controlled by the diffusion of the ionic species through the oxide scale. At this stage the oxide scale was NiO for both melt coating and the diffusion rate should be same for both cases. The reaction rate did not depend on the coating amount if the coating was larger than 20 \( \text{mgcm}^{-2} \). If the large amount of the carbonate was placed on the metal, the total carbonate could not hold on the metal since the melt could easily flow away from the metal specimen. From these data the maximum amount of the melt that could hold on the metal was estimated to be 20 \( \text{mgcm}^{-2} \) in this experiment.

Figure 8 shows the parabolic plot of the corrosion of Ni at the temperature range from 873 K to 1073 K. Although the reaction obeyed the parabolic law after 60 h, something curious is the temperature dependence. In the very initial period of the reaction (<2h), the corrosion rate became larger at higher temperatures. However, the temperature dependence was reversed as the reaction proceeded and the parabolic rate constant decreased as the temperature increased. Usually the reaction rate should increase at higher temperatures. Since the reaction obeyed the parabolic law, the rate determining step is the diffusion of the ions through the scale. The diffusion path or the mechanism might be changed as the temperature changed.

Figure 9 shows the surface of the specimen after the corrosion test. At 1073 K the surface of the scale was covered by the fine crystals. On the other hand the surface of the specimen after corroded at 873 K was covered by the large crystals and the scale was looked porous. This difference might be caused by the solubility of the oxide scale. The solubility of NiO is \( 14\times10^{-6} \) and \( 46\times10^{-6} \) (mole fraction) at 1073 K and 873 K, respectively, in 67%CO2-33%O2(10). Since the solubility of the scale is high at 873 K, the large crystal can be easily formed by the dissolution-reccrystallization mechanism. If the scale is porous, the oxidant(O2) can easily diffuse through the pore that is filled with carbonate melt. This might be the reason for the inverse temperature dependence of the corrosion rate.

Figure 10 shows the Arrhenius plot of \( k_p \) for the corrosion of Ni with and without carbonate melt coating. Clearly the negative dependence of \( k_p \) on temperature is observed for (Li\text{0.62}K\text{0.38})\text{2CO3} coating. The activation energy of \( k_p \) for Li\text{2CO3} coating was 156 kJ/mol that is same as that without carbonate coating. Since the solubility of NiO in Li\text{2CO3} melt is very low compared to that in (Li\text{0.62}K\text{0.38})\text{2CO3} (10), the oxide scale that is formed during the corrosion is very similar to that
without carbonate. The corrosion reaction depended on the gaseous atmosphere, namely CO₂ pressure and O₂ pressure.

Figure 11 shows the corrosion curves under the several CO₂ pressures at 1073 K. At the CO₂ pressure above 8.5x10⁻³ atm the corrosion reaction obeyed the parabolic law and the catastrophic corrosion could not be seen. However, at the CO₂ pressure below 10⁻³ atm the corrosion reaction proceeded tremendously after the initial induction period and the hot corrosion was observed.

Figure 12 shows the dependence of the corrosion amount on the CO₂ pressure. At 1073 K the amount of corrosion becomes larger under lower CO₂ pressure because the hot corrosion takes place more easily. On the other hand the corrosion reaction obeyed the parabolic law and the hot corrosion could not be seen at 923 K.

Figure 13 shows the cross section of the corroded specimen for 100 h under CO₂ pressure of 8.5x10⁻⁵ atm at 1073 K. At this condition the hot corrosion took place and the most metal was consumed. According to the EPMA study, K was detected throughout the whole scale formed. Since K compound was not formed with Ni, the carbonate melt penetrated through the scale. This observation was same as that of previous papers(7,8). If the carbonate melt was present through the scale, the dissolution and the deposition of the oxide scale could take place throughout the scale. The hot corrosion took place more easily at higher temperature and lower CO₂ pressure. This phenomenon is closely related to the dissolution of the NiO scale to the carbonate melt. At low CO₂ pressure NiO showed the basic dissolution and the solubility increased at lower CO₂ pressure(10). In the basic dissolution region the solubility increased at higher temperatures(10). At 1073 K and low CO₂ pressure the solubility of NiO scale to the carbonate melt is larger than that at 923 K. If the dissolution reaction obeyed the basic dissolution, the solubility of NiO at the scale/gas interface was smaller than that of the metal/scale interface. At this condition the basic fluxing of the oxide scale could easily take place(2). This might be the reason for the hot corrosion at 1073 K under low CO₂ pressure. At 923K the corrosion reaction obeyed the parabolic law.

Figure 14 shows the dependence of kp on CO₂ pressure. kp clearly increased as the increase of CO₂ pressure at the pressure higher than 0.1 atm(10). At this condition the acid dissolution of NiO takes place and the solubility of NiO increased as the CO₂ pressure increased. This solubility might affect the corrosion reaction and the corrosion rate increased owing to the increase of the solubility. The corrosion rates at PO₂=0.15 are larger than those at PO₂=0.3. Usually the parabolic rate constant becomes smaller or keeps constant at the lower PO₂, since the oxidant activity decreases(12). The results of Fig.14 are reversed. Since the solubility of NiO does not depend of the O₂ pressure(10), the results can not be explained by the solubility of the oxide scale. Since kp represents the diffusivity of the ions through the oxide scale, the oxide scale that is formed at low O₂ pressure
might be more defective. In other words, the stable oxide scale could be formed more easily at higher O$_2$ pressure.

CONCLUSION

The high temperature corrosion of Ni with alkaline carbonate coating was deeply affected by the solubility of NiO that was formed on metal. In this study the parabolic rate law was observed except 1073 K under low CO$_2$ pressure. This tendency is different from that of Shores(7). Although the reason is not clear, the metallic characteristics such as impurities, grain size may affect the corrosion reaction.

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Table 1 Chemical composition of specimen (wt. ppm)

|    | Co  | Fe  | Cu  | Mn  | Al  | Ti  | Zn  | Si  |
|----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ni | 99.7% | 85  | 335 | 14  | 1320| 922 | 8   | 5   | 31  |

Fig. 1 Parabolic plots of the corrosion of Ni without molten carbonates at 923 K–1173 K under 67%CO₂-33%O₂ for 100 h.

Fig. 2 Parabolic plots of the corrosion of Ni coated with Li₂CO₃ under 67%CO₂-33%O₂ at 1073 K.
Fig. 3 Relation between the parabolic rate constant \( k_p \) and the coated amount of \( \text{Li}_2\text{CO}_3 \) at 1073 K under 67\%\text{CO}_2-33\%\text{O}_2.

Fig. 4 Parabolic plots of the corrosion of Ni coated with 35 mg/cm\(^2\) of \( \text{Li}_2\text{CO}_3 \) at 1023 K–1173 K under 67\%\text{CO}_2-33\%\text{O}_2.

Fig. 5 SEM micrograph of the cross section of the corroded Ni coated with 22 mg/cm\(^2\) of \( \text{Li}_2\text{CO}_3 \) under 67\%\text{CO}_2-33\%\text{O}_2 at 1073 K for 100h.
Parabolic plot of the corrosion of Ni coated with (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ under 67%CO$_2$-33%O$_2$ at 1073 K.

Relation between the parabolic rate constant $k_p$ and the coated amount of (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 1073 K under 67%CO$_2$-33%O$_2$.

Parabolic plot of the corrosion of Ni 32 mg/cm$^2$ of (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 873 K-1073 K under 67%CO$_2$-33%O$_2$. 
Fig. 9 SEM micrograph of the surface of the corroded Ni coated with 32 mg/cm² of $\text{(Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ under 67%CO₂-33%O₂ for 100 h.

Fig. 10 Arrhenius plots of $k_p$ for the corrosion of Ni with and without molten carbonate.
Fig. 11 TGA curves for the corrosion of Ni coated with 35–41 mg/cm² of (Li₀.₆₂K₀.₃₈)₂CO₃ under several CO₂ pressure at 1073 K.

Fig. 12 Corrosion amount of Ni coated with 35–41 mg/cm² of (Li₀.₆₂K₀.₃₈)₂CO₃ at 1073 K and 923 K as a function of CO₂ pressure for 100 h.
Fig. 13 SEM micrograph of the cross section of the corroded Ni coated with 37 mg/cm² of (Li₀.₆₂K₀.₃₈)₂CO₃ at 1073 K under P₀₂ = 8.5 x 10⁻⁵ for 100 h.

Fig. 14 Parabolic rate constant k_p of the corrosion of Ni coated with 35 mg/cm² of (Li₀.₆₂K₀.₃₈)₂CO₃ at 923 K as a function of CO₂ pressure for 75 h.