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Dependence of Ni Corrosion with a $(Li_{0.62}K_{0.38})_2CO_3$Coating on the Temperature and Atmosphere

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The corrosion of Ni coated with alkali carbonates was measured in a CO_2/O_2 atmosphere at 873—1173 K. The corrosion of Ni coated with carbonates generally obeyed a parabolic rate law under a 67% CO_2–33% O_2 atmosphere. The parabolic rate constant decreased with an increase in the temperature with a $(Li_{0.62}K_{0.38})_2CO_3$ coating under a 67% CO_2–33% O_2 atmosphere. This was explained by the solubility of NiO that was formed on Ni metal during corrosion. Hot corrosion was observed several times with $(Li_{0.62}K_{0.38})_2CO_3$ under low CO_2 pressure at 1073 K. This hot corrosion could be explained by the dissolution/reprecipitation mechanism of the NiO scale, due to the solubility gradient in the carbonate film.

The molten carbonate fuel cell (MCFC) has the advantage that a wide variety of fuels, such as hydrogen, hydrocarbons, carbon monoxide, as well as 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. Although the MCFC can serve as a cogeneration system, regarding the durabilities of the components of the MCFC cause problems long-time operation.[1] Corrosion of the metallic materials caused by molten carbonate is one such problem. Metals are easily attacked by molten salts at high temperature, and catastrophic corrosion occasionally occurs in the presence of a thin film of molten salt on the metal surface. This is called "hot corrosion". Hot corrosion is usually studied in the presence of a molten Na_2SO_4 film.[2] A fluxing model is preferred for hot corrosion, where the solubility of the metal oxide that is formed by the corrosion reaction and the dissolution mechanism of the oxide are important factors.[2] Although hot corrosion has been reported in presence of a molten carbonate film,[3—6] no discussion has been made in relation to the solubility of the corrosion product, which is the key factor related to the effects of the molten salt. In this study Ni was selected as the metallic material, since Ni is an important component for high-temperature alloys and is used in the electrodes of the MCFC. The corrosion of Ni in the presence of molten carbonate films has been reported in only a few papers.[7—9] Ting reported that the corrosion of Ni was accelerated by a molten carbonate coating in O_2 and CO_2.[8] Shores also reported on the hot corrosion of Ni, and found that molten carbonate penetrated through the oxide scale, reaching the metal/oxide interface.[7,8] However, the results were obtained only at 923 K.

In order to elucidate the high-temperature corrosion machanism of Ni coated with carbonate melts, wider reaction conditions, such as the temperature, amount of melt and gaseous compositons should be studied. In this paper the corrosion of Ni coated with carbonate melts was studied in a CO_2/O_2 atmosphere. The results were correlated with the solubility of NiO.[10]

Experimental

Ni specimens $(6\times10^{-3}\,m)\times(1.2\times10^{-2}\,m)$ were cut from sheet Ni (10^{-3} m thickness and 99.7% purity; the impurities are given in Table 1) and were polished successively with #600—#1500 SiC abrasive paper, followed by degreasing with a neutral detergent, washing with ethanol, drying and weighing before testing. 0—60×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ or Li_2CO_3 were coated onto the surface of a Ni specimen by dipping into a carbonate–ethanol mixture and drying. The amout of corbonate on the metal was determined by the weight change of the Ni specimen before and after the coating process. The Ni specimen with carbonate was placed in a gold cell. Before the corrosion test, the specimen was held at 463 K for 20 min in order to remove any remaining moisture. The weight-gain of the specimen was measured and monitored continuously by TGA (Shimadzu DT-40). The atmosphere was normally a 67% CO_2–33% O_2 gas mixture with a flow rate of 75×10^{-6} m^3 min^{-1}. To examine the effect of the gas composition, CO_2 and O_2 pressures were varied from 10^{-5} to 0.85 atm and from 0.1 to 0.3 atm, respectively. The reaction temperature was varied 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 weight loss of a carbonate melt was checked. $(Li_{0.62}K_{0.38})_2CO_3$ of 0.238×10^{-3} kg was placed in the test cell and the weight change were measured for 100 h under 67% CO_2–33% O_2 at 1073 K. The observed weight loss was less than 0.1×10^{-6} kg. Since the vapor pressure of Li_2CO_3 is smaller than that of $(Li_{0.62}K_{0.38})_2CO_3$ the vaporization loss of Li_2CO_3 was estimated to be smaller than that of $(Li_{0.62}K_{0.38})_2CO_3$. Since a weight loss could not be detected below this

Table 1. Chemical Composition of Ni Specimen (wt ppm)

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

temperature, the weight loss due to vaporization of the carbonate was neglected in this study.

Figure 1 shows weight-gain curves for the corrosion of Ni without carbonates under 67% CO_2–33% O_2 at 923—1173 K for 100 h. The corrosion reacton obeyed a parabolic rate law and the rate constants were very close to those obtained in air by Gulbransen.[11]

1. Corrosion of Ni Coated with Li_2CO_3. With the presence of a Li_2CO_3 film, the corrosion reaction proceeded faster than without only a film. Figure 2 shows the weight-gain curves obtained for the corrosion of Ni coated with Li_2CO_3 under 67% CO_2–33% O_2 at 1073 K. The reaction obeyed a parabolic rate law.

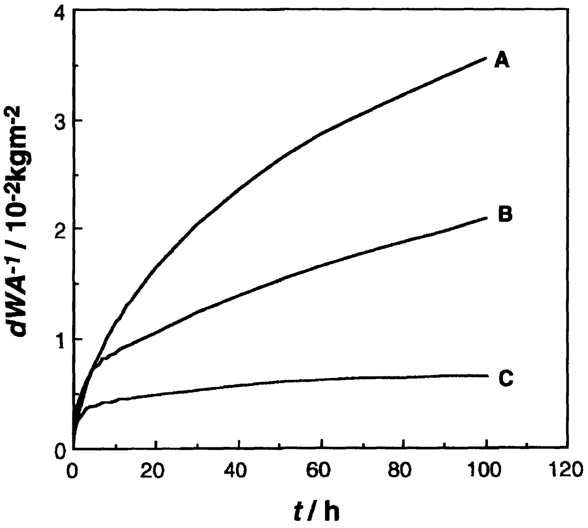


Fig. 1. Weight-gain curves for the corrosion of Ni without molten carbonates at 923—1173 K under 67% CO_2–33% O_2. A: 1173 K, B: 1073 K, C: 923K.

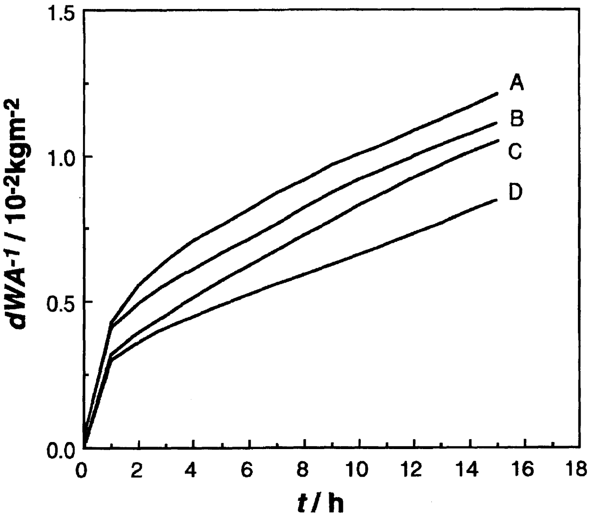


Fig. 2. Weight-gain curves for the corrosion of Ni coated with Li_2CO_3 under 67% CO_2–33% O_2 at 1073 K. Coated amount; A: 7.2×10^{-2} kg m^{-2}, B: 2.3×10^{-2} kg m^{-2}, C: 14.1×10^{-2} kg m^{-2}, D: 44.9×10^{-2} kg m^{-2}.

Figure 3 shows the relation between the parabolic rate constant (k_p) and the coated amount of Li_2CO_3 under 67% CO_2–33% O_2 at 1073 K. k_p increased with an increase in the amount of coated Li_2CO_3 up to 7×10^{-2} kg m^{-2}, and reached a maximum of 0.093×10^{-4} kg^2 m^{-2} h^{-1} at 7×10^{-2} kg m^{-2}. The reaction rate was independent of the coated amount of melt if the amount was larger than 20×10^{-2} kg m^{-2}.

Figure 4 shows the weight-gain curves for the corrosion of Ni coated with 30×10^{-2} kg m^{-2} of Li_2CO_3 over a temperature range of 1023 to 1173 K. Clearly, the corrosion reaction obeyed the parabolic rate law from the initial period of the reaction at 1023—1123 K. At 1173 K the parabolic rate law was observed after 10 h.

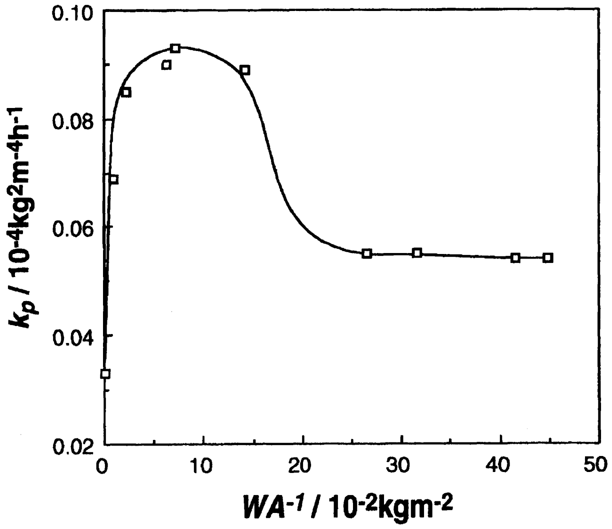


Fig. 3. Relation between the parabolic rate constant (k_p) and the coated amount of Li_2CO_3 at 1073 K under 67% CO_2–33% O_2.

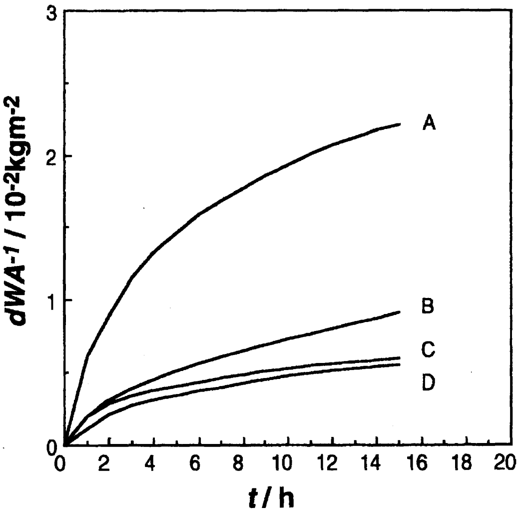


Fig. 4. Weight-gain curves for the corrosion of Ni coated with 35×10^{-2} kg m^{-2} of Li_2CO_3 at 1023—1173 K under 67% CO_2–33% O_2. Temperature; A: 1173 K, B: 1123 K, C: 1023 K, D: 1023 K.

Figure 5 shows the cross section of the corroded specimen after 100 h at 1073 K. The corrosion scale comprised of two layers. Although the inner layer was compact and had good adhesion to the metal, the outer layer was relatively porous.

2. Corrosion of Ni Coated with $(Li_{0.62}K_{0.38})_2CO_3$. Figure 6 shows the weight-gain curves for the corrosion of Ni coated with $(Li_{0.62}K_{0.38})_2CO_3$. The other reaction conditions were same as those given in Fig. 2. During the initial several hours the reaction did not obey a parabolic rate law and the amount of corrosion was 2- or 3-times larger than that with Li_2CO_3. This might have been caused by a difference in the solubilities of NiO in molten carbonate. Under these conditions, the solubility of NiO is 4×10^{-6} (mole fraction) in Li_2CO_3 melt and 13×10^{-6} in $(Li_{0.62}K_{0.38})_2CO_3$ melt.[10] Since the solubility of the oxide scale is higher in the $(Li_{0.62}K_{0.38})_2CO_3$ melt than in the Li_2CO_3 melt, the oxide scale that was formed during corrosion with $(Li_{0.62}K_{0.38})_2CO_3$ coating was more detective compared with the scale formed with Li_2CO_3 coating; the corrosion reaction with a $(Li_{0.62}K_{0.38})_2CO_3$ coating would therefore proceeded faster. After 40—60 h, the rate of uptake of oxygen became small with the growth of the scale, and the corrosion reaction obeyed the parbolic rate law.

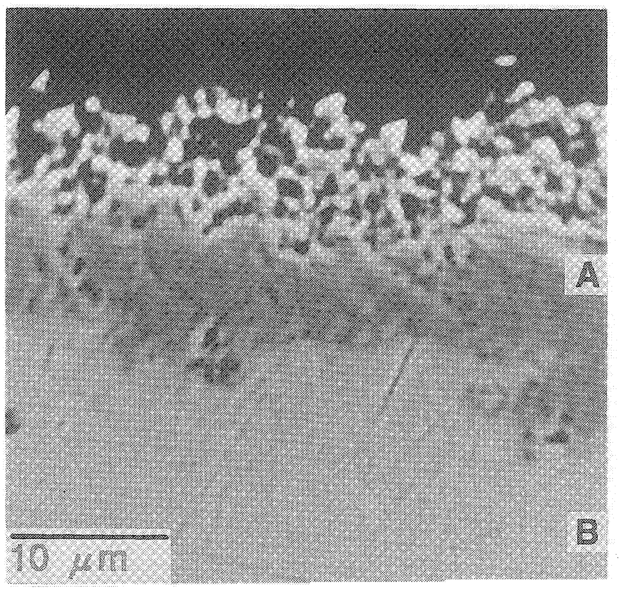


Fig. 5. SEM micrograph of the cross section of corroded Ni coated with 22×10^{-2} kg m^{-2} of Li_2CO_3 under 67% CO_2–33% O_2 at 1073 K for 100 h. A: scale, B: metal.

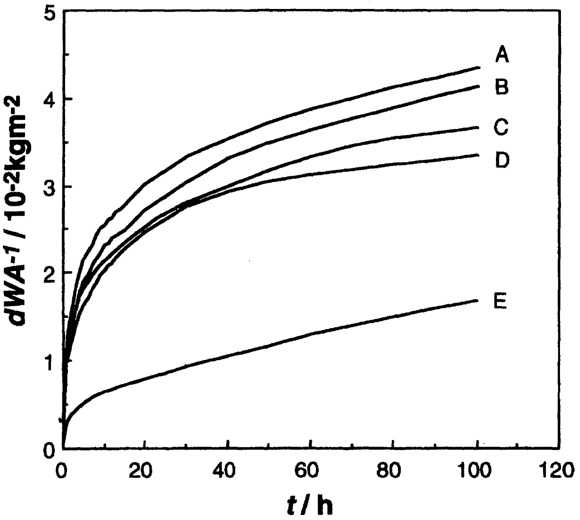


Fig. 6. Weight-gain curves for the corrosion of Ni coated with $(Li_{0.62}K_{0.38})_2CO_3$ under 67% CO_2–33% O_2 at 1073 K. Coated amount; A: 3.46×10^{-2} kg m^{-2}, B: 1.25×10^{-2} kg m^{-2}. C: 10.58×10^{-2} kg m^{-2}, D: 33.76×10^{-2} kg m^{-2}, E: 0×10^{-2} kg m^{-2}.

Figure 7 shows the relation between the parabolic rate constant and the amount of $(Li_{0.62}K_{0.38})_2CO_3$ melt coated on the specimen under 67% CO_2–33% O_2 at 1073 K. The maximum reaction rate was 0.12×10^{-4} kg^2 m^{-4} h^{-1} for a coating of 4×10^{-2} kg m^{-2}. Although this value is larger than that with Li_2CO_3, the difference is very small compared with that observed during the initial period. Since the corrosion reaction obeyed a parabolic rate law, the reacton was controlled by the diffusion of Ni ions through the oxide scale. At this stage, the oxide scale was NiO for both carbonate melts, and the diffusion rate should have been the same for both cases. The reaction rate did not depend on the coated amount when the coating was greater than 20×10^{-2} kg m^{-2}. Even if a larger amount of carbonate was coated on the metal, the total amount of carbonate was kept constant, since the excess melt easily flowed away from the metal specimen. From these data the maximum amount of the carbonate melt adhering to the

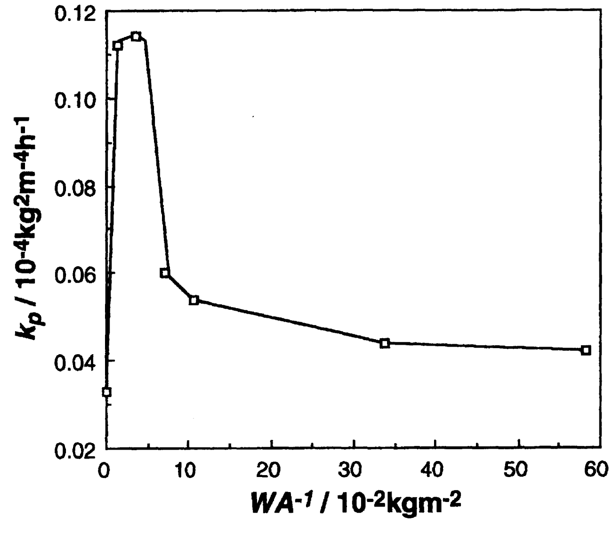


Fig. 7. Relation between the parabolic rate constant (k_p) and the coated amount of $(Li_{0.62}K_{0.38})_2CO_3$ at 1073 K under 67% CO_2–33% O_2.

metal was estimated to be 20×10^{-2} kg m^{-2}. In order to avoid any effect due to the coated amount, most of the measurements were conducted with coatings greater than 25×10^{-2} kg m^{-2}.

Figure 8 shows the weight-gain curves for the corrosion of Ni coated with 32×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 873—1073 K under 67% CO_2–33% O_2. Although the reaction obeyed the parabolic rate law after 60 h, the temperature dependence is curious. During the initial period of the reaction (<2 h), the corrosion rate became higher at higher temperatures. However, the temperature dependence reversed as the reaction proceeded, and the parabolic rate constant decreased as the temperature increased. Normally, the reaction rate should increase at higher temperatures. Since the reaction obeyed a parabolic law, the rate-determining step might be the diffusion of ions through the scale. The diffusion path of the ions might have changed with temperature.

Figure 9 shows the surface of the specimen after the corrosion test. At 1073 K the surface of the scale was covered by fine crystals and the scale was dense. On the other hand the surface of the specimen at 923 K was covered by large crystals and the scale looked porous. This difference might have been caused by a difference in the solubility of the NiO scale at the two temperatures. The solubility of NiO is 14×10^{-6} and 46×10^{-6} (mole fraction) at 1073 and 873 K, respectively, under 67% CO_2–33% O_2.[10] Because the solubility of the NiO scale is higher at 873 K, a large crystal can be easily formed by the dissolution–recrystallization mechanism. If the NiO scale is porous, the oxidant (O_2) can easily diffuse through the pores that are filled with the carbonate melt. This might be the cause of the inverse temperature dependence of the corrosion rate on the temperature.

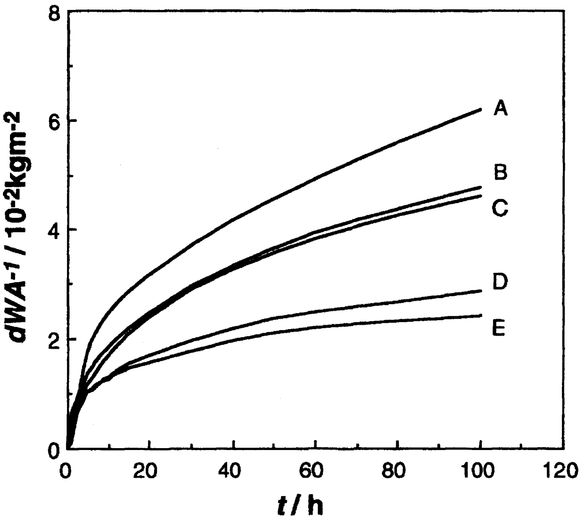
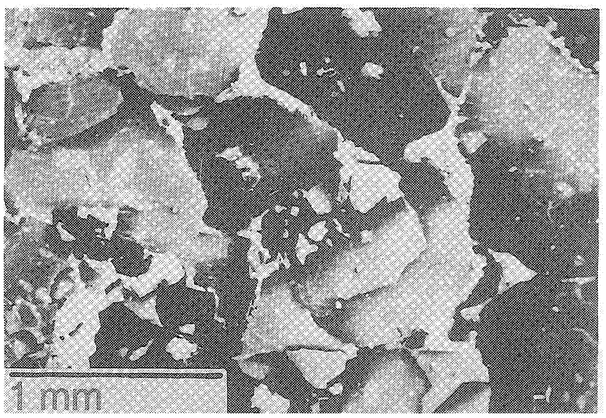
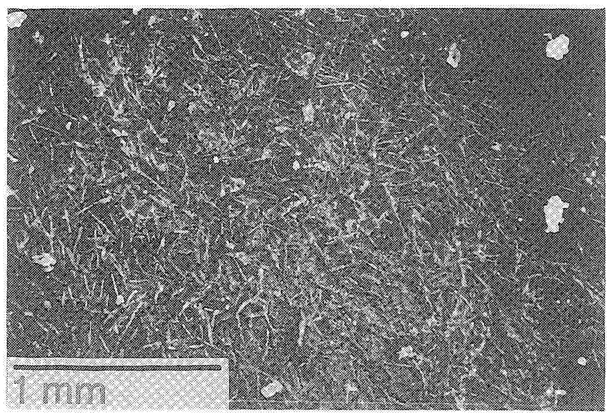


Fig. 8. Weight-gain curves for the corrosion of Ni coated with 35×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 873—1073 K under 67% CO_2–33% O_2. A: 873 K, 8: 923 K, C: 973 K, D: 1023 K, E: 1073 K.



(a) 923 K



(b) 1073 K

Fig. 9. SEM micrograph of the surface of corroded Ni coated with 32×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ under 67% CO_2–33% O_2 for 100 h.

Figure 10 shows Arrhenius plots of k_p for the corrosion of Ni with and without molten carbonates under 67% CO_2–33% O_2 at 873—1173 K. Clearly, a reverse dependence of k_p on the temperature was observed for the $(Li_{0.62}K_{0.38})_2CO_3$ coating. The activation energy of k_p for the Li_2CO_3 coating was 156 kJ mol^{-1}, the same as that without molten carbonate. Since the solubility of NiO in the Li_2CO_3 melt is very low compared with that in $(Li_{0.62}K_{0.38})_2CO_3$,[10] the oxide scale that is formed with a Li_2CO_3 coating is similar to that without a carbonate melt.

The corrosion reaction depended on the components of the gaseous atmosphere, namely the CO_2 and O_2 pressures. Figure 11 shows the weight-gain curves for the corrosion of Ni coated with 35—41×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ under various CO_2 pressures at 1073 K. At CO_2 pressures above 8.5×10^{-3} atm the corrosion reaction obeyed the parabolic rate law, and no catastrophic corrosion was observed. However, at

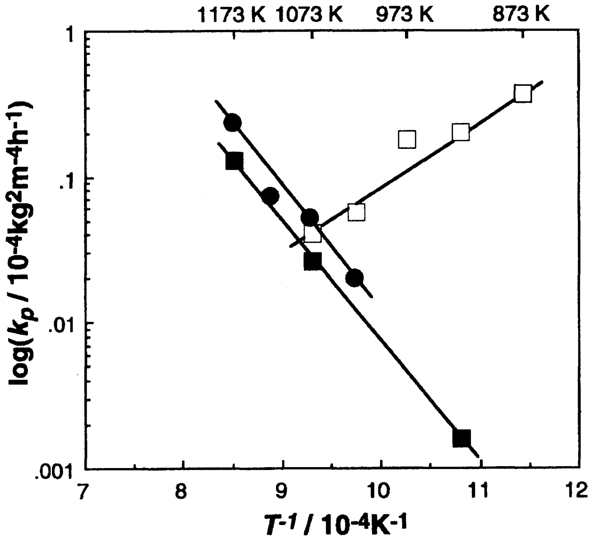


Fig. 10. Arrhenius plots of k_p for the corrosion of Ni with and without molten carbonates under 67% CO_2–33% O_2. □: 35×10^{-2}kg m^{-2} $(Li_{0.62}K_{0.38})_2CO_3$, ●: 35×10^{-2}kg m^{-2} Li_2CO_3, ■: without melt.

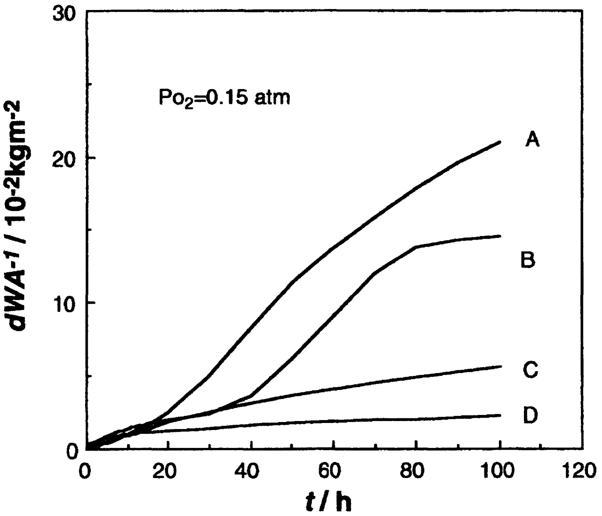


Fig. 11. Weight-gain curves of Ni coated with 35—41×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ under P_{O_2}=0.15 atm at 1073 K. P_{CO_2}; A: 8.5×10^{-5} atm, B: 1.0×10^{-3} atm, C: 8.5×10^{-3} atm, D: 1.0×10^{-1} atm.

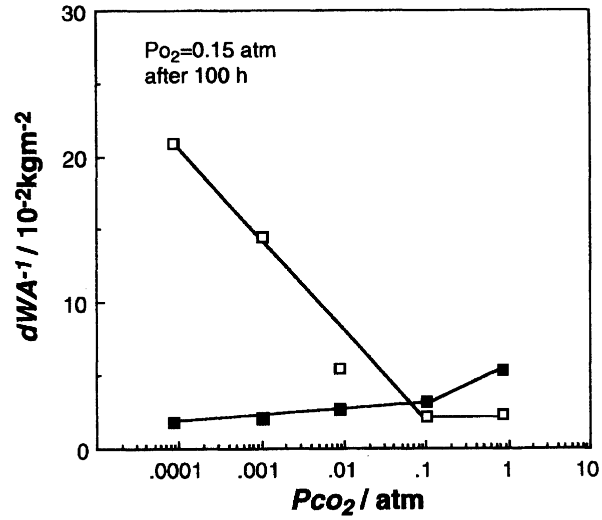


Fig. 12. Dependence of the amount of corrosion of Ni coated with 35—41×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 1073 and 923 K for 100 h on P_{CO_2}. □: 1073 K, ■: 923 K.

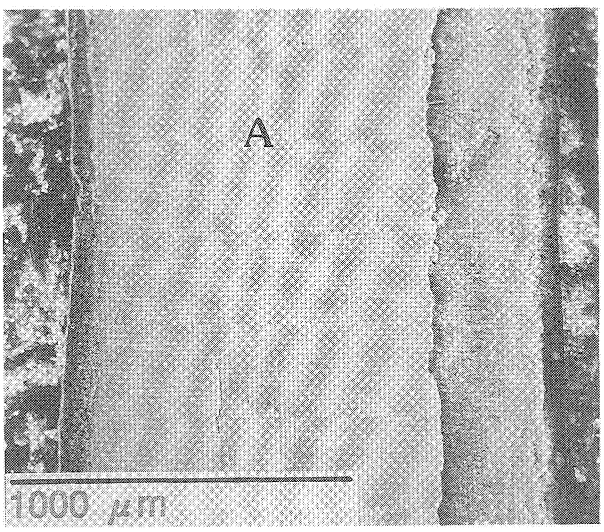


Fig. 13. SEM micrograph of the cross section of corroded Ni coated with 37×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 1073 K under P_{CO_2}=8.15×10^{-5} atm (P_{O_2}=0.15 atm) for 100 h. A: metal.

CO_2 pressures below 10^{-3} atm, the corrosion reaction proceeded rapidly after the initial induction period and hot corrosion was observed.

Figure 12 shows the dependence of the amount of corrosion on the CO_2 pressure with 35—41×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 923 and 1073 K. At 1073 K the amount of corrosion increased at lower CO_2 pressures, because hot corrosion takes place more easily. On the other hand, the corrosion reaction obeyed the parabolic rate law at 923 K, and no hot corrosion was observed.

Figure 13 shows the cross section of the corroded specimen after 100 h under a CO_2 pressure of 8.5×10^{-5} atm (P_{O_2}=0.15 atm) at 1073 K. Under these conditions hot corrosion took place and the metal was almost consumed. According to an EPMA study, K was present throughout the entire scale. Since the K compound was not formed with Ni, the carbonate melt is thought to have penetrated through the scale. This observation is the same as those mentioned in previous papers.[7,8] If the carbonate melt was present throughout the scale, a dissolution and deposition of the oxide scale could take place throughout the scale. Hot corrosion took place more easily at higher temperature and at lower CO_2 pressures. This tendency is closely related to the dissolution of the NiO scale in a molten carbonate melt. At

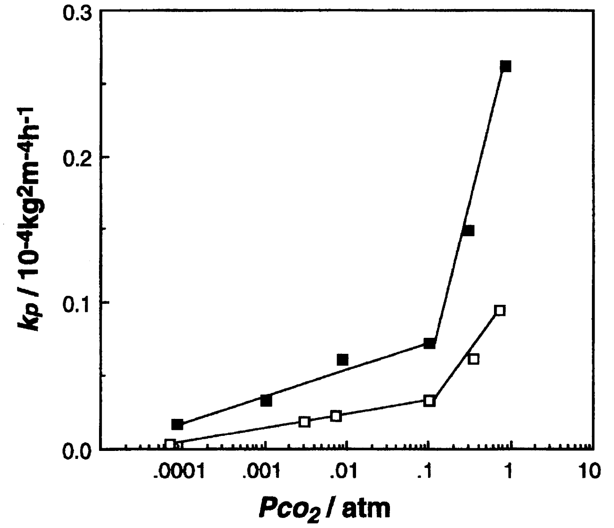


Fig. 14. Dependence of the parabolic rate constant (k_p) for the corrosion of Ni coated with 35×10^{-2} kg m^{-2} of $(Li_{0.62}K_{0.38})_2CO_3$ at 923 K on P_{CO_2}. ■ : P_{O_2}=0.15 atm, □ : P_{O_2}=0.3 atm.

low CO_2 pressure NiO shows a basic dissolution mechanism and the solubility of NiO increases with decreasing CO_2 pressure.$^{10)}$ In the basic dissolution region the solubility of NiO increases at higher temperatures.$^{10)}$ At 1073 K and low CO_2 pressure, the solubility of the NiO scale in the carbonate melt is higher than at 923 K. Since the CO_2 potential at the scale/gas interface is higher than at the metal/scale interface, the melt at the metal/scale interface is more basic than that at the scale/gas interface. If the dissolution reaction occurred by a basic dissolution mechanism, the solubility of NiO at the scale/gas interface would be lower than at the metal/scale interface. Under such conditions, 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 CO_2 pressure. At 923 K the solubility of NiO was too low to generate fluxing of the oxide scale, and the corrosion reaction obeyed the parabolic rate law.

Figure 14 shows the dependence of k_p on CO_2 pressure at 923 K. The value of k_p clearly increased with increasing CO_2 pressure at pressures higher than 0.1 atm, where acid dissolution of NiO takes place and the solubility of NiO increases as the CO_2 pressure increases.$^{10)}$ This change in solubility might affect the corrosion reaction; the corrosion rate is considered to have increased due to the increase in the solubility of NiO. The corrosion rates at $P_{O_2}=0.15$ atm were larger than that at $P_{O_2}=0.3$ atm. Usually, the parabolic rate constant becomes smaller, or remains constant, at lower P_{O_2} if the activity of oxidant in the gas decreases.$^{12)}$ However, a reverse relation was obtained, as shown in Fig. 14. Since the solubility of NiO is independent of the O_2 pressure,$^{10)}$ the results can not be explained by the solubility of the oxide scale. Since k_p is proportional to the diffusivity of the ions throughout the oxide scale, the oxide scale formed at low O_2 pressure might contain more defects. In another words, a stable oxide scale could be formed more easily at higher O_2 pressure.

Conclusion

The high-temperature corrosion of Ni coated with alkali carbonates was greatly affected by the solubility of NiO formed on Ni. From the reported results, the solubility of the scale in the carbonate melt was confirmed to be one of the important factors for studying the durability of metallic materials in the presence of a carbonate melt.

In this study the corrosion reaction obeyed the parabolic rate law and no hot corrosion was observed, except for at 1073 K under low CO_2 pressure. This tendency is different from that reported in previous papers.$^{7)}$ Although the reason is not yet clear, the material characteristics, such as impurities and grain size, may affect the corrosion reaction.

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