

Molten Carbonate-Induced Hot Corrosion of Nickel

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The accelerated oxidation of pure nickel in the presence of a molten carbonate mixture has been studied in O₂ and CO₂-containing atmospheres. The oxidation rate of nickel with carbonate coatings was at least four orders of magnitude faster than that without salt coatings. The extent of oxidation, in terms of unit area weight gain, depended on both the amount of carbonate mixture coatings and the gas atmosphere. The unit area weight gain due to oxidation increased with increasing amounts of salt coatings up to a certain value. These observations suggest that the termination of nickel oxidation results from the exhaustion of either the salt coatings or metallic nickel. Porous and particulate oxide products were observed from scanning electron microscopic (SEM) examinations. The energy-dispersive analysis of x-rays (EDAX) shows that no salt remains on the specimen surface after the oxidation experiment.

KEY WORDS: Hot corrosion; nickel; TGA; kinetics; mechanism.

INTRODUCTION

In the development of molten carbonate fuel cells, the hot corrosion of the electrodes induced by the molten carbonate electrolyte in both oxidizing and reducing environments has been the major concern in the selection of electrode materials.^{1,2} To evaluate the material behavior in fuel-cell environments, commercially available stainless steels and chromium-plated stainless steels have been tested in both the reducing (anode) and the oxidizing (cathode) gas atmospheres.² It was observed that commercial stainless steels

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corroded in both environments, but deteriorated faster in the anodic reducing condition. Chromium-plated stainless steels, on the other hand, showed good corrosion resistance in the anodic reducing atmosphere. The catastrophic corrosion of chromium-plated steels, however, occurred in the cathodic oxidizing atmosphere. The corrosion attack led to oxide spallation and dissolution of the protective chromium oxide.³ To increase the corrosion resistance in both anode and cathode gas atmospheres, bimetallic sheets have been suggested for use as both the electrodes and the separators. This results in the use of nickel-clad stainless steel bipolar sheets in fuel cells.⁴ The objectives of the present study are to explore the oxidation resistance of nickel in a simulated cathodic environment of molten carbonate fuel cells and to contribute to the development of the corrosion mechanism of nickel and other alloys in hot-corrosion environments.

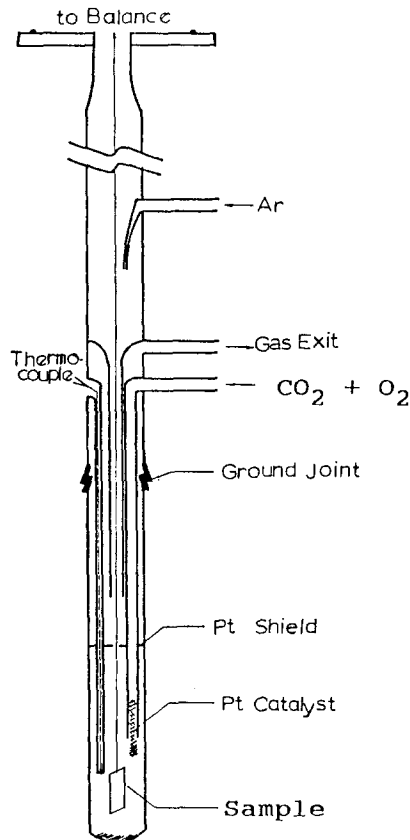


Fig. 1. Experimental apparatus.

EXPERIMENTAL

Apparatus

A thermogravimetric analysis (TGA) system was used to determine the oxidation kinetics under a controlled temperature and atmosphere. The system consists of a reactor, a Cahn C-1000 thermobalance, a Leeds and Northrup Model Speedomax 15-Pen recorder, a Marshall furnace, a Eurotherm temperature controller, and a gas train. In the gas train, gases were dried in drying columns with anhydrous phosphorus pentoxide before entering the capillary flowmeters. Gases of known flow rates from the capillary flowmeters were mixed in the mixer, led into the reactor, and blown on top of the specimen. The detailed drawing of the quartz reactor is shown in Fig. 1. The specimen was suspended with a quartz fiber onto the Cahn C-1000 thermobalance. The weight of the specimen was continuously monitored during each experiment and recorded with the Leeds and Northrup recorder. The temperature of the specimen was measured continuously with an S-type thermocouple placed near the specimen surface and monitored by the recorder. It has been observed that there was no temperature difference between the specimen surface and the tip of the recording thermocouple during the calibration. The furnace temperature was controlled by a Model 984 Eurotherm PID controller, such that during each experiment the specimen temperature was kept to within $\pm 1^\circ\text{C}$ of the desired temperature.

Sample Preparation

High-purity nickel foil ($>99.9\%$ pure) with a thickness of 0.025 mm was purchased from Johnson & Matthey, Inc. The nickel foil was cut into approximately 1×1 cm coupons, and a small suspension hole was punched out near one end of the coupon. All nickel coupons were cleaned by acetone ultrasonically and weighed before being coated with the carbonate mixture. In the early experiments, the sample surface area was determined by measuring the dimensions. Since the variation of the nickel-foil thickness is small (undetectable with a micrometer), the surface area calculated from the dimensions agreed very well with the area calculated from the sample weight, density, and thickness. In the later experiments, therefore, the surface area was determined only by the weight of samples. The solution of the carbonate mixture was made by dissolving 1.40 g of Li_2CO_3 and 1.60 g of K_2CO_3 in 300 cc distilled water in a spray bottle. Therefore, the solution consisted of a $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ mixture with a molar ratio of 62:38. Both sides of the nickel coupons were coated with the carbonate mixture by spraying this solution on the coupons in an oven at 90°C . The amount of carbonate mixture coated on each sample was carefully controlled.

Experimental Procedures

The salt-coated coupon was suspended in the TGA reactor and flushed with the reaction gas for at least 20 min at room temperature before each experiment. The preheated furnace was then raised to a preset position. Through this arrangement, the specimen in the reactor was brought up to the experimental temperature, 660°C, in less than 10 min. Most of the experiments were conducted in a gas atmosphere of 50 v/o CO₂ + 50 v/o air. A few experiments were conducted in pure Ar, pure CO₂, or air. To minimize the thermal fluctuation of the specimen-weight reading, the flow rate of the reaction gases was maintained to be at least 100 cc/min. This corresponds to a linear flow rate of at least 16 cm/min. At the end of each experiment, the furnace was quickly lowered down to expose the entire reactor to the ambient environment while maintaining the flow of the reaction gases. Normally, the specimen temperature dropped to below 100°C within 5 min.

Analysis

A number of analyses have been carried out for each specimen. First, the amount of water-soluble salt remained on the specimen after the experiment was determined. This residual salt was removed by soaking the specimen in cold distilled water for 5–10 min. The weight difference of the specimen before and after soaking in water gave the amount of the residual salt. Any trace amount of spalled scales in the solution was retrieved by filtering the solution. The weight of filtered and dried solid was included in the final sample weight. The actual net weight gain of each specimen was determined by subtracting the weight of the residual salt from the total weight gain. The crystal structure of the corrosion product was characterized by a Philip x-ray diffractometer, and the microstructure was examined using a Cambridge A-600 Scanning Electron Microscope (SEM). The chemistry of the surface product was analyzed using an Energy Dispersive Analysis of x-ray (EDAX) device attached to the SEM.

RESULTS

Since the main purpose of this study is to examine the effect of salt coatings on the oxidation characteristics of nickel, samples with various amounts of coatings were exposed to a number of different environments, including pure argon, pure CO₂, air, and CO₂/air mixture at 1:1 volumetric ratio. The amount of salt coatings on the samples varied from 0 mg/cm² to 1.12 mg/cm². Table I summarizes the experimental results. The reaction rates listed in this table were determined from the kinetics curves 5 min

Table I. The Unit Area Net Weight Gain,^a Net Oxygen Pick-Up, Reaction Rate, and Residual Salt for Various Conditions

Atmosphere	Coatings (mg/cm ²)	Reaction time (Hr)	Weight gain (mg/cm ²)	Oxygen pick-up (mg/cm ²)	Reaction rate (mg/cm ² /min)	Residual salt (mg)
Ar	0.99	12	0.00	0.00	—	1.91
CO ₂	1.12	48	0.57	0.26	10 ⁻⁴	1.16
Air	0.00	0.5	0.03	0.03	—	—
Air	1.00	0.5	1.67	1.27	0.14	0.55
CO ₂ /air	0.05	2	1.09	1.06	—	0.00
CO ₂ /air	0.09	3	1.23	1.18	—	0.00
CO ₂ /air	0.09	6	1.24	1.19	—	0.00
CO ₂ /air	0.15	2	1.97	1.90	—	0.04
CO ₂ /air	0.19	2	2.01	1.92	—	0.20
CO ₂ /air	0.25	4	2.50	2.34	—	0.18
CO ₂ /air	0.27	6	2.72	2.57	—	0.00
CO ₂ /air	0.30	3	2.88	2.71	—	0.00
CO ₂ /air	0.38	2	2.67	2.55	—	0.54
CO ₂ /air	0.50	2.5	2.76	2.64	—	0.56
CO ₂ /air	0.00	48	0.08	0.08	—	—
CO ₂ /air	0.10	48	1.42	1.36	0.68	0.00
CO ₂ /air	0.26	48	2.63	2.49	1.08	0.00
CO ₂ /air	0.27	48	2.74	2.59	—	0.00
CO ₂ /air	0.52	48	2.91	2.62	0.76	0.00
CO ₂ /air	0.64	48	3.03	2.68	1.26	0.00
CO ₂ /air	1.05	48	3.22	2.64	1.13	0.05

^aThe weight gain was determined after the coatings, if any remained, were washed away.

after reaching the experiment temperature. For the salt-coated samples, the oxidation behavior of all 2 to 6-hr tests were similar to that of 48-hr tests. No oxidation rate, thus, was calculated for any 2- to 6-hr experiments.

Pure Ar Atmosphere

The specimen was coated with 0.99 mg/cm² salt. After being tested for 12 hr in pure Ar atmosphere, no detectable weight gain was observed. Visual examination shows that the salt remained on the specimen surface after the reaction. X-ray and SEM examinations show no reaction on the surface. This experiment reveals that (a) the salt alone does not react with nickel, and (b) the decomposition of the salt in the inert atmosphere is minor.

Pure CO₂ Atmosphere

The specimen was coated with 1.12 mg/cm² salt. After being tested for 48 hr in pure CO₂ atmosphere, the sample weight gain was only 0.57 mg/cm².

The SEM result (Fig. 2a) shows that oxide products are in the form of spherical grains. Very small portions of the specimen surface appeared to have maintained the original nickel surface due to the incomplete reaction. Weight loss was observed after soaking the reacted specimen in distilled water. This indicates that salt remained on the sample at the end of the experiment. However, the EDAX result (Fig. 3b) of the washed specimen shows only a nickel peak and no chemical ingredient of the salt. It is suggested that a portion of the salt has reacted with nickel and oxygen to form alkaline oxides which are dissolved in nickel oxide and, in the mean time, CO_2 was released as a result of the reaction. The concentration of the alkaline oxides was so small that EDAX with a lower detection limit of about 1% failed to detect them. The remaining salt is believed to have

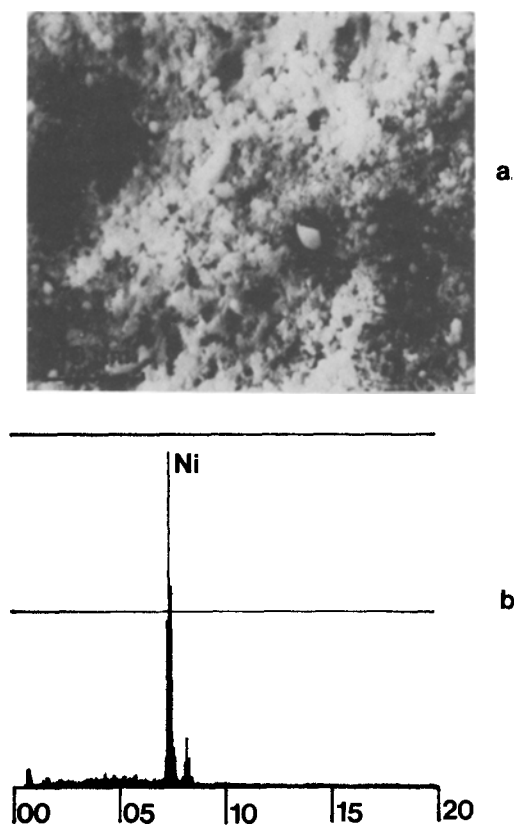


Fig. 2. (a) SEM photograph and (b) EDAX patterns of the sample coated with 1.12 mg/cm^2 salt and reacted in pure CO_2 atmosphere.

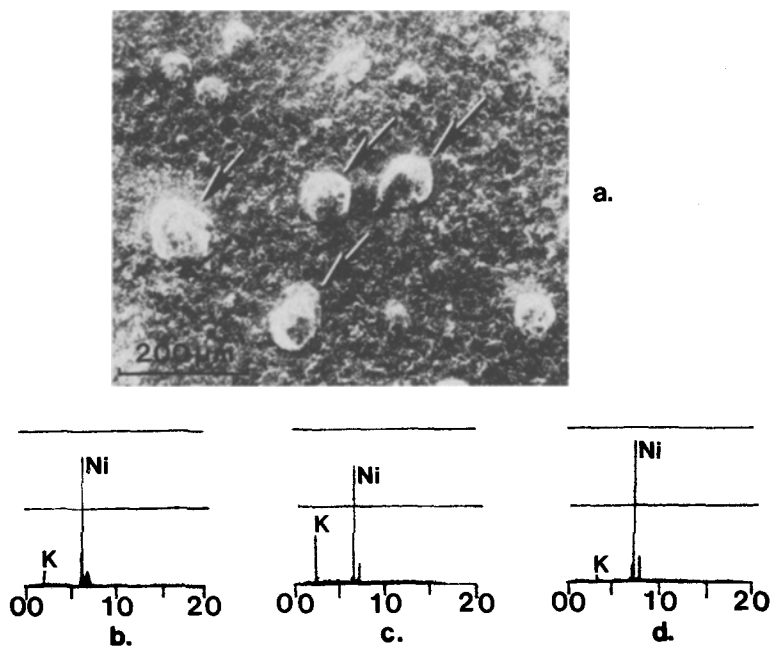


Fig. 3. SEM and EDAX analyses of the sample coated with 1.00 mg/cm² salt and reacted in air. (a) SEM photograph, (b) EDAX analysis of the bulk sample surface, (c) EDAX analysis of one of the spheres indicated by arrows, and (d) EDAX patterns of the area outside the spheres.

migrated inward to the interface between unreacted nickel and the oxide layer, as to be discussed later. Since the entire amount of alkaline oxides in carbonate salt for more heavily coated samples could be accounted, both Li₂O and K₂O were considered not volatile in this study. As shown in Table I, the reaction rate was only 10⁻⁴ mg/cm²min. Such a slow reaction can be realized since the oxygen available was limited. The possible oxygen source could result from the following equilibrium reaction,



or the oxygen impurity (less than 10⁻³ atm.) in CO₂. From thermochemical data,⁵ the oxygen partial pressure of the above reaction at 660°C was calculated to be $P_{\text{O}_2} = 1.91 \times 10^{-8}$ atm. At such a low oxygen partial pressure, the reaction rate was expected to be slow. It was found that even after 48 hr of experiment, the reaction was incomplete and still continuing.

Air-only Atmosphere

The specimen was coated with 1.00 mg/cm² salt and tested for 48 hr in air. The net specimen weight gain was 1.67 mg/cm². Although there was

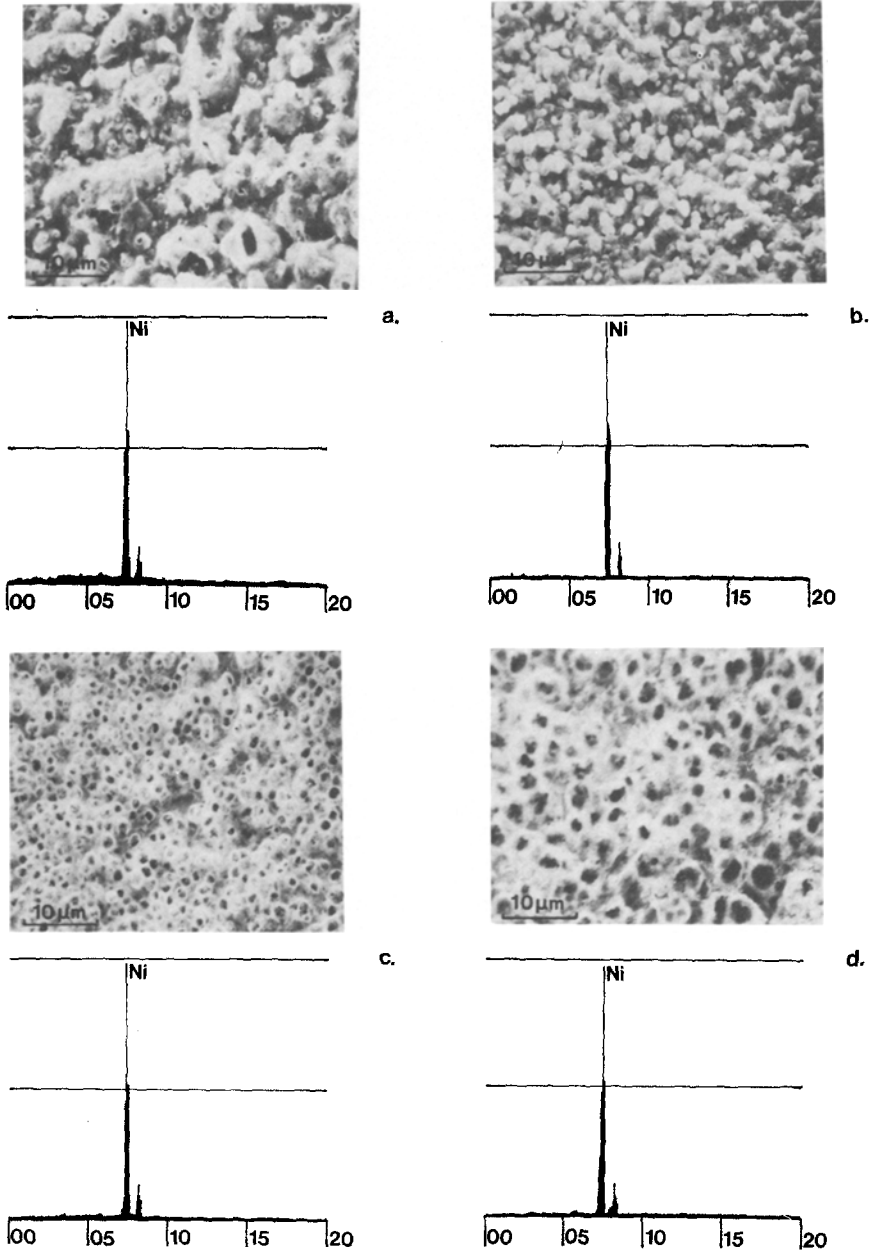


Fig. 4. Surface morphology and EDAX analysis of the samples reacted in CO_2 -air atmosphere: (a) 0.10 mg/cm^2 ; (b) 0.19 mg/cm^2 ; (c) 0.26 mg/cm^2 ; (d) 0.64 mg/cm^2 ; and (e) 1.05 mg/cm^2 coatings.

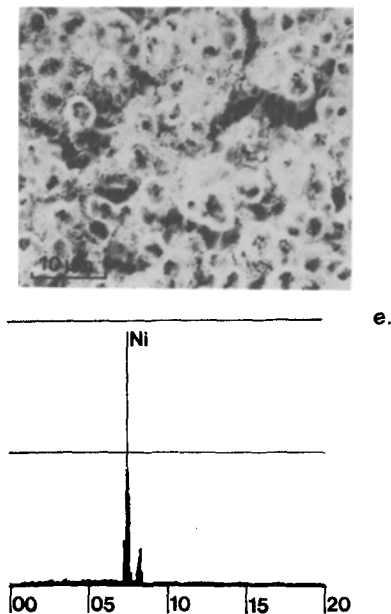


Fig. 4. Continued.

oxygen in the reaction zone, the experimental result from the TGA kinetics curve shows that the extent of oxidation was limited. The reaction rate was $0.14 \text{ mg/cm}^2/\text{min}$, a rate faster than that in the pure CO_2 oxidation but slower than that in the CO_2 -air mixture by a factor of at least five (Table I). This indicates that both O_2 and CO_2 are necessary ingredients to form the proper atmosphere for rapid oxidation. The SEM and EDAX results are shown in Fig. 3. It appears that the reaction product was porous. Salt was found on the specimen surface after the reaction, as pointed out by the arrows in Fig. 3.

CO_2 -Air Atmosphere

In this condition, the oxidation rate of the nickel specimen coated with salt was much faster than those without salt coatings. Compared to those in pure air, the reaction rate in the mixed-gas atmosphere was about an order of magnitude higher (Table I). However, there is no correlation between the reaction rate and the amount of salt deposits. Spallation of the oxide scale was obvious with visual observations. The surface morphologies of the oxide scales of selected samples are shown in Fig. 4. It appears that the lower the amount of the salt coatings, the finer the oxide particles. All oxide scales formed were porous.

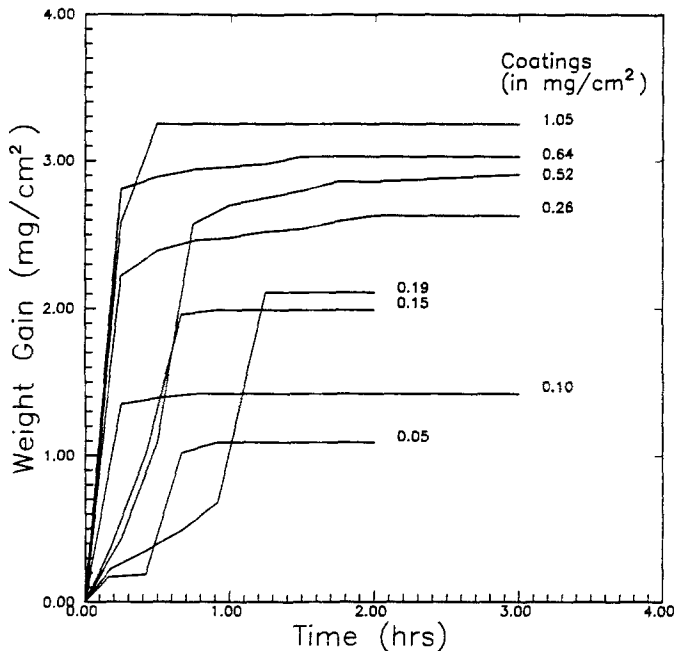


Fig. 5. The net weight gain per unit area as a function of the reaction time.

Figure 5 shows the weight gain as a function of the reaction time. Some experiments exhibited incubation periods. However, once the reaction started, the oxidation rate was so fast that the reaction appeared to have been completed in ~ 30 min. After this stage, the sample weight change tended to cease. As shown in Table I, the final net weight gain is proportional to the initial amount of salt deposit. A plot showing the curve of the net weight gain per unit area vs. the amount of salt is given in Fig. 6. The data in this figure may be grouped into two regions as shown. In region I, the net weight gain increases as the amount of salt increases. In region II, although the amount of salt increases further, the increase in the net weight gain was only minor. Such a small increase in the net weight gain with increasing salt coatings in region II is equal to the weight of alkaline oxides in the excess carbonate salt coatings. In a separate study (J. M. Ting and R. Y. Lin, unpublished observations), the saturation of net weight gain exhibited in region II was not observed when thicker (one order of magnitude thicker) nickel coupons were used. As shown in Fig. 7, the metallic nickel can be observed from the cross section of the reacted thick sample. This indicates that the saturation phenomenon was due to the exhaustion of the metallic nickel.

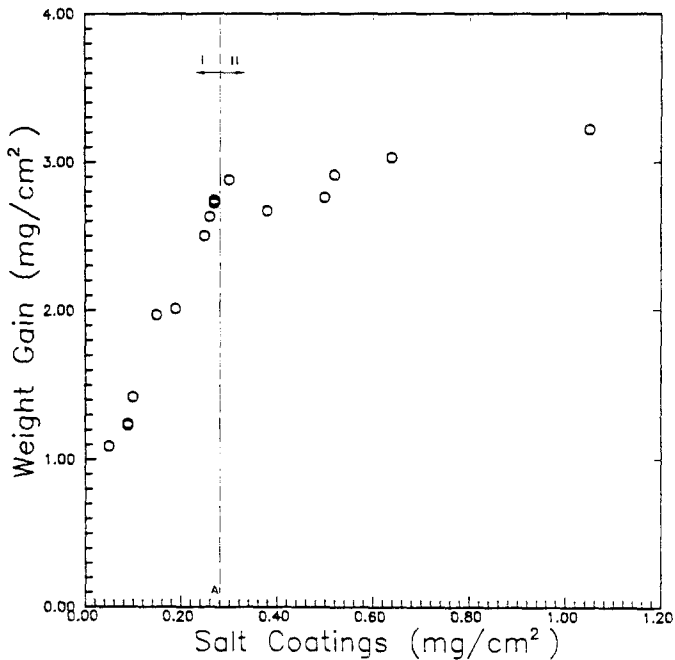


Fig. 6. The net weight gain per unit area as a function of the amount of salt coatings.

Table I also shows that for the specimens tested for 48 hr, there was no residual salt left on the specimens. However, for those samples tested for only 2–4 hr, although reactions had been completed, residual salt was detected. In general, the amount of the residual salt increased with increasing amount of coatings for experiments of the same duration. The EDAX analysis on the reacted coupon surface of unwashed specimen with 0.25 mg/cm² salt coatings, as shown in Fig. 8, indicates that there was no salt existing on the specimen surface. However, Table I shows that there was 0.18 mg salt left on this sample. It is believed, therefore, that salt has “migrated” toward the substrate and “mixed” with the oxides; but due to the porous nature of the oxide, the salt was washed out when the specimens were soaked in water. To further prove that the salt “migrated” toward the substrate, EDAX was used to monitor one of the salt ingredients, K, inside the oxide product. This was done on the inner surface of the oxide scale of a corroded specimen. These specimens were coated with 0.8, 1.2, and 1.6 mg/cm² salt, respectively, before the experiment. It was found that indeed there was K inside the oxide scale (Fig. 9).

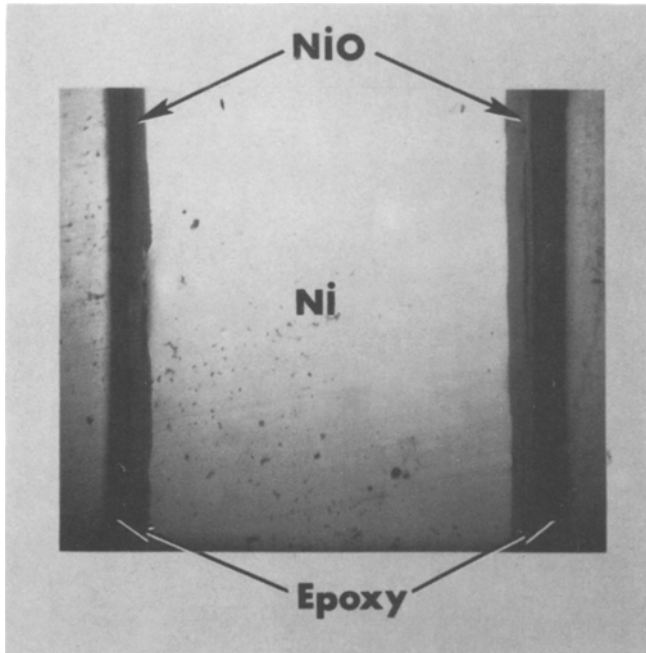


Fig. 7. SEM micrograph of the cross section of a corroded thick nickel sample.

From the SEM surface morphology of coupons tested with salt coatings, it was observed that oxidation products evenly covered the sample surface. This suggests that salt coatings homogeneously spread over the entire sample surface during the experiments. To further verify the wetting characteristics of the salt on the sample surface, a few experiments were carried out with only one side of the sample surface being coated with the salt. It was found that the salt crept from the coated side to the other uncoated side. Some other experiments were designed to examine whether the melt vaporized. In these experiments, a nickel coupon without a salt coating was placed, in parallel, next to a heavily coated ($>1.5 \text{ mg/cm}^2$) nickel coupon. The distance between these coupons was maintained to $<1 \text{ mm}$. After 24-hr experiments at 660°C , no reaction was detected on the uncoated coupon. This indicated that the salt did not vaporize to any significant extent.

DISCUSSION

A total of six different oxidation conditions were used in this study. They are (a) argon atmosphere with salt coatings, (b) pure CO_2 atmosphere

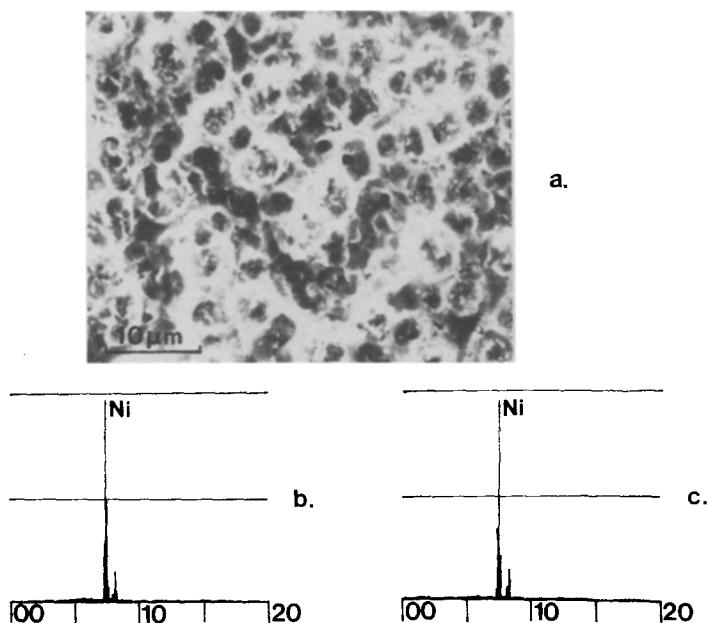


Fig. 8. Oxidized samples before soaking in distilled water. (a) A SEM photograph, (b) and (c) the EDAX analysis on the surfaces of two different samples similarly tested.

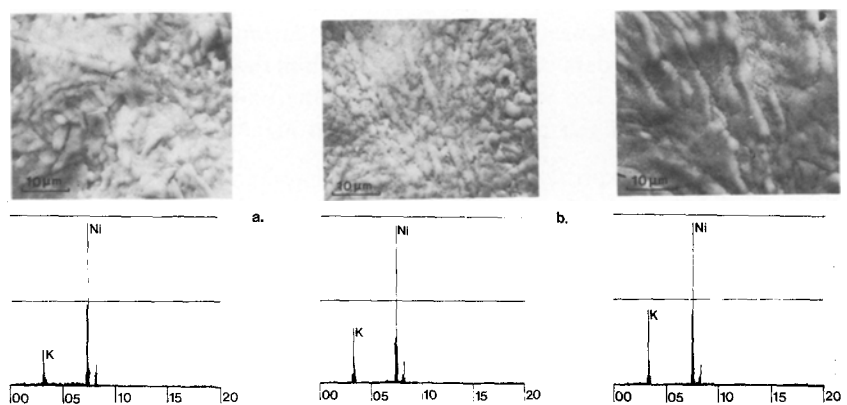


Fig. 9. SEM photograph and EDAX analysis showing that a salt ingredient, K, was found in the inner surface of the oxide scale of samples with various coatings. (a) 0.8 mg/cm², (b) 1.2 mg/cm², and (c) 1.6 mg/cm² coatings.

with salt coatings, (c) air atmosphere without salt coatings, (d) air atmosphere with salt coatings, (e) CO₂-air mixture without salt coatings, and (f) CO₂-air mixture with salt coatings. The results from this study on the hot corrosion of nickel in the molten eutectic Li-K carbonates may be summarized as follows.

1. Without salt coatings, the oxidation of nickel in either air or CO₂-air mixture was negligible. Oxidation in such a condition formed a protective NiO layer which prevented the nickel from further oxidation.
2. In argon with salt-coated samples, no oxidation was observed apparently due to the lack of oxygen. The decomposition of salt was minor, and there was no reaction between salt and nickel.
3. In pure CO₂ with salt-coated samples, moderate oxidation of nickel was observed. The reaction was retarded by the limited amount of oxygen in the reactor. This small amount of oxygen might come from either the dissociation of the carbon dioxide or the oxygen impurity in the carbon dioxide gas.
4. As the amount of oxygen in the reactor increased e.g., in the case of the air atmosphere, the reaction rate also increased. However, although there was enough oxygen in the air, the reaction was still limited compared with the case where both CO₂ and air were present. This indicated that a proper gaseous environment is necessary for catastrophic hot corrosion to occur. In this study, it was observed that in a 50 v/o air + 50 v/o CO₂ atmosphere, the molten salt indeed induced accelerated corrosion of nickel.
5. The catastrophic hot corrosion of nickel coated with salt occurred in a 50/50 mixture of CO₂-air. The oxidation rate in such a case was several orders of magnitude faster than that of samples without salt coatings. The weight gain due to the oxidation depended on the amount of salt coatings as shown in Fig. 6.

A model to explain the hot corrosion phenomena is the salt fluxing mechanism.⁶⁻⁸ This model states that the catastrophic corrosion of a material occurs when the protective oxide layer of the material dissolves in molten salt on its surface. The dissolved oxides gradually diffused outward to the salt-gas interface and re-precipitate near the interface as porous oxides. In this model, the molten salt acts only as a fluxing medium where oxides can dissolve in and migrate through.

Based on this model, hot corrosion will continue regardless of the amount of salt presented on the sample surface. This is contrary to the results from this study in which the extent of the hot-corrosion reaction of nickel was observed to depend on the amount of salt coatings to a certain

limit. The observations made in this study suggest that the role of molten salt during hot corrosion is something other than only a fluxing medium. Salt, in fact, is consumed during the oxidation reaction. It is believed that a hot-corrosion mechanism would have to consider the reaction between molten salts and oxides.

As shown in Fig. 6, the weight gain increases with increasing coatings in region I. With more salt present, there was more weight gain, and the oxidation proceeded to a greater extent. When the amount of salt coatings increased to that of point A in Fig. 6, the oxidation of nickel was complete or, in other words, metallic nickel was exhausted. At heavier salt deposits i.e., in region II, there was no further weight gain due to oxygen pick-up. The x-ray diffraction patterns of the samples in region II show only NiO (hcp structure) in the product (Fig. 10). The small increase in the net weight corresponded to the extra amount of alkaline oxides as the residual of the decomposed carbonates. In order to illustrate the net weight gain of only the oxygen pick-up, Fig. 11 plots the net weight gain minus the corresponding amount of alkaline oxides as a function of the amount of salt coatings. It clearly shows that in region II, the net oxygen pick-up is a constant. It is to be noted that the net oxygen pick-up of nickel in the presence of salt

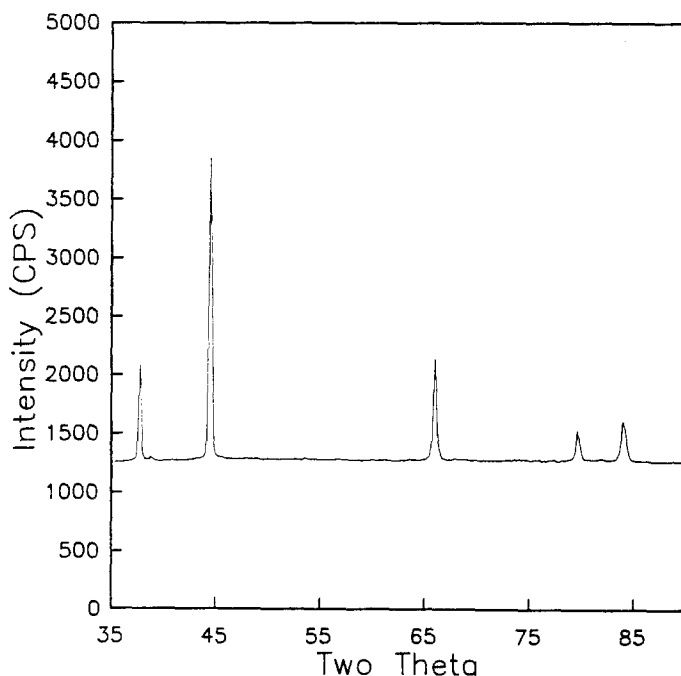


Fig. 10. X-ray diffraction patterns of a sample in region II of Fig. 7.

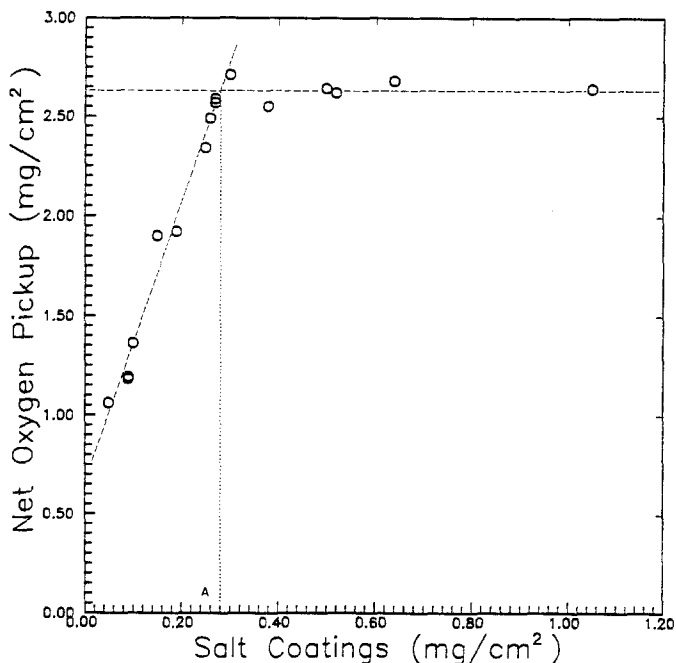


Fig. 11. The net oxygen pick-up per unit area vs. the amount of salt coatings.

and CO₂-air mixture corresponds to a formula of NiO_{0.857}. Such a highly oxygen-deficient formula, although surprising, is rather consistent in this study. This seems to suggest that nickel oxide, similar to nickel sulfide, may be stable in the form of Ni₃O₂ or Ni₄O₃, particularly in the presence of alkaline carbonates.

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