

Corrosion of Iron Coexisting with Molten Sodium Hydroxide and Sodium Peroxide

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(Received December 20, 2001)

Liquid sodium is used in new energy conversion systems such as fast breeder reactors and sodium-sulfur batteries. Liquid sodium forms high-temperature molten salts once it is exposed to air by reactions with oxygen or moisture. These molten salts might cause the severe corrosion of metals. In this study, the high-temperature corrosion of iron was studied in the presence of sodium salt using thermogravimetry in an air-simulated atmosphere. The corrosion reaction with coexisting NaOH obeyed a parabolic rate law. On the other hand, severe corrosion occurred with coexisting Na₂O₂. The corrosion reaction changed from a parabolic rate law to a linear rate law as the amount of melt increased, because the dissolution on the corrosion of the corrosion layer would increase with the amount of melt. Since the oxidation ability of Na₂O₂ is not as high as that of O₂, dissolution of an oxide scale on iron would be the main reason for severe corrosion.

Liquid sodium will be used for new energy systems, such as fast breeder reactors (FBRs) and sodium-sulfur batteries because sodium metal has a low melting point, high heat and electrical conductivities, and a low electrochemical potential. Sodium is an active chemical, especially in the presence of oxygen or water. In the case of a sodium leakage incident in a FBR, the liquid sodium would form molten salts (NaOH, Na₂O₂, Na₂O, etc.) together with heat once it is exposed to air, which might cause severe corrosion of metallic materials.¹ The corrosion rate generally increases with increasing temperature, regardless of the coexistence of molten salts.² In many cases, the corrosion rate increases with the coexistence of molten salts. Most of the molten salts have low corrosion activity, themselves, compared to that of oxygen. The solubility of the corrosion scale should be considered in evaluating the stabilities of metals with the coexistence of molten salt. This might be the most important factor, where the amount of molten salt may affect the corrosion reactions. When a large amount of molten salt coexists, the corrosion scales dissolve easily. However, the diffusion of oxygen (oxidant) through the molten salt is decreased. When a small amount of molten salt coexists, the corrosion mechanism is complicated. This is because the corrosion scale is soluble in the salt, and thus an oxidant can be provided smoothly. Severe corrosion that is enhanced by molten salt is called "hot corrosion".^{3–6}

In order to analyze the corrosion reactions of metals, oxidants should be considered. Generally, oxygen in air is an oxidant.⁷ NaOH and Na₂O have a smaller ability each as an oxidant for corrosion. The oxidation ability of Na₂O₂ should be

lower than that of oxygen in air, because Na₂O₂ forms in the reaction between Na and air.

Huber investigated the high-temperature corrosion of metals, simulating sodium leakage from a FBR. He observed that the sodium caught fire, and the temperature of the metal pan rose to 1373 K after leakage at 873 K. The metal was corroded, especially sheathed thermocouples.⁸ Newman investigated the corrosion of steels with coexisting NaOH at 1063–1273 K. The corrosion reaction followed a parabolic rate law, and the existence of water and Na₂O accelerated the corrosion.⁹ However, the high-temperature corrosion of metal with coexisting sodium compounds is not very clear.

In this study, to facilitate greater safety in using sodium metal as a heat medium, the high-temperature corrosion of iron with the coexisting sodium compounds, NaOH and Na₂O₂, was investigated.

Experimental

High-purity (99.99%) Fe sheets were used as specimens. The major impurities in the specimens are listed in Table 1. Sodium compounds were NaOH (purity 96%) and Na₂O₂ (Merck Japan, purity 95%), which were the products of sodium combustion.

An Fe sheet was cut into a rectangular shape of 6×6×1 mm and polished with emery paper (#400–#1500). After the specimen was degreased and dehydrated by acetone, it was weighed with an electric microbalance. Both sodium compounds of 1–500 mg cm⁻² coexisted on the Fe specimens in a nitrogen gas-filled dry box. The sample was put in an Au–Pd cell (Fig. 1) and placed in a thermobalance (Shimadzu TGC-41). The cell, the Fe specimen,

Table 1. Impurities in Specimen (Mass ppm)

	C	Si	Mn	Cu	Ni	Cr	O	N
99.99% Fe	11	< 20	< 2	< 2	2	< 2	430	< 5

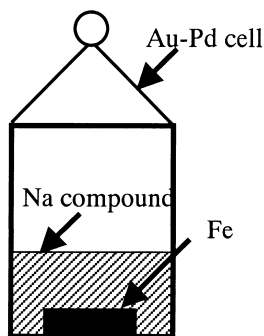


Fig. 1. Measurement cell for thermogravimetry.

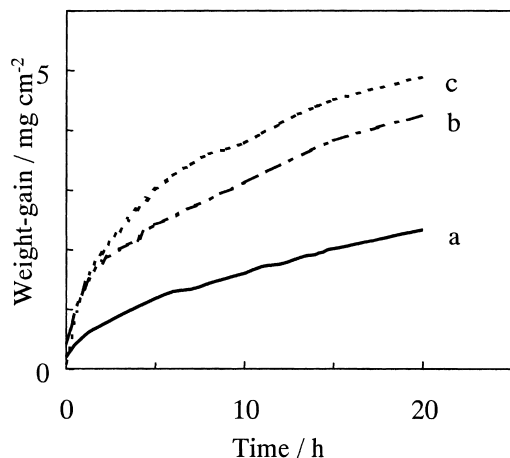
and the sodium compound were weighted together by the thermobalance.

Corrosion tests were performed by thermogravimetry at 823 K under a simulated air N_2 - O_2 gas mixture to simulate the corrosion of metals under sodium leakage. The total pressure was 1 atm and the total gas flow rate was 50 mL min^{-1} . The weight change due to the corrosion reaction was measured continuously using the thermobalance. The temperature was increased from room temperature to 473 K at 30 K min^{-1} , and was then held for 30 min to undergo dehydration. After the dehydration period, the temperature was increased to 823 K at a rate of 30 K min^{-1} and the corrosion test was started. Under this condition, the evaporation of sodium compounds was too little to affect the weight change.

After the corrosion test, the surface of a specimen was analyzed by X-ray diffraction. A cross section of the specimen was observed using a scanning electron microscope (SEM) and an electron probe X-ray microanalyzer (EPMA).

Results and Discussion

Weight-gain curves of Fe with 40 mg cm^{-2} of the sodium compound coating at 823 K under $N_2/O_2 = 80/20$ are shown in Fig. 2. The horizontal axis is the time after reaching 823 K, and the vertical axis is the weight-gain over the weight at 473 K. About 12 minutes were required from 473 K to 823 K. The weight-gain of Fe corroded with the sodium compound was

Fig. 2. Oxidation of Fe with or without sodium compound at 823 K. a: without, b: 40 mg cm^{-2} NaOH, c: 40 mg cm^{-2} Na_2O_2 .

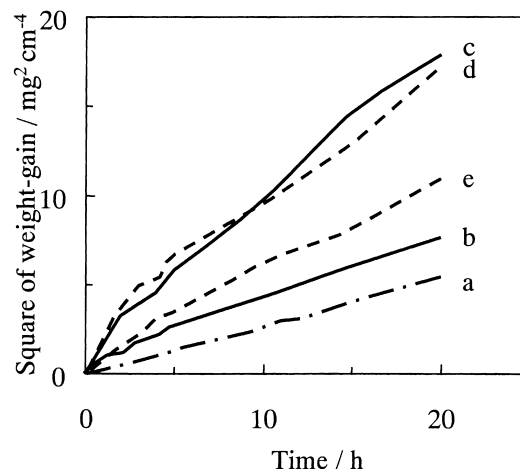
larger than that without the sodium compound. If the corrosion protection layer were stable, the corrosion of the metal would not be accelerated. The dissolution of the layers caused the layer to become unstable, and the oxidant could permeate to the metal interface smoothly. In the case of NaOH and Na_2O_2 coexisting on Fe, the weight-gain might be larger than that without the sodium compounds.

The Na_2O_2 melt contains peroxide ion (O_2^{2-}), which is an oxidizing agent, but the ability for oxidation is smaller than that of oxygen, because Na_2O_2 is an oxidized agent of sodium by oxygen in air. Oxygen would be most effective for corrosion.

The dissolution rate of the corrosion protection layer in the melt and the permeability of oxygen in the melt film are important factors in hot corrosion. The dependence of Fe corrosion on the amount of sodium compound has now been investigated. Weight-gain curves of Fe corroded with NaOH at 823 K under $N_2/O_2 = 80/20$ are shown in Fig. 3. The vertical axis is the square of the weight change, and the horizontal axis is time. The square of the weight-gain with NaOH was proportional to time. The corrosion obeyed a parabolic rate law whose rate-determining step is the diffusion of a reactant through the corrosion protection layer.¹⁰ With NaOH, the corrosion rates during the initial few hours were higher than those after, in spite of the constant corrosion rate without NaOH. During the initial period, the dissolution of a corrosion product would affect the corrosion rate. The parabolic rate constant, which is the slope of the curves in Fig. 3, was highest at 40 mg cm^{-2} . In this region, NaOH film on Fe would not be uniform, and the corrosion would be accelerated by an increase of the effective metal surface area.

Weight-gain curves of Fe corroded in the range of 20 to 500 mg cm^{-2} of Na_2O_2 at 823 K under $N_2/O_2 = 80/20$ are shown in Fig. 4. The weight-gain at 20 hours increased with the amount of Na_2O_2 . Especially, the weight-gain with as large an amount of Na_2O_2 as 500 mg cm^{-2} was much larger than that with NaOH.

X-ray diffractions of Fe after a 20-hour corrosion test are shown in Fig. 5. The condition of the corrosion tests was ei-

Fig. 3. Oxidation of Fe with NaOH depending on the amount of melt at 823 K. a: without, b: 10 mg cm^{-2} , c: 40 mg cm^{-2} , d: 50 mg cm^{-2} , e: 100 mg cm^{-2} .

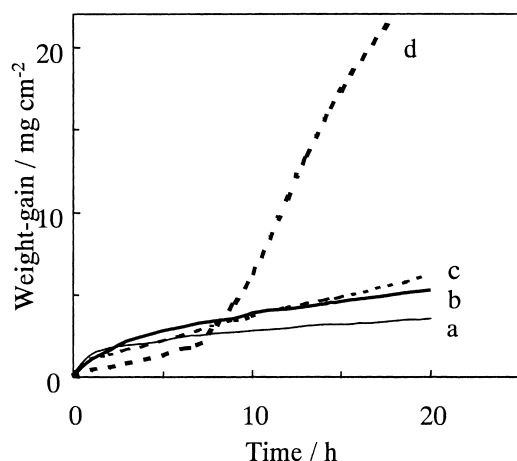


Fig. 4. Oxidation of Fe with Na_2O_2 depending on the amount of melt at 823 K. a: 20 mg cm^{-2} , b: 60 mg cm^{-2} , c: 100 mg cm^{-2} , d: 500 mg cm^{-2} .

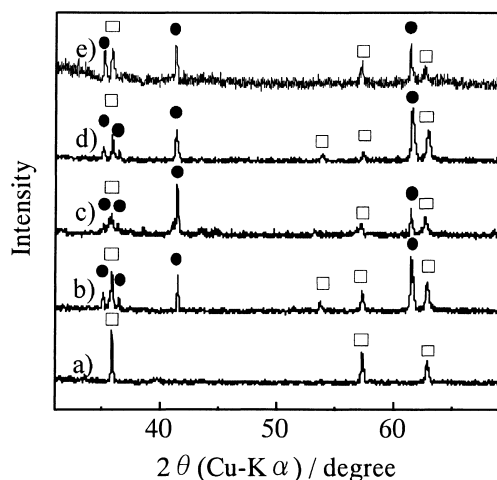


Fig. 5. X-ray diffraction of the Fe with NaOH and Na_2O_2 after 20 h at 823 K. a) dry, b) 40 mg cm^{-2} NaOH, c) 500 mg cm^{-2} NaOH, d) 40 mg cm^{-2} Na_2O_2 , e) 500 mg cm^{-2} Na_2O_2 ; $\square$: Fe_3O_4 , $\bullet$: $\alpha\text{-NaFeO}_2$.

ther without a sodium compound, with 40 mg cm^{-2} of NaOH, with 500 mg cm^{-2} of NaOH, 40 mg cm^{-2} of Na_2O_2 , or with 500 mg cm^{-2} of Na_2O_2 . Only Fe_3O_4 was detected as the corro-

sion product for dry corrosion, while $\alpha\text{-NaFeO}_2$ was also detected for corrosion with NaOH or Na_2O_2 , regardless of the amount of NaOH or Na_2O_2 .

SEM images of the cross section of Fe after a 20-hour corrosion test are shown in Fig. 6. The thicknesses of the corrosion layers formed at 20 hours with 40 mg cm^{-2} NaOH, 40 mg cm^{-2} Na_2O_2 , and 500 mg cm^{-2} Na_2O_2 were 23.8, 18.8, and $18.4 \mu\text{m}$, respectively, while the weight-gains were in the opposite order i.e., 4.24, 4.88, and 25.0 mg cm^{-2} , respectively. The weight-gain corresponds to the weight of oxygen that reacted with Fe. When a large amount of Na_2O_2 was present, the weight-gain was large, but the corrosion layer did not grow. The dissolution reaction of the corrosion layer in the melt would cause this phenomenon. When a large amount of Na_2O_2 existed on Fe, the reaction mechanism obeyed a linear rate law and severe corrosion took place. This is because the corrosion layer did not prevent the oxidation reaction of Fe because of dissolution of the layer in the melt. The solubility of the corrosion layer in a Na_2O_2 melt might be larger than that in NaOH, taking into account the difference in the corrosion behavior of Fe with these Na compounds.

An EPMA analysis after a 20-hour corrosion test with 500 mg cm^{-2} of Na_2O_2 is shown in Fig. 7. The corrosion obeyed a linear rate law for this condition (Fig. 4-d), and the corrosion products were Fe_3O_4 and $\alpha\text{-NaFeO}_2$ according to X-ray diffraction. The corrosion layer had a double-layer structure. The outer layer was sodium iron oxide, and the inner layer was iron oxide, as determined by EPMA. The outer layer would then be $\alpha\text{-NaFeO}_2$, and the inner layer would be Fe_3O_4 . This structure is similar to the corrosion product with coexisting molten carbonate.¹¹

The logarithm of the weight-gain of Fe corroded in the range of 10 to 100 mg cm^{-2} of Na_2O_2 as a function of the logarithm of time is shown in Fig. 8. The slope changes from 1/2 to 1 as the amount of Na_2O_2 increases. The corrosion reaction obeyed a parabolic rate law in the case of 20 mg cm^{-2} of Na_2O_2 , but obeyed a linear rate law for 100 mg cm^{-2} of Na_2O_2 . The corrosion protection layer would not grow, and severe corrosion, which obeyed the linear rate law, occurred with as large an amount of Na_2O_2 as 100 mg cm^{-2} .

Weight-gain curves of Fe corroded with 160 and 500 mg cm^{-2} Na_2O_2 for 40 hours at 823 K are shown in Fig. 9. The weight-gain rate decreases after the initial linear weight-gain. The time when the weight-gain rate decreased is defined as the

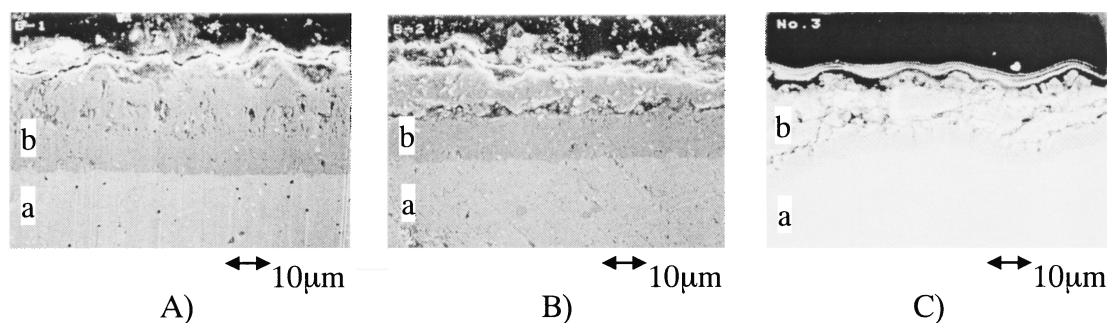


Fig. 6. Cross section of Fe after 20 h corrosion tests with sodium compounds at 823 K. A) 40 mg cm^{-2} NaOH, B) 40 mg cm^{-2} Na_2O_2 , C) 500 mg cm^{-2} Na_2O_2 ; a: metal b: corrosion layer.

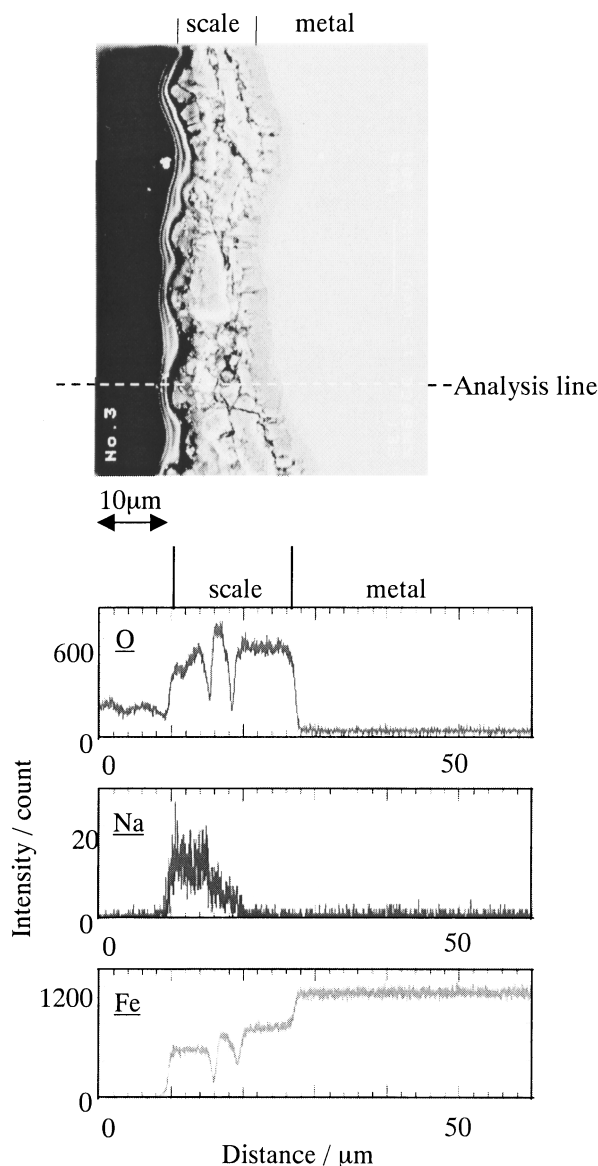


Fig. 7. Line analysis of cross section of Fe with 500 mg cm⁻² Na₂O₂ at 823 K after 20 h.

“turning point”. Before the turning point, the corrosion reaction obeyed a linear rate law, but it obeyed a parabolic rate law after the turning point. The relationship between the weight-gain at the turning point and the amount of Na₂O₂ is shown in Fig. 10. The weight-gain at the turning point was proportional to the amount of Na₂O₂. The ratio of the weight-gain at the turning point to the amount of the Na₂O₂ was 5.2 mg cm⁻² weight-gain to 100 mg cm⁻² Na₂O₂. The reason why the reaction mechanism changed would be saturation of the metal oxide in the melt or a melting-point increase due to a melt composition change with dissolution of the metal. Before the turning point, the corrosion layer would not grow, because the corrosion product would dissolve in the melt. The corrosion reaction then obeyed a linear rate law. After the turning point, the corrosion layer would grow, because the dissolution of the corrosion product had stopped. The corrosion reaction then obeyed the parabolic rate law. The dissolution quantity of the

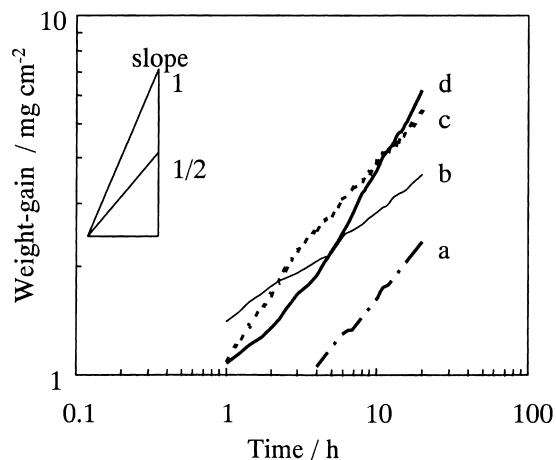


Fig. 8. Oxidation of Fe with Na₂O₂ depending on the amount of melt at 823 K. a: without, b: 20 mg cm⁻², c: 60 mg cm⁻², d: 100 mg cm⁻².

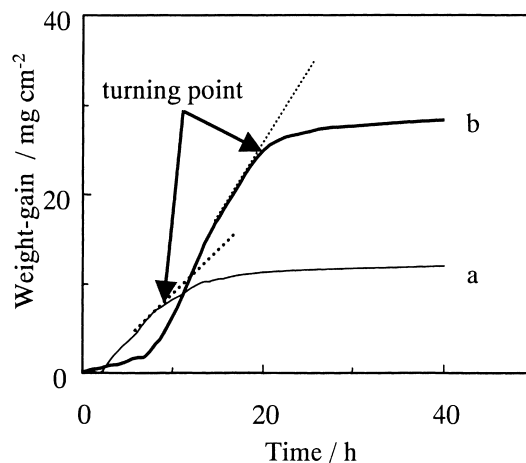


Fig. 9. Oxidation of Fe with Na₂O₂ depending on the amount of melt at 823 K. a: 160 mg cm⁻², b: 500 mg cm⁻².

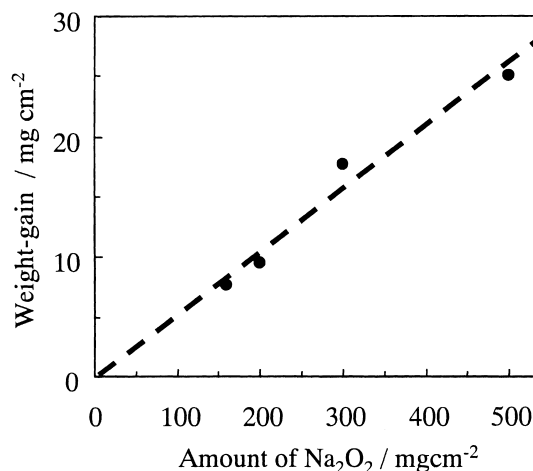


Fig. 10. Dependence of the weight-gain at the turning point for Fe on the amount of Na₂O₂ at 823 K.

corrosion product would be an important factor in corrosion with Na_2O_2 .

The ratio of the inner-layer thickness to the total corrosion-layer thickness for cases with 500 mg cm^{-2} of Na_2O_2 was 41% for a 20-hour corrosion test, while it was 59% for a 40-hour corrosion test. The 20-hour period nearly corresponded to the turning point, while the 40-hour period was after the turning point. This indicates that the inner layer grew selectively after the turning point. With 40 mg cm^{-2} of NaOH , the ratio of the inner-layer thickness was 71% after a 20-hour corrosion test. When the inner-layer ratio was higher, the corrosion tended to obey a parabolic rate law. The diffusion control layer of a parabolic rate law would be the inner layer that was made of Fe_3O_4 , and the outer layer that was of $\alpha\text{-NaFeO}_2$ would be a porous layer.

The solubility and the dissolution rate of the corrosion layer in the sodium compounds, and the diffusion coefficient of iron in the corrosion layer may affect this corrosion. However, these physical properties would not be available in the literature. Therefore, it would be not possible to perform quantitative analysis using these factors. The parabolic rate law can be described as follows in differential form:

$$\partial w / \partial t = k / w, \quad (1)$$

where w , t , and k are the amount of the corrosion layer, the time, and the rate constant that is determined by the diffusion coefficient, respectively. If the dissolution of the corrosion layer is affected, the corrosion could be described as follows in the differential form:

$$\partial w / \partial t + \partial s / \partial t = k / w, \quad (2)$$

where $\partial s / \partial t$ is the dissolution rate that can be determined by the solubility, the dissolution rate, and the amount of melt. The weight-gain for our TGA is expressed as $\partial w / \partial t + \partial s / \partial t$. In the region of $\partial w / \partial t \ll \partial s / \partial t$, the corrosion is controlled by dissolution where the corrosion layer cannot exist, and a linear rate law would be observed. In the region of $\partial w / \partial t \approx \partial s / \partial t$, the behavior of the weight-gain would also show a linear rate law. Before the turning point, a corrosion layer existed. Therefore, the corrosion in this study would be in the region $\partial w / \partial t \approx \partial s / \partial t$. After the saturation of iron species in the sodium compounds, $\partial s / \partial t$ becomes zero and the weight-gain would follow a parabolic rate law.

For the corrosion of Fe by sodium compounds, the corrosion layer has a double structure with an outer $\alpha\text{-NaFeO}_2$ layer and an inner Fe_3O_4 layer. Dissolution of the corrosion product seems to be an important factor. The $\alpha\text{-NaFeO}_2$ solubility in Na_2O_2 would be higher than that in NaOH , because corrosion with Na_2O_2 indicated a larger weight-gain and a lower corro-

sion layer growth than those with NaOH . With the coexistence of Na_2O_2 , the corrosion of Fe was severe, especially if a large amount of Na_2O_2 was present. To prevent severe corrosion, selecting a material of lower solubility in sodium compounds seems to be desirable.

Conclusion

To facilitate greater safety in using metallic sodium, the higher temperature corrosion of Fe with NaOH and Na_2O_2 , separately, has been investigated. The corrosion rates of Fe with NaOH or Na_2O_2 were higher than that without the sodium compound. The corrosion products were $\alpha\text{-NaFeO}_2$ and Fe_3O_4 , not only for NaOH , but also for Na_2O_2 . The corrosion with NaOH obeyed a parabolic rate law. The corrosion with a small amount of Na_2O_2 obeyed a parabolic rate law, but the corrosion with a large amount of Na_2O_2 changed to a linear rate law behavior. This behavior seems to be caused by the higher solubility of Fe in Na_2O_2 than that in NaOH . The growth of a corrosion layer with Na_2O_2 was then lower than that with NaOH . To prevent severe corrosion, a material needs to be designed for lower solubility in sodium compounds.

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