Research Paper

Oxidation of Iron in molten Alkali Nitrate*

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The oxidation kinetics of iron in molten alkali nitrate was studied gravimetrically in the temperature range from 350°C to 470°C. It was found that the oxidation proceeds according to a parabolic rate law. The parabolic rate constant k depends on the temperature and the activation energy was estimated to be 33.8 and 35.0 kcal/mol in NaNO_3 melt and KNO_3 melt, respectively. An X-ray examination reveals that the oxidation product, iron oxide, formed on iron was magnetite. These results are compared with the oxidation kinetics of iron in dry oxygen or air. It is also shown that either acid or base has little effect on the iron oxidation in nitrate melt in the concentration range of acid or base from 10^{-3} and 10^{-2} mole fraction.

1 Introduction

Alkali metal nitrates have been widely used as the surface and heat treatment-baths for steels, iron-based alloys, and aluminium and its alloys. Moreover, it is recently receiving attention as heat transfer media suitable for high temperature heat exchangers. Application of nitrate melt has also been made in these days to high temperature batteries in which mixtures of alkali nitrate and chloride are often used as the electrolyte¹⁾, and to the reaction media for nitration of benzen²⁾.

The corrosion study of metals in molten nitrates are therefore of importance and of necessity in designing corrosion resistant materials to be used for vessels with the melts. Although many studies have been reported on the oxidation of iron and low carbon steels in oxidizing gases, such as oxygen, air and steam, the present knowledge of the oxidation of iron and steels in molten alkali nitrates is very limited. Gurovich³⁾ reported some data on the weight change of low carbon steels and other metals after they were immersed for a short period of time in molten alkali nitrates at a temperature range of 400°C to 500°C. Brough and Kerridge⁴⁾ investigated the reactions between pure iron and LiNO_3 - KNO_3 eutectic melt at 500°C, but gave no quantitative description on the reaction products except the gases which evolves during the reaction.

The present investigation has been undertaken to obtain the fundamental corrosion (oxidation) behavior of iron in molten NaNO_3 or KNO_3 in the temperature

range from 350 to 470°C. Furthermore, comparison has been made between the present results of iron oxidation in molten salts and the previously reported results^{7,9-10)} obtained in oxygen or air.

2 Experimental

The iron specimens ($5 \times 7 \times 0.1$ cm) were cut from a carbonyl iron sheet (C; 0.008, P; 0.004, S; 0.009, Si; 0.20, Mn; 0.043, Cu; 0.006%) and punched to make a small hole near the top edge, the hole was used to support the specimen using a nichrom wire hook. They were then abraded with No. 600 emery paper and stored in a desiccator. Reagent grade sodium nitrate and potassium nitrate were used to prepare the melts. The salt of 600 g was placed in a glass vessel and vacuum-dried at 150°C for 24 hrs. The temperature was then raised to a given temperature gradually and then it was melted. Argon gas was then bubbled through the melt for 2 hrs to exclude a trace of moisture remained in it. The glass vessel was placed in a quartz container, 60 mm diameter, 35 cm height and 1.5 cm thick, and it was located in a vertical electric furnace whose temperature could be automatically controlled using an electric thermoregulator (EC-51 type Okura Denki Co., Ltd.) connected to a variac-transformer. The temperature of the system was controlled within $\pm 2^\circ\text{C}$ and it was at equilibrium in about 10 min. after immersing the specimen in the melt. The equipments used are given schematically in Fig. 1. All the experiments were carried out in open to air. The weighed iron specimens were immersed into the melt. At the end of the reaction period, the

* Corrosion Studies of Metals in Molten Alkali Nitrates
(Part 5)

specimens were withdrawn from the bath and washed with distilled water to remove the salt, dried and weighed. Oxide films formed on the iron specimen were examined by X-ray analysis using Cr-K α radiation filtered by vanadium.

Fig. 1 The equipment for the corrosion test

3 Results and Discussion

When the specimen immersed in the nitrate melt at 350°C~470°C, blue-black oxide scales were formed on the specimen within an 1 hr and one of the main products in the melt was alkali nitrite⁵⁾.

The weight gain can be considered to the oxide film thickness because the amount of iron dissolved in the melt after the reaction was found by chemical analysis to be negligibly small. It was observed that small amounts of gaseous products evolved from the

specimen at the initial stage of oxidation, and that the spots where bubbles of the gases (nitrogen and/or nitrogen oxides) attached on the specimen, were prevented further oxidation, though the gas evolution diminished gradually with time. The results of the oxidation of iron at various temperatures in NaNO₃ melt and in KNO₃ melt under the stagnant condition are given in Fig. 2 and Fig. 3, respectively, where the weight gain in mg/cm² was plotted as a function of the exposure time in hour. As is seen in the figures, the weight gain of the specimen increases with the lapse

Fig. 3 Weight gain of iron vs. time curves in KNO₃ melt

Fig. 2 Weight gain of iron vs. time curves in NaNO₃ as well as NaNO₂ melt

of time in a parabolic fashion, and a similar oxidation behavior is found both in NaNO₃ melt and in NaNO₂ melt at 360°C, as is shown in Fig. 2 and in KNO₃ melt in Fig. 3. At all temperatures studied iron was oxidized a little more rapidly in NaNO₃ melt than in KNO₃ melt, though the plotted values are rather scattered. This results is in agreement with Gurovich's data³⁾ that gave the oxidation rate of a carbon steels to decrease in the order of molten LiNO₃>NaNO₃>KNO₃ for 4 hrs at 400°C. Agitation with oxygen gas by means of bubbling through the melt resulted in a slight increase in weight gain. Photo. 1 and Photo. 2 are both photomicrographs of the surface of the oxides formed at 400°C in NaNO₃ melt and in KNO₃ melt. X-ray analysis of the corrosion product formed in both NaNO₃ and KNO₃ melts at 400°C for long periods of time showed that it was mainly consisted of Fe₃O₄, while α-Fe₂O₃ and iron nitrides were not detected. Microscopic examination of a cross section of the specimen revealed that there was only a layer of Fe₃O₄ on the specimen surface. X-ray diffraction patterns obtained with the specimens immersed in molten alkali nitrate and in molten alkali nitrite are shown in Fig. 4.

Iron is known to oxidize in accordance with the

Fig. 4 X-ray patterns for the iron oxide formed on the specimen

($\times 10,000$, two stage replication method)

Photo. 1 Microphotograph of the iron surface immersed in NaNO_3 melt for 3 hrs at 350°C

($\times 10,000$, two stage replication method)

Photo. 2 Microphotograph of the iron surface immersed in KNO_3 melt for 3 hrs at 350°C

parabolic rate law in air at temperatures 250 – 500°C ⁶⁾. To demonstrate the parabolic rate law of the oxidation of iron in the melts, the data obtained with different melts are replotted in Fig. 5. The apparent parabolic rate constants calculated from the slopes of the curves in Fig. 5 are plotted against reciprocal of the absolute temperature in Fig. 6, where the previously reported data^{7)–10)} together with the present data are shown.

The experimental values of the activation energy are 33.8 and 35.0 kcal/mol in NaNO_3 and KNO_3 melt, respectively. These data are in fairly good agreement with the published data obtained in air or oxygen environment.

The rate constant changed continuously in the initial period of oxidation, for example, at 410°C in NaNO_3

Fig. 5 Parabolic plot of the oxidation data

Reciprocal of absolute temperature
 $K = Ae^{-Q/RT}$

- : NaNO_3 33.8 kcal/mol
- : KNO_3 35.0 kcal/mol
- : E.A. Gulbransen (O_2)
- ▲ : D.E. Davies, et al., (Air)
- ⊖ : M.H. Davies, et al., (O_2)
- ⊙ : D. Caplan, et al., (O_2)

Fig. 6 Arrhenius plot of the oxidation data in molten nitrate with data reported which were obtained in oxygen or air

melt, it was found to increase in 3 hrs from 4.16×10^{-1} to $6.18 \times 10^{-1} \mu\text{g}^2/\text{cm}^4 \cdot \text{sec}$, and to remain approximately constant at this value during further oxidation up to 10 hrs, while in KNO_3 melt it increased from 4.63×10^{-1} in 4 hrs and then remained constant at $4.50 \times 10^{-1} \mu\text{g}^2/\text{cm}^4 \cdot \text{sec}$. The plotted values in Fig. 6 are the average ones obtained for 10 hrs. The similarity between the molten salt oxidation and the oxidation in air or oxygen can be seen, and in molten salts the rate of oxidation is higher than that in air or oxygen. It is known that carbon content exert influence

Fig. 7 Effect of acid or base on the corrosion (oxidation) of iron in molten NaNO_3 and KNO_3

on the oxidation of steel in oxygen. The carbon content in low carbon steels (C; 0.04~0.14%), however, has little effect upon their oxidation behavior in alkali nitrate melt.

The acid and base of the melt was expected to play an important role in corrosion of metals. Namely,

increase of the alkalinity (basicity) resulting from metal dissolution and decomposition of the melt due to local overheating, would make a favorable effect on the corrosion of metals. To examine the effect of the acid and base, either $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{S}_2\text{O}_7$ was added to the melt as an acid, while either KOH or Na_2O_2 was added to it as a base. It was then found that red colored oxide, probably Fe_2O_3 , was formed on the specimen surface in a melt containing high concentration of $\text{K}_2\text{S}_2\text{O}_7$. On the other hand brownish gas evolved by addition of the acid, probably NO_2 gas, may oxidize Fe_3O_4 to Fe_2O_3 . However, there was no appreciable dependence of acid and base on the thickness of the oxide in the concentration range shown in Fig. 7.

4 Summary

Iron corrosion (oxidation) in molten KNO_3 or NaNO_3 was studied gravimetrically at 350–470°C. The oxidation behavior of iron in molten nitrate is found to be similar to that in air or oxygen. This suggests that the kinetics of high temperature oxidation of iron and iron-based alloys in oxygen can directly be applied to the oxidation in molten nitrates.

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