Improvement of Cyclic Oxidation Resistance of Fe-23 mass% Cr Alloy by Molten Salt Electrodeposition of Lanthanum

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A La-containing surface layer was formed on a Fe-23 mass% Cr alloy by electrodepositing La and alloying it with the alloy in molten salt. The electrodeposition of La was carried out using a potentiostatic polarization method at constant potential in an equimolar NaCl-KCl melt containing La₂O₃ and NH₄Cl at 1023 K. EPMA analysis of the cross-section of the alloy after the electrodeposition showed that a surface region containing La of less than 1 mass% was formed. The cyclic oxidation test showed that the La-electrodeposited alloy was more resistant than the bare alloy to cyclic oxidation. On the La-electrodeposited alloy after cyclic oxidation, formation of a thin scale consisting of Cr₂O₃ was observed.

Key Words: lanthanum, electrodeposition, molten salt, Fe-Cr alloy, cyclic oxidation

1. Introduction

Stainless steels have a high oxidation resistance in an oxidizing atmosphere at high temperature. This is attributable to the formation of a protective oxide film consisting mainly of Cr₂O₃. However, the oxidation resistance of the stainless steel decreases under thermal cycles because the protective oxide film is broken or spalled due to the stress caused in the film under the cooling. Therefore, for high oxidation resistance for stainless steels under thermal cycles, the resistance against the breakage and spallation of the oxide film must be improved.

It has been known that improvement of the resistance against the breakage and the spallation of the oxide film is achieved by the addition of a small amount of a rare earth element into the steel [1, 2]. However, the addition of a rare earth element into the steel leads to an increase in the price of the steel. Therefore, for high oxidation resistance for stainless steels under thermal cycles, the resistance against the breakage and spallation of the oxide film must be improved.

The electrodeposition method is advantageous because the equipment is cheaper in comparison with the ion implantation method. The traditional method of electrodeposition uses an aqueous solution bath, but metals with a precipitation potential less noble than the reduction potential of water cannot be electrodeposited. Rare earth elements are one type of elements that cannot be electrodeposited from an aqueous solution phase. Some metals that cannot be electrodeposited from aqueous solution, however, can be electrodeposited from molten salt. We have, in fact, electrodeposited tantalum and silicon from molten salt to improve some substrate materials [5-8]. For example, electrodeposition of aluminum on a nickel substrate in a molten salt bath resulted in the formation of a nickel aluminate surface layer due to mutual diffusion of aluminum and nickel, thereby dramatically improving the oxidation resistance [9]. We anticipated that electrodeposition of lanthanum, which is one of the rare earth elements, onto the Fe-23 mass% Cr alloy might lead to addition of lanthanum into the surface region of the Fe-23 mass% Cr alloy in order to improve the cyclic oxidation resistance of the alloy.

Driven by this thought, the electrodeposition of lanthanum on the Fe-23 mass% Cr alloy from NaCl-KCl molten salt containing La₂O₃ and NH₄Cl at 1023 K was carried out by potentiostatic electrolysis. Furthermore, the cyclic high-temperature oxidation resistance of the electrodeposited Fe-23 mass% Cr alloy was evaluated with reference to that of the untreated Fe-23 mass% Cr alloy.

2. Experimental

2.1 Specimen materials and molten salts

Fe-23 mass% Cr alloy was used as the substrate material for electrodeposition. The alloy was produced by vacuum melting using a high frequency induction furnace. The alloy ingot was cut into specimens, 10 x 10 x 1.5 mm³. Nickel (99.6 mass%) sheet having dimensions of 10 x 10 x 1 mm³ also was used as an electrode to examine cathodic reduction behavior of the molten salt used in the experiment. Their surfaces were polished with emery paper up to #800 and washed ultrasonically in acetone prior to the electrochemical measurement. Equimolar NaCl-KCl salts containing various concentrations of La₂O₃ and NH₄Cl were used as a test salt. La₂O₃ and NH₄Cl were added into the salt to form LaCl₃, which provided lanthanum ion into the molten salt. The salts were dried in a vacuum at 543 K for 8.4 ks before using them for the test.
2.2 Cathodic polarization curve measurement and electrodeposition experiment

Figure 1 shows the setup for cathodic polarization curve measurement and the electrodeposition experiment. An alumina crucible (internal diameter 35 mm and height 160 mm) was used as a container of the electrolytic cell. This cell was placed in a quartz tube held in an electric furnace. The reference electrode and thermocouple protected with a sheath were set in the cell before the cell was filled with the test salt. The amount of the salt was adjusted so that the surface of the molten salt was 10 mm higher than the top of the working electrode. The working electrode and the counter electrode were put into the molten salt after the temperature of the molten salt reached 1023 K. After these electrodes were put into the molten salt, the electrochemical measurement was immediately carried out. A graphite rod of 5 mm diameter was used as the counter electrode. The reference electrode was a silver wire immersed in an equimolar NaCl-KCl melt containing 10 mol% AgCl placed in a mulite (3Al2O3-2SiO2) tube. The electrolyte was melted under an argon atmosphere. The argon gas was blown on the surface of the electrolyte at the rate of $3.3 \times 10^6 \text{m}^3 \cdot \text{s}^{-1}$. In order to determine the cathodic reduction reaction of lanthanum ion in the molten salt, cathodic polarization curves were measured by a potential-sweeping method. The sweeping rate was $1.7 \times 10^{-3} \text{V} \cdot \text{s}^{-1}$. In order to electrodeposit lanthanum on the specimen, the specimen was polarized potentiostatically at various potentials, at which the cathodic reduction reaction of lanthanum ion was presumed to occur actively.

The cross-section and surface of the specimen after the electrodeposition were examined by a scanning electron microscope (SEM) and electron probe micro-analysis (EPMA).

2.3 Cyclic oxidation test

The cyclic oxidation test was performed in pure O2 atmosphere at 1273 K, using a horizontal tube furnace. The test cycles involved exposing the specimens for 36 ks and cooling quickly to room temperature, measuring mass gain including spalled oxides. The cooling of the specimen was carried out as follows; the specimen was taken out of the furnace to the air at the room temperature within 3 s. Subsequently, the specimen was allowed to stand in the air at the room temperature. The average cooling rate from 1273 K to 373 K was about $7 \text{K} \cdot \text{s}^{-1}$. The specimens during the cyclic oxidation were given a total exposure of 360 ks (10 cycles). The cross-section of the specimen after the oxidation test was examined using SEM and EPMA. The oxide scale formed on the specimen was identified by X-ray diffraction measurement.

3. Results and discussion

3.1 Cathodic polarization curves

Figure 2 shows the cathodic polarization curves of nickel measured in the NaCl-KCl melts without and with 2, 4 and 6 mol% La2O3. Each curve showed an increase in cathodic current density in the potential region lower than about $-2.0 \text{V}$. It has been reported that the standard electrode potential of Na(+1)/Na(0) on the basis of Ag(+1)/Ag(0) in the equimolar NaCl-KCl melt at 1000 K was $-1.931 \text{V}$ [10]. Therefore, the increase in cathodic current density seems to correspond to the cathodic reduction reaction of Na+ to Na. The difference in the cathodic polarization curve due to the concentration of La2O3 in the molten salt was not observed. This suggests that La2O3 did not dissolve as La3+ and O2- ions in the molten salt and that La3+ ion was not reduced electrochemically.

Next, NH4Cl was added with La2O3 in the molten salt and the molten salt was maintained at 973 K for 1.8 ks in order to allow the following reactions to proceed [11].

\[
\text{La}_2\text{O}_3 + 6\text{NH}_4\text{Cl} \rightarrow 2\text{LaCl}_3 + 6\text{NH}_3 + 3\text{H}_2\text{O} \quad (1)
\]

\[
\text{LaCl}_3 \rightarrow \text{La}^{3+} + 3\text{Cl}^- \quad (2)
\]

As the equilibrium constant at 973 K of the chemical reaction...
shown by Eq. (1) is $10^{3.9}$, it is presumed that this reaction proceeds to form $\text{LaCl}_3$. Figure 3 shows the cathodic polarization curves of nickel measured in the NaCl-KCl melts without and with both $\text{La}_2\text{O}_3$ and $\text{NH}_4\text{Cl}$. The curves measured in the NaCl-KCl containing both $\text{La}_2\text{O}_3$ and $\text{NH}_4\text{Cl}$ showed an increase in cathodic current density in the potential region lower than about $-1.5$ V. The degree of the increase in cathodic current density increased with an increase in the concentrations of both $\text{La}_2\text{O}_3$ and $\text{NH}_4\text{Cl}$. This suggests that $\text{La}^{3+}$ ion formed by Eqs. (1) and (2) was reduced in the potential region lower than about $-1.5$ V.

3.2 Morphology of the cathode surface after electrodeposition

The electrodeposition on nickel and Fe-23 mass% Cr alloy substrates was carried out by potentiostatic polarization at $-2.0$ V, using NaCl-KCl molten salt containing 4 mol% $\text{La}_2\text{O}_3$ and 24 mol% NH$_4$Cl.

Figure 4 (a) and (b) show the surface micrograph (secondary electron image: SEI) and cross-sectional micrograph (back-scattered electron image: BEI) of the nickel cathode after potentiostatic polarization for 1.8 ks. The surface micrograph showed that the surface of the deposit material consisted of many rectangular crystals. The cross-sectional micrograph showed that a lamellar deposit layer of about 50 μm thickness was formed on the nickel substrate. The X-ray diffraction results showed that this deposit layer consisted of two-phase intermetallic compounds, $\text{LaNi}_3$ and $\text{LaNi}_5$. The EPMA results showed that the phase observed as dark color, (A), and the phase observed as white color, (B), in the deposit layer shown in Figure 4 (b) corresponded to $\text{LaNi}_3$ and $\text{LaNi}_5$, respectively. It is thought that such lanthanum-nickel intermetallic compounds were formed by the cathodic reduction reaction of $\text{La}^{3+}$ ion to La, shown by Eq. (3) and a mutual diffusion between the deposited lanthanum and the substrate nickel.

$$\text{La}^{3+} + 3e^{-} \rightarrow \text{La}$$  \hspace{1cm} (3)

Figure 5 shows the surface micrograph (SEI) of Fe-23 mass% Cr alloy after potentiostatic polarization at $-2.0$ V for 0.18 ks in the NaCl-KCl melt containing 4 mol% $\text{La}_2\text{O}_3$ and 24 mol% NH$_4$Cl at 1023 K.

Figure 3 Cathodic polarization curves of nickel measured at 1073 K in the NaCl-KCl melt without $\text{La}_2\text{O}_3$ and $\text{NH}_4\text{Cl}$ and the NaCl-KCl melts containing 2 mol% $\text{La}_2\text{O}_3$ and 12 mol% $\text{NH}_4\text{Cl}$, 4 mol% $\text{La}_2\text{O}_3$ and 24 mol% $\text{NH}_4\text{Cl}$, and 6 mol% $\text{La}_2\text{O}_3$ and 36 mol% $\text{NH}_4\text{Cl}$.

Figure 4 Surface (a) and cross-sectional (b) micrographs of nickel after potentiostatic polarization at $-2.0$ V for 1.8 ks in the NaCl-KCl melt containing 4 mol% $\text{La}_2\text{O}_3$ and 24 mol% NH$_4$Cl at 1023 K.

Figure 5 Surface micrograph of Fe-23 mass% Cr alloy after potentiostatic polarization at $-2.0$ V for 0.18 ks in the NaCl-KCl melt containing 4 mol% $\text{La}_2\text{O}_3$ and 24 mol% NH$_4$Cl at 1023 K, and the EDS spectrum obtained from the surface.
alloy after potentiostatic polarization at $-2.0 \text{ V}$ for 0.18 ks, and the EDS spectrum obtained from the surface. The micrograph showed that small, flake-shaped deposits were numerously formed on the alloy. It was found from EDS spectrum that the surface region containing the deposit consisted of lanthanum, chlorine, iron and chromium elements. It is presumed that the lanthanum and chlorine spectrum and the iron and chromium spectrum corresponded to the chemical composition of the deposit and that of the alloy substrate, respectively.

Figure 6 shows the cross-sectional micrograph (BEI) of Fe-23 mass\% Cr alloy, whose surface micrograph was shown in Figure 5, and the concentration profiles of iron, chromium and lanthanum across the surface vicinity area of the alloy substrate, obtained by EPMA analysis. As shown in Figure 4, when lanthanum electrodeposition was carried out on the nickel substrate at the same potential for 1.8 ks, the deposit layer consisting of La$_3$Ni and LaNi$_5$ with about 50 $\mu$m thickness was formed. On the other hand, when the lanthanum electrodeposition was carried out on the Fe-23 mass\% Cr alloy for 0.18 ks, the result that not more than 1 mass\% of lanthanum was contained in the region within 0.25 $\mu$m depth from the alloy surface, was observed (Figure 6). It was thought that this low lanthanum content in the alloy resulted from the short deposition time and the small solubility limit of lanthanum in $\alpha$-Fe phase [12]. Further, a thin and flake-shaped deposit was observed on the alloy (Figures 5 and 6). This deposit seems to consist of lanthanum chloride because the deposit contained lanthanum and chlorine as shown in the EDS spectrum (Figure 5). It was presumed that this lanthanum chloride was formed by the chemical reaction shown by Eq. (1) and was deposited on the alloy.

3.3 Cyclic oxidation behavior of lanthanum-electrodeposited Fe-23 mass\% Cr Alloy

Before the cyclic oxidation test, the deposit consisting of lanthanum chloride formed on the electrodeposited Fe-23 mass\% Cr alloy was removed by polishing with an emery paper of #400. However, this alloy contained a small amount of lanthanum in the surface vicinity area of the alloy, as described in section 3.2. Figure 7 shows the mass gain curve of this alloy during the cyclic oxidation test at 1273 K in a pure O$_2$ atmosphere. For comparison, the figure includes the curve of untreated Fe-23 mass\% Cr alloy during the cyclic oxidation test in the same atmosphere. The mass gain of the electrodeposited alloy was far smaller than that of the untreated alloy. After 108 ks (3 cycles), especially, the difference in the mass gain between both alloys became large.

Figure 8 shows the cross-sectional micrographs of the electrodeposited alloy and the untreated alloy after oxidation for 10 cycles (360 ks). It was found that the maximum scale thickness for the untreated alloy was about 250 $\mu$m. Pores were observed in the scale. It was found from the X-ray diffraction measurement that the scale consisted of iron oxides such as Fe$_3$O$_4$ and FeO. On the other hand, the scale formed on the electrodeposited alloy was extremely thin. Therefore, the scale could not be observed in the micrograph.

As the scale formed on the electrodeposited alloy could not be observed, the cross-section of the scale was observed with a higher magnifying power. The result is shown in Figure 9. This figure includes the characteristic X-ray images of iron, chromium and oxygen corresponding to the micrograph (BEI). It was found that scale of 7–8 $\mu$m thickness was formed on the alloy and that chromium was contained in the scale while iron was not contained in the scale. It is presumed that the scale formed on the electrodeposited alloy consisted mainly of Cr$_2$O$_3$. Though the...
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Consequently, it was found that a thin scale consisting mainly of Cr₂O₃ was formed on the lanthanum-electrodeposited Fe-23 mass% Cr alloy and that this alloy had a high cyclic oxidation resistance.

3.4 High cyclic oxidation resistance mechanism of lanthanum-electrodeposited Fe-23 mass% Cr alloy

As described in section 3.3, the lanthanum-electrodeposited Fe-23 mass% Cr alloy had a high cyclic oxidation resistance in comparison with the untreated alloy. In this section, a reason for this observation is discussed.

As shown in Figure 6, the electrodeposition of lanthanum on the Fe-23 mass% Cr alloy led to the addition of lanthanum lower than 1 mass% in the surface vicinity region of the alloy. Therefore, the formation of the thin scale consisting mainly of Cr₂O₃ for the lanthanum-electrodeposited Fe-23 mass% Cr alloy was attributable to the addition of a small amount of lanthanum in the surface vicinity region of the alloy. It has been known that the cyclic oxidation resistance of an alloy forming Cr₂O₃ such as Fe-Cr alloy is improved by the addition of small amounts of rare earth elements into the alloy. As a reason for this improvement, "the void absorption effect in the alloy/scale interface [13]" has been proposed. For the stainless steel, chromium is preferentially oxidized to form a protective Cr₂O₃ scale. At this time, in the alloy under the scale, chromium concentration decreases, whereas iron concentration increases. Because of this, in the alloy under the scale, chromium diffuses from the bulk side to the surface side, whereas iron diffuses from the surface side to the bulk side. At this time, vacancies generate at the alloy/scale interface due to Kirkendall effect on the basis of a difference in the diffusion rate between chromium and iron. The vacancies condense to form a void. This void lowers the adhesion of the scale to the alloy.

"The void absorption effect in the alloy/scale interface" is that the rare earth element and its micro oxide in the alloy inhibit the void formation at the alloy/scale interface to inhibit the breakage of the scale. As the radius of the rare earth element is larger than that of iron or chromium, a complex of the rare earth element in the alloy and of the vacancy formed at the alloy/scale interface is formed to reduce the strain energy for the solid solution. As the result, the rare earth element acts as the annihilation site of the vacancy. In the same way, the micro oxide particle of the rare earth element formed in the vicinity of the alloy/scale interface acts as the annihilation site of the vacancy formed at the interface. It has been thought that this effect induces the adherence of scale to increase and cause the resistances of the breakage of the scale during the cyclic oxidation to increase. In the present work, it was found that for the lanthanum-electrodeposited alloy the thin Cr₂O₃ scale adhesively formed on the alloy even if the oxidation time was reached at 360 ks (10 cycles) (Figure 9). This result is attributed to the fact that coverage of the Cr₂O₃ scale formed at the initial stage of the oxidation was continuously maintained without causing the breakage of the scale during the cyclic oxidation. On the other hand, the oxidation for the untreated alloy seems to proceed with a repetition of breakage and reformation of the Cr₂O₃ scale. In this case, if the chromium concentration in the alloy at the alloy/scale interface becomes a value less than the critical concentration at which the Cr₂O₃ scale cannot be formed, it becomes impossible for the Cr₂O₃ scale to reform. As the result, the oxidation of the iron component occurs to form the oxide scale containing iron oxide. This induces the protective ability of the scale to decrease. As shown in Figure 7, the oxidation mass gain of the untreated alloy abruptly increased after 108 ks (3 cycles). It is thought that the result was attributed to the fact that after this time the scale changed from that mainly consisting of Cr₂O₃ to that much containing iron oxide. Finally, after 360 ks (10 cycles) the scale formed on the untreated alloy consisted mainly of iron oxide.
4. Conclusion

Lanthanum was successfully electrodeposited by potentiostatic electrolysis using equimolar NaCl-KCl molten salts containing La₂O₃ and NH₄Cl. When nickel was used as a cathode, a surface layer consisting of LaNi₅ and the LaNi₃ was formed. When Fe-23 mass% Cr alloy was used as a cathode, on the other hand, the surface region containing a small amount of lanthanum less than 1 mass% was formed. The cyclic oxidation test showed that the oxidation resistance of the lanthanum-electrodeposited Fe-23 mass% Cr alloy was far higher than that of untreated Fe-23 mass% Cr alloy. A thick scale consisting mainly of Fe oxides was formed on the untreated Fe-23 mass% Cr alloy, while a thin scale consisting of Cr₂O₃ was formed on the lanthanum-electrodeposited Fe-23 mass% Cr alloy.

References