Straining Electrode Behavior of Fe-Cr and Ni-Cr Alloys in High Temperature and High Pressure Borate Buffer Solution

By Toshio Shibata* and Shinji Fujimoto**

In order to discuss the role of chromium in the passivity of Fe-Cr and Ni-Cr alloys in a high temperature and high pressure water environment, the initial process of repassivation of newly created surface of these alloys has been analyzed by a straining electrode technique, and also the depth profile of the composition of films formed on these alloys in the same environment is examined by Auger electron spectroscopy.

It is observed that chromium addition simply increases the initial current density on bare surface of both the Fe-Cr and Ni-Cr alloys. The repassivation rate for the Fe-Cr alloys was enhanced by chromium addition of more than 8 mass%, but was rather retarded by the addition of 3 mass% chromium. On the other hand, the repassivation currents of the Ni-Cr alloys were increased by chromium addition and no promotion of repassivation rate was observed during the short period of the straining electrode test. Auger analysis showed that enrichment of chromium in the film occurred only for the high chromium Fe-Cr alloy, but no enrichment occurred for the low chromium Fe-Cr alloy and for all the Ni-Cr alloys. The contribution of the chromium addition to the repassivation behavior of the Fe-Cr and Ni-Cr alloys was discussed in consideration of the effect of chromium on the film composition.

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I. Introduction

Stainless steels and high nickel alloys have been widely used in the high temperature and high pressure water environment of the light water nuclear power plants⁽¹⁾⁽²⁾. Extensive studies have been performed on these commercial materials to understand and prevent corrosion failures including SCC, IGA, crevice corrosion and others⁽³⁾⁽⁴⁾. It is commonly accepted that alloying elements such as chromium, nickel and molybdenum play an important role in supplying corrosion resistance for these alloys. However, few studies have been performed to understand the basic electrochemical behavior of these elements in this environment.

In order to discuss the role of chromium in the initial process of repassivation of

chromium containing alloys, a rapid straining electrode test⁽⁵⁾ is performed for two series of the binary alloys of Fe-Cr and Ni-Cr. A high temperature and high pressure borate buffer solution was used as the test environment, because iron and nickel showed no localized corrosion in this solution⁽⁶⁾⁻⁽¹⁰⁾.

The composition of passive films formed on the alloys in the same environment was analyzed by Auger electron spectroscopy, referring to their repassivation behavior.

II. Experimental

Materials used in the present study are Fe- x Cr alloys and Ni- x Cr alloys ($x=3, 8, 18$ and 22) in addition to pure iron and pure nickel. Their chemical compositions are shown in Table 1. These materials were melted in a vacuum, cast and drawn to thin wire of 0.35 mm diameter. The wire specimens were degreased, then annealed in a vacuum and subjected to water quenching. The annealing temperature was 1073 K for pure nickel, pure iron and iron base alloys, and 1323 K for nickel

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Table 1 Chemical composition of the specimen materials (mass%).

	C	N	Si	Mn	P	S	Al	Ni	Cr	Fe
pure Fe	0.001	0.0004	0.003	<0.001	0.002	0.001	<0.001	0.001	—	bal.
pure Ni	0.028	—	0.066	0.38	0.003	0.004	—	bal.	0.001	0.09
Fe-3Cr	0.039	0.0069	0.32	0.31	0.003	0.002	0.15	<0.01	3.20	bal.
Fe-8Cr	0.028	0.0049	0.28	0.30	0.003	0.002	0.14	<0.01	8.23	bal.
Fe-18Cr	0.025	0.0064	0.30	0.30	0.003	0.002	0.17	<0.01	18.59	bal.
Fe-22Cr	0.025	0.0099	0.30	0.30	0.003	0.002	0.15	<0.01	22.48	bal.
Ni-3Cr	0.027	0.0019	0.27	0.30	0.002	0.001	0.14	bal.	3.26	0.17
Ni-8Cr	0.025	0.0037	0.27	0.30	0.002	0.001	0.15	bal.	7.66	0.01
Ni-18Cr	0.027	0.0045	0.30	0.31	0.002	0.001	0.13	bal.	18.07	<0.01
Ni-22Cr	0.024	0.0044	0.27	0.31	0.002	0.001	0.16	bal.	21.92	<0.01

base alloys. The electrolyte used was the borate buffer solution of $0.15 \text{ kmol} \cdot \text{m}^{-3} \text{ H}_3\text{BO}_3 + 0.0375 \text{ kmol} \cdot \text{m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$, prepared with reagent grade chemicals and distilled water, and was deaerated with high purity N_2 gas at room temperature before heating.

The straining electrode technique has been described in previous publications^{(5)–(10)}. The wire electrode was elongated rapidly to yield a small amount of newly created surface at a constant applied potential. The anodic current increases rapidly to a maximum and decays with time due to formation of passive film. The change in strain and anodic current with time was recorded. Measurements of polarization curves were carried out for $10 \text{ mm} \times 10 \text{ mm}$ sheet specimens of 2 mm thickness, which were obtained from the same materials prepared for the straining electrode specimen and were polished with SiC paper up to 1200 grid. The reference electrode for these electrochemical measurements was an internal $\text{Ag}/\text{AgCl}/0.01 \text{ M KCl}$ electrode.

A specimen for Auger analysis was prepared as follows. $10 \text{ mm} \times 15 \text{ mm}$ coupons were cut from the same sheet used for the measurement of polarization curve. The specimen surface was polished with SiC paper up to 1500 grid, finished with $0.3 \mu\text{m}$ alumina paste and then degreased with acetone and methanol in an ultrasonic bath. The passive films were formed at 523 K and at a constant potential of $-0.2 V_{\text{SHE}}$ for 3600 s in the borate buffer solution.

III. Results

1. Polarization behavior

Polarization curves of the iron base and nickel base alloys in the borate buffer solution at 523 K are shown in Fig. 1.

For the iron base alloys, the current density in the passive region decreased with increasing chromium content. A small peak of current density was observed around $-0.5 V_{\text{SHE}}$ for Fe-3Cr. Another peak appeared at around $0 V_{\text{SHE}}$ for 8Cr, 18Cr and 22Cr-Fe alloys except for pure Fe and Fe-3Cr alloy. This peak is called an over passive peak. After the over passive peak, a secondary passive region was observed for every alloy.

The nickel base alloys showed nobler corrosion potentials than the iron base alloys. The over passive peak was also observed for the nickel base alloys around $0 V_{\text{SHE}}$. Therefore, the passive potential region for the nickel alloys was narrower than that of the iron base alloys. The current density in the passive state for the Ni-Cr alloys did not depend so much on the chromium content and was in the same order as those for Fe-18Cr and Fe-22Cr alloys. In contrast, the over passive peak current density of the Ni-Cr alloys depended clearly on the chromium content, but was fairly smaller than those of the Fe-Cr alloys.

Consequently, it is concluded that the anodic polarization curves of the Fe-Cr alloys clearly change with the chromium content. On the other hand, the Ni-Cr alloys showed

Fig. 1 Polarization curves of (a) the Fe-Cr alloys and (b) the Ni-Cr alloys in a borate buffer solution at 523 K.

almost the same polarization curves except for the current density of the over passive peak.

2. Straining electrode behavior of the Fe-Cr alloys

Figure 2(a) shows the changes in the current density with time on the newly created surface of the Fe-Cr alloys at $-0.2 V_{SHE}$ and 523 K. The current density, i , decayed following a power law,

$$i = at^{-n}, \quad (1)$$

from few ms for about 3 decades. The power,

Fig. 2 Changes in the anodic current density with time on the newly created surface of (a) the Fe-Cr alloys of various chromium contents at 523 K and $-0.2 V_{SHE}$, and (b) Fe-18Cr at various potentials at 523 K.

n , was in the range between 0.8 and 0.95 for the Fe-Cr alloys and was larger than that of pure iron in the same environment⁽¹⁰⁾. The dependence of i on the chromium content, however, can not be seen clearly in the $\log i - \log t$ plot. Figure 2(b) shows the changes in the current density with time of Fe-18Cr alloy at various potentials at 523 K. The current density on the newly created surface decayed following also the power law. i at the early stage for about 10 ms showed a positive potential dependence, while the current density at the later stage did not show any significant potential dependence. The current density at 0 V_{SHE} , however, decreased for a period up to about 0.5 s and then remained at a large value for few tens of seconds. This potential was in the over passive region in the polarization curve. This change in the feature of the repassivation behavior in this potential region seems to be brought about by the oxidation of chromium, which was enriched in the initially formed film, from Cr^{3+} to Cr^{6+} as discussed later.

An analysis of the relation between the current density, i , and the charge density, Q , provides the information to discuss the repassivation process, because Q is directly related to the thickness of the film. The charge density which has passed at time t after the straining was stopped, $Q(t)$, is defined by

$$Q(t) = Q_0 + \int_0^t i(t) dt, \quad (2)$$

where Q_0 is the charge density passed during elongation. $Q(t)$ was obtained by graphical integration of i vs t curves measured in the experiment.

Figure 3 shows the decay in the current density on the newly created surface, i , with the increase in the charge density, Q , for the Fe-Cr alloys at $-0.2 V_{SHE}$ and 523 K. The alloy with the higher chromium content shows the smaller current density at the same charge density Q except for Fe-3Cr alloy. On the other hand, Fe and Fe-3Cr alloy showed a larger current density than that of the other alloys at the same Q . In other words, the repassivation of Fe and Fe-3Cr alloy was slower than that of the other alloys. Similar $\log i$ vs Q plots for Fe

Fig. 3 Changes in current density, i with increasing charge density, Q , for the Fe-Cr alloys of various chromium contents at 523 K and $-0.2 V_{SHE}$.

and the Fe-Cr alloys were observed at 423, 473 and 553 K.

3. Straining electrode behavior of the Ni-Cr alloys

Figure 4(a) shows the change in i with time for the Ni-Cr alloys at $0.2 V_{SHE}$ at 523 K. A significant difference in $\log i$ vs $\log t$ curve was observed between pure nickel and the Ni-Cr alloys. Decays of the current density on both nickel and the Ni-Cr alloys followed the power law of eq. (1), but the values of n were found to be 0.5–0.8 for pure nickel and 0.8–0.95 for the Ni-Cr alloys. The initial current density, i_0 , the current density just after the straining was stopped, for the Ni-Cr alloys was fairly larger than that for pure nickel and increased with the increase in the chromium content.

The potential dependence of the i vs t curve for Fe-18Cr alloy is shown in Fig. 4(b). The current density increased with increasing applied potential. On the other hand, the value n in eq. (1) did not depend on the applied potential. Namely, the repassivation rate of Ni-18Cr alloy was independent of potential, contrasting with that of Fe-18Cr alloy which depended on the potential.

Relations between the current density and the charge density for the Ni-Cr alloys at $-0.2 V_{SHE}$ and 523 K are shown in Fig. 5. A

Fig. 4 Changes in the anodic current density with time on the newly created surface of (a) the Ni-Cr alloys of various chromium contents at 523 K and 0.2 V_{SHE}, and (b) Ni-18Cr at various potentials for 523 K.

Fig. 5 Changes in the current density, i with increasing charge density, Q , for the Ni-Cr alloys of various chromium contents at 523 K and -0.2 V_{SHE}.

similar repassivation behavior was observed for all the Ni-Cr alloys examined, although a larger current density during repassivation was observed for the larger chromium content alloy.

4. Auger electron spectroscopy

Auger analysis of the film was conducted for Fe-8Cr, Fe-18Cr, Ni-8Cr, Ni-18Cr and Ni-30Cr alloys. Figure 6 shows the depth profiles for (a) Fe-8Cr and (b) Fe-18Cr alloys. It is

Fig. 6 Auger depth profiles for the films formed on (a) Fe-8Cr and (b) Fe-18Cr alloys in a borate buffer solution at 523 K and -0.2 V_{SHE} for 3.6 ks. (Sputtering rate: (a) 0.385 nm/s (231 Å/min) as SiO₂, (b) 0.0417 nm/s (25 Å/min) as SiO₂).

difficult to estimate the exact thickness of the film from the sputtering time, because the sputtering rate for the oxide film formed on each alloy was not determined directly. The sputtering rate, however, was measured for SiO_2 . The sputtering rate for Fe-8Cr was larger than that of Fe-18Cr, as is described in the caption of the figure, and Fe-8Cr alloy needed a longer sputtering time for the peak to peak height of Fe reaching a constant value, comparing with Fe-18Cr alloy. Therefore, it is concluded that a fairly thicker film was formed on Fe-8Cr alloy than on Fe-18Cr alloy. This result was confirmed by the fact that a brown interference color was observed for Fe-8Cr alloy specimen, while Fe-18Cr alloy showed only metallic luster without color. Figure 7 shows depth profiles for (a) Ni-8Cr, (b) Ni-18Cr and (c) Ni-30Cr alloys. An identical sputtering rate was used for all the Cr-Ni alloys. In comparison between these three figures, it is readily seen that the thicknesses of the films formed on the Ni-Cr alloys were almost the same. In addition, the surface of the Ni-Cr alloys showed the same metallic luster without interference color.

The peak to peak heights of chromium and iron in the depth profile for Fe-8Cr alloy simply increased with the sputtering time, as shown in Fig. 6(a). No enrichment of chromium in the film occurred, although a slight increase of the Cr/Fe ratio in the outer layer was observed. On the other hand, a significant enrichment of chromium was clearly observed for the Fe-18Cr alloy. It has been reported similarly that the enrichment of chromium in the film occurs for more than 12 at% chromium Fe-Cr alloys in 1 N H_2SO_4 at room temperature⁽¹¹⁾. The profile for Fe-18Cr alloy showed a maximum peak to peak height of chromium in the outer layer of the film, while the peak to peak height of iron in the outer layer increased with depth. Thus, it is concluded that the outer layer of the film for Fe-18Cr alloy consists mainly of chromium oxide.

The peak to peak height profiles for every Ni-Cr alloy show that a nearly constant Cr/Ni ratio was attained throughout the whole profile from the outer surface to the bulk alloy. Therefore, it is concluded that the Cr/Ni ratio

Fig. 7 Auger depth profiles for the films formed on (a) Ni-8Cr and (b) Ni-18Cr and (c) Ni-30Cr alloys at 523 K and $-0.2 \text{ V}_{\text{SHE}}$ for 3.6 ks. (Sputtering rate: 0.385 nm/s as SiO_2).

in the film is nearly equivalent to that of the substrate alloy. It should be noted that no enrichment of chromium in the film occurs for the Ni-Cr alloys, contrasting with the

remarkable enrichment for Fe-18Cr alloy.

IV. Discussion

1. Active dissolution on the newly created surface

The initial stage of repassivation showed that the anodic current tended to increase with increasing chromium content. It is reasonable to suppose that the initial current density is proportional to the activity of metal or alloy for active dissolution.

The initial current density, i_0 , that is, the current density just after the straining has been stopped, however, is no true initial current density on the bare surface, because a short time of about 20 ms is always needed to give a constant amount of elongation. Thus, the film formation had already started even before the straining was stopped. Therefore, i_0 includes the influence of both active dissolution and the early stage of the film formation.

In the following discussion, a bare surface current density without any influence of film formation is estimated quantitatively by a numerical method, the outline of which is shown as follows. The details of the treatment will be described elsewhere.

It is assumed that the current density on a bare surface which emerges instantaneously is expressed by an unknown function, $C(t)$. In actual, the area of the bare surface changes with time during the limited time to reach a constant value, because an emergence of bare surface needs a limited time. Namely, the area of the bare surface can be described as a function of time, $S(t)$. Thus, the observed change in current with time, $I(t)$, is expressed as a convolution of $S(t)$ and $C(t)$, as shown in the following equation:

$$I(t) = \int_0^t C(\tau)S(t-\tau)d\tau. \quad (3)$$

In the present experiment, $I(t)$ and $S(t)$ can be expressed as a series of data with the same intervals, because $I(t)$ and $S(t)$ are recorded as digital data measured at constant intervals. Therefore, if $C(t)$ is also defined as a series of variables, the integral in eq. (3) for a given t is

Fig. 8 Effect of chromium content on the estimated bare surface current density, $i_{e,b}$ and the current density just after straining was stopped, i_0 , for the Fe-Cr and Ni-Cr alloys at 523 K at $-0.2 V_{SHE}$.

modified to a polynomial. Thus, eq. (3) is also modified to a series of polynomials, namely, simultaneous equations. Thus, the unknown function $C(t)$ can be obtained by solving these simultaneous equations. Consequently, the estimated bare surface current density, $i_{e,b}$, is given from the function $C(t)$ thus obtained.

Figure 8 shows $i_{e,b}$ of iron and nickel alloys at 523 K and $-0.2 V_{SHE}$ as a function of chromium content. In this figure, i_0 is also plotted in broken lines. $i_{e,b}$ of both the Fe-Cr and Ni-Cr alloys increases with increasing chromium content in a similar way to i_0 . $i_{e,b}$ of pure iron is larger than that of pure nickel by about one order. It is also clearly shown that the addition of chromium to iron and nickel increases the initial current. Therefore, it is concluded that the activity for dissolution of chromium is larger than that of iron and nickel. It is noticeable that the effect of chromium content on the current density is more pronounced for the Ni-Cr alloys than for the Fe-Cr alloys.

There have been few reports which deal thermodynamically with the anodic dissolution of alloys. Bockris *et al.*⁽¹²⁾ discussed on the partial dissolution current of constituent elements in a binary alloy in consideration of the change in

activation energy for dissolution of elements due to alloying. It is known that the reversible potential for an element in an alloy can be defined in consideration of the change in activity of the element in the alloy. It has been reported that a curve of the partial dissolution current density of an element vs potential for the binary alloy obeys the Tafel's relation. In this case, the decrease in the logarithm of the partial anodic current density is proportional to the increase in the reversible potential⁽¹³⁾. In the present experiment, however, a detailed discussion on the contribution of chromium to the total dissolution current could not be given, because the observed current density could not be separated into each partial current.

On the other hand, Mueller⁽¹⁴⁾ has discussed on the derivation of the anodic polarization curves of alloy from its constituent elements on the assumption that the alloy is a heterogeneous mixture of single metallic components and that each component contributes a fraction of the total current density:

$$I_a = I_x(A_x/A_a) + I_y(A_y/A_a) + I_z(A_z/A_a) + \dots, \quad (4)$$

where, I_a is the current density of the alloy. I_x , I_y and I_z are the current densities of single metals of x, y and z. A_x , A_y and A_z are exposed areas of the metals, and A_a is the total exposed area of the alloy.

As previously reported, the initial dissolution current of pure iron⁽¹⁰⁾ and pure nickel⁽⁹⁾ in the same solution was independent of potential nobler than about $-0.2 V_{\text{SHE}}$ at 523 K. Furthermore, the temperature dependence of the initial dissolution current proved that this process in the potential independent region was diffusion controlled. A similar potential independent region was also observed in this experiment for the initial current of the Fe-Cr and Ni-Cr alloys at potentials nobler than $-0.2 V_{\text{SHE}}$. Thus, the dissolution current, $i_{e,b}$, at $-0.2 V_{\text{SHE}}$ seems to be also diffusion controlled. Therefore, the dissolution rate is determined by the concentration of metal ion adjacent to the metal surface. It may be fairly accepted that the ratio among the concentrations of elements adjacent to the bare metal is proportional to the ratio in the substrate alloy for the very initial period after the emergence

of bare surface. If there is no interaction among alloying elements, the relation presented in eq. (4) holds. Thus, if the data exhibited in Fig. 8 are plotted in $i_{e,b}$ vs the chromium content in normal scales, the extrapolation of the plots to 100% chromium content provides I_{Cr} , i.e., the current density on the bare surface of pure chromium. The current density on the bare surface of chromium thus obtained is in the range between 10^6 and 10^7 Am^{-2} . The current density on the bare surface of chromium is by more than one order of magnitude larger than that of iron, and in turn the value for iron is by about one order of magnitude larger than that of nickel. Consequently, the contribution of chromium to the initial current density of alloys is apparently larger for the Ni-Cr alloys than for the Fe-Cr alloys, as can be seen in Figs. 2(a), 4(a) and 8.

In other words, most of the current for the initial period of repassivation of the Fe-Cr and Ni-Cr alloys derives from dissolution of chromium. This fact seems to be important for considering the mechanism of localized corrosion of the Fe-Cr-Ni alloys, because the larger dissolution rate is expected for the larger chromium content alloys for the very initial period after the film breakdown, in spite of their improved passivity. Moreover, the faster initial dissolution seems to enhance the localized corrosion.

2. Repassivation rate

As stated before, the chromium addition to the Ni-Cr alloys simply increased the current density during repassivation but did not accelerate the repassivation. On the other hand, the addition of chromium to the Fe-Cr alloys also increased the initial dissolution current, and the alloying with more than 8 mass% chromium increased the repassivation rate of the Fe-Cr alloys. The addition of 3 mass% chromium, however, rather retarded the repassivation of the Fe-Cr alloy, as shown in Fig. 3.

The transient current density on the newly created surface should be discussed in consideration not only of the active dissolution rate but also of the nature of film formed during the repassivation. The information on the

nature of the passive film on these alloys is provided by the polarization curves and the results of Auger analysis.

The Auger electron analysis showed that the enrichment of chromium in the film occurred for Fe-18Cr alloy, whereas no enrichment of chromium occurred for Fe-8Cr alloy and all the Ni-Cr alloys. It is very likely that the change in polarization curves with chromium content corresponds to the chromium content in the passive film. The small current density in the passive region for Fe-18Cr and Fe-22Cr alloys seems to be caused by the chromium enrichment in the passive film. It is also supposed that the large over passive peak current density is brought about by the oxidation of Cr^{3+} thus enriched in the film. On the other hand, the little contribution of chromium to decrease the passive current density and the small over passive peak for the Ni-Cr alloys compared with that of the Fe-Cr alloys are the result of no enrichment of chromium in the film for the Ni-Cr alloys.

It is considered that the enrichment of chromium in the steady state film corresponds to the change in the repassivation behavior observed in the straining electrode test, although the film on each alloy subjected to Auger analysis was formed after a long time passivation compared with the short time of the straining electrode test.

The more rapid decrease in the current density, namely, the faster repassivation was always observed for the higher chromium content Fe-Cr alloys, as shown in Fig. 3. It is reasonably assumed that the chromium enriched passive film depresses effectively the dissolution current, although the larger anodic current flows for the very initial period owing to the higher activity of chromium. On the other hand, the little addition of chromium also enhances the initial dissolution. However, it does not suppress effectively the repassivation current, because the chromium content in the alloy is not sufficient to form any chromium enriched passive film. Consequently, the repassivation current of Fe-3Cr alloy was larger than that of the other Fe-Cr alloys. The enrichment of chromium, however, did not occur for Fe-8Cr, as shown in Fig. 6, but the

enhancement of the repassivation was observed for this alloy. It seems that the structure of the newly created surface was different from that of the surface prepared for Auger analysis. Therefore, the repassivation behavior in the straining electrode did not correspond to the film composition obtained by Auger analysis for the Fe-Cr alloy of the intermediate chromium content.

In the case of the Ni-Cr alloys, the chromium addition increases significantly the initial current, because the dissolution activity of chromium is fairly larger than that of pure nickel as mentioned before. However, changes in the current density with time or the charge density are quite similar for all the Ni-Cr alloys, regardless of the chromium content. In other words, the increase in the chromium content has no effect on the repassivation rate for the Ni-Cr alloys, corresponding to no enrichment of chromium in the passive film formed on the Ni-Cr alloys.

V. Conclusion

The initial stage of repassivation process of the Fe-Cr and Ni-Cr alloys of various chromium contents was investigated in the high temperature and high pressure borate buffer solution by the rapid straining electrode technique. Moreover, the composition of the film formed on these alloys was analyzed by Auger electron spectroscopy.

(1) The initial current on the newly created surface increased with increasing chromium content for both the Fe-Cr and Ni-Cr alloys. The chromium addition of more than 8 mass% accelerated the repassivation of the Fe-Cr alloys, while the addition of 3 mass% chromium rather retarded it. On the other hand, the increasing chromium content for the Ni-Cr alloys simply increased the current density during repassivation, although it did not accelerate the repassivation.

(2) A bare surface current density without influence of film formation was estimated by a numerical method. It was concluded that the bare surface current density of chromium was by more than one order of magnitude larger than that of pure iron. The bare surface cur-

rent density of pure iron was in turn by about one order of magnitude larger than that of pure nickel.

(3) Auger analysis showed that chromium was enriched in the passive film of Fe-18Cr alloy, while chromium enrichment did not take place for the Fe-Cr alloy of small chromium content and all the Ni-Cr alloys examined.

(4) The results of straining electrode tests and the Auger analysis showed that the acceleration of repassivation was always associated with the chromium enrichment in the passive film.

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