Interfacial Impedance of Austenitic Stainless Steel under Anodic Polarization

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Variations in the interfacial impedance of the electrode of AISI Type 304 stainless steel in electrolytic solutions of sodium sulphate have been measured as a function of polarizing voltage under anodic polarization. The capacitive component of the impedance exhibits three characteristic changes with potential and these changes correspond to the transitions from the passive to the transpassive state, from the transpassive to the secondary passive state and from the secondary passive to the oxygen evolution state which are observed in the current-potential curve of this steel. However, the changes observed in the capacitance-potential curve always appear at more negative potentials than the potentials at which the corresponding changes are observed in the polarization curve. These phenomena are discussed on the basis of compositional changes in the passive film.

1. Introduction

The interfacial impedance of austenitic stainless steel electrodes in aqueous solutions of sodium sulphate has been investigated over a region of the corrosion potential to the oxygen evolution potential in order to clarify changes in properties of surface films formed during anodic polarization. The typical example of the variations in capacitance, resistance and anodic current with potential for a commercial AISI Type 304 stainless steel in a neutral solution of 1 M- Na_2SO_4 is shown in Fig. 1. Two minimums and one maximum of capacitance are usually observed in the capacitive component-potential curve (C - E curve), which are herein designated C_1 , C_2 , and C_3 , respectively. One maximum of resistance is also observed in the resistive component-potential curve (R - E curve), which is designated R_1 . A similar behavior of the C - E and R - E curves for Type 304 stainless steel measured by an A.C. bridge method has been observed by Pražák,¹⁾ Morioka,²⁾ Okamoto,³⁾ and the present authors.⁴⁾

However, there arises a question as to whether the changes in the C - E curve correspond to those in the anodic polarization curve measured at the same time with the C - E curve because the potentials of C_1 , C_2 and C_3 in the C - E curve are more negative by 150–200 mV than the transition potentials from passivity to transpassivity, transpassivity to secondary passivity and secondary passivity to oxygen evolution in the anodic

polarization curve, respectively. The present study was carried out so as to determine the electrode reactions by which the changes of C_1 , C_2 and C_3 in the C - E curve and R_1 in the R - E curve are caused.

To make clear the influence of alloying elements on the electrode impedance for Type 304 stainless steel, the C - E and R - E curves of Type 304 stainless steel were compared with those for pure iron, pure chromium, pure nickel, binary Fe-Cr alloys and a binary Fe-Ni alloy. Further, to investigate the correspondence between the changes in electrode impedance and electrode reactions, the dependence of the potentials for C_1 , C_2 , C_3 and R_1 on the pH of solutions was compared with those of the transition potentials in the anodic polarization curves.

2. Experimental Procedure

Experimental arrangement composed of a potentiostat and an A.C. bridge was used for measurements of the electrode impedance during potentiostatic polarization.^{5,6)} Balance points of the bridge were detected by using a synchroscope with an amplitude of vertical axis up to 5 mV/cm. If necessary, a differential amplifier with a gain of 60 dB was used to increase the amplification of the synchroscope. The frequency of the applied A.C. wave was 1000 Hz and its amplitude was less than 7 mV. A specimen and an auxiliary platinum electrode for the D.C. supply were placed separately in two compartments of an H-type cell made of Pyrex glass and a platinized

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Fig. 1. The typical example of the variations in capacitance, resistance and anodic current with potential for Type 304 stainless steel in 1 M-Na₂SO₄ solution at pH 6.4.

platinum electrode for the impedance measurement was set in one of the compartments at a distance of 2 cm from the specimen.

Electrode impedances and anodic currents were measured at the same time at given potentials. Both measurements were made after holding electrode potential for 5 min at each setting potential which was obtained by changing potentials from the corrosion potential toward the positive direction at intervals of 50 mV. The bridge was balanced by using an equivalent RC network having a series combination of a capacitor and a resistor. A saturated calomel electrode was used for the reference in potential measurements.

A commercial AISI Type 304 stainless steel was used as specimens. Effects of alloying elements, such as Fe, Cr, and Ni, on the impedance were also examined by using pure iron, pure chromium, pure nickel, binary Fe-Cr alloys (20–70% Cr) and a binary Fe-40% Ni alloy. The chemical compositions and the heat treatment conditions of the specimens are listed in Table 1. Specimen surfaces were prepared by finishing with cloth after polishing with emery papers up to No. 6/0. The rest of the specimen surface except the exposed area of 1 cm² was covered with a resin insulator.

In most cases, a neutral solution of 1 M-Na₂SO₄ at pH 6.4 was used as the electrolyte. When

Table 1. Chemical compositions and heat treatment conditions of specimens.

Specimen	Cr	Ni	C	Si	P	S	Mo	Cu	Mn	Heat treatment
Type 304	18.53	8.82	0.06	0.73	0.029	0.005	0.13	0.10	1.69	1100°C, 30 min→WQ
pure iron			0.003	0.006	0.002	0.004	0.008	0.011		as cast
pure chromium	99.29		0.020	0.008	0.001	0.024		0.0005		820°C, 5 min→AC
pure nickel		99.96	0.002	0.008			<0.001	0.002		1000°C, 30 min→WQ
Fe-20%Cr	21.20	<0.01	0.001	0.01	0.002	0.010	0.01	0.01		830°C, 5 min→WQ
Fe-30%Cr	32.30	<0.01	0.001	0.03	0.002	0.012	0.01	0.01		830°C, 5 min→WQ
Fe-40%Cr	42.31	0.18	0.002	0.42	0.016	0.019	0.01	0.01		830°C, 5 min→WQ
Fe-60%Cr	58.20	0.16	0.002	0.45	0.011	0.021	0.01	0.01		1100°C, 60 min→WQ
Fe-70%Cr	72.10	0.13	0.001	0.48	0.010	0.024	0.01	0.01		1100°C, 60 min→WQ
Fe-40%Ni	<0.01		0.001	<0.01	0.002	0.006	0.01	0.01		1000°C, 30 min→WQ

necessary, the pH of the solutions was adjusted in the range of 0 to 8.0 by adding a small amount of H_2SO_4 or NaOH solution keeping the concentration of SO_4^{2-} ion in the solutions constant (1 g-ion/L). The electrolytes were prepared from reagent-grade chemicals and distilled water with the specific conductivity of $2 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$. Purified nitrogen gas was bubbled through the cell for more than 20 min before measurements. Measurements were made in a nitrogen atmosphere at a temperature of $25 \pm 0.5^\circ\text{C}$ under the condition of a stationary state.

3. Experimental Results

3.1 Relations between alloy compositions and variations in the C - E and R - E curves

3.1.1 Iron

The C - E curve, the R - E curve and the anodic polarization curve for pure iron measured in 1 M- Na_2SO_4 solution (pH 6.4) are shown in Fig. 2. The shape of the C - E curve for pure iron is quite different from that for Type 304 stainless steel; that is, neither maximum nor minimum of capacitance corresponding to C_1 and C_2 for Type 304 stainless steel appears in the C - E curve for pure iron, and the values of capacitance in the potential range of $+0.30$ to $+1.15$ V corresponding to the passivity of iron decrease with increasing in potential.

3.1.2 Chromium

The anodic polarization curves for pure chromium and binary Fe-Cr alloys measured in

Fig. 2. Variations in capacitance, resistance and anodic current with potential for pure iron in 1 M- Na_2SO_4 solution at pH 6.4.

1 M- Na_2SO_4 solution (pH 6.4) are shown in Fig. 3. The C - E and R - E curves for them are also shown in Figs. 4 and 5, respectively.

The C - E curves for pure chromium and binary Fe-Cr alloys containing 60 and 70% chromium which exhibit transpassivity but no secondary passivation in the anodic polarization curves show only one minimum of capacitance corresponding to C_1 at $+0.30$ V, while those of binary Fe-Cr alloys containing 20 to 40% chromium have two maxima at -0.30 and $+0.70$ V, which are designated $C_{(\text{Fe-Cr})0}$ and $C_{(\text{Fe-Cr})2}$,

Fig. 3. Anodic polarization curves for pure chromium and binary Fe-Cr alloys in 1 M- Na_2SO_4 solution at pH 6.4.

Fig. 4. Variations in capacitance with potential for pure chromium and binary Fe-Cr alloys in 1 M- Na_2SO_4 solution at pH 6.4.

respectively, and two minimums at $+0.35$ and $+0.95$ V, which are designated $C_{(\text{Fe-Cr})1}$ and $C_{(\text{Fe-Cr})3}$, respectively.

The relations between the potentials of $C_{(\text{Fe-Cr})1}$, $C_{(\text{Fe-Cr})2}$ and $C_{(\text{Fe-Cr})3}$ in the C - E curves and the chromium content for Fe-Cr alloys are shown in Fig. 6. The potential of $C_{(\text{Fe-Cr})1}$ depends on the chromium content of the binary alloys and shifts in negative direction with an increase in chromium content, while the potentials of $C_{(\text{Fe-Cr})2}$ and $C_{(\text{Fe-Cr})3}$ are independent of the chromium content. Not only the potentials but also the capacitance values of $C_{(\text{Fe-Cr})1}$, $C_{(\text{Fe-Cr})2}$ and $C_{(\text{Fe-Cr})3}$ for Fe-Cr alloy containing chromium about 18% agree quite well with those of

Fig. 5. Variations in resistance with potential for pure chromium and binary Fe-Cr alloys in 1 M-Na₂SO₄ solution at pH 6.4.

Fig. 6. Relations between the potentials of $C_{(\text{Fe-Cr})1}$, $C_{(\text{Fe-Cr})2}$ and $C_{(\text{Fe-Cr})3}$ in the C - E curves and the chromium content of Fe-Cr alloys.

C_1 , C_2 and C_3 for Type 304 stainless steel (see Fig. 1).

The maximum of resistance is observed at about $+0.50$ V in the R - E curves for pure chromium and binary Fe-Cr alloys containing chromium up to 70%, which is designated $R_{(\text{Fe-Cr})1}$. The potential of $R_{(\text{Fe-Cr})1}$ is also almost equal to that of R_1 for Type 304 stainless steel.

3.1.3 Nickel

The C - E , R - E and anodic polarization curves for pure nickel and a binary Fe-40%Ni alloy measured simultaneously in 1 M-Na₂SO₄ solution (pH 6.4) are shown in Fig. 7. The C - E curve of Fe-40%Ni alloy has one maximum at -0.20 V in the potential region of active dissolution and one minimum near a middle potential of the passivity region, $+0.45$ V, which are designated $C_{(\text{Fe-Ni})0}$ and $C_{(\text{Fe-Ni})1}$, respectively. The potential and capacitance of $C_{(\text{Fe-Ni})1}$ are nearly equal to those of C_1 for Type 304 stainless steel. Pure nickel exhibits the transpassivity, secondary passivation and oxygen evolution in the anodic polarization curve. The C - E curve for pure nickel has two maximums (at -0.20 and $+0.75$ V) and three minimums (at -0.4 , 0.0 and $+1.05$ V). The shape of the C - E curve between about -0.20 V

Fig. 7. Variations in capacitance, resistance and anodic current with potential for pure nickel and Fe-40%Ni alloy in 1 M-Na₂SO₄ solution at pH 6.4.

and +1.20 V bears close resemblance to that for Type 304 stainless steel. However, the potentials and capacitances for the minimums and the maximums are different from those for Type 304 stainless steel.

The R - E curve for Fe-40%Ni alloy shows only one maximum at +0.65 V, which is designated $R_{(\text{Fe-Ni})1}$. The potential of $R_{(\text{Fe-Ni})1}$ is nearly equal to that of R_1 for Type 304 stainless steel.

3.2 Effects of the pH of solutions on the C - E and R - E curves

Variations of the C - E and R - E curves for Type 304 stainless steel with the pH of 1 M- Na_2SO_4 solutions are shown in Figs. 8 and 9, respectively. Variations of the anodic polarization curves with the pH of the solutions are also shown in Fig. 10. With a decrease in pH of the solutions, the variations in current corresponding to the active dissolution, passivity, transpassivity, secondary passivation and oxygen evolution are clearly distinguishable in the anodic polarization curves.

The relations between the pH of solutions and transition potentials in the anodic polarization curves in Fig. 10 are shown in Fig. 11. Linear relations are obtained for the potentials E_1 , E_2

and E_3 , which are the transition potentials from the passive to the transpassive state, the transpassive to the secondary passive state, and the secondary passive to the oxygen evolution state, respectively.

$$E_1: E = 0.900 - 0.063 \text{ pH}, \quad (1)$$

$$E_2: E = 1.313 - 0.137 \text{ pH}, \quad (2)$$

$$E_3: E = 1.647 - 0.103 \text{ pH}. \quad (3)$$

The capacitances and potentials of C_1 , C_2 and

Fig. 8. Variations in the C - E curves for Type 304 stainless steel with the pH of 1 M- Na_2SO_4 solutions.

Fig. 9. Variations in the R - E curves for Type 304 stainless steel with the pH of 1 M- Na_2SO_4 solutions.

Fig. 10. Variations of the anodic polarization curves with the pH of 1 M- Na_2SO_4 solutions.

C_3 depend on the pH of solutions; that is, the potentials of C_1 , C_2 and C_3 shift in positive direc-

Fig. 11. Relations between the pH of solutions and transition potentials in the anodic polarization curves for Type 304 stainless steel.

Fig. 12. Relations between the pH of solutions and the potentials of C_1 , C_2 and C_3 for Type 304 stainless steel.

tion and the variations in capacitance with potential become pronounced as the pH of solution decreases. The relations between the potentials of C_1 , C_2 and C_3 and the pH of solutions are shown in Fig. 12. Linear relations as expressed by Eqs. (4) to (6) are obtained for C_1 , C_2 and C_3 when the pH is lower than 4.0.

$$C_1: E = 0.727 - 0.058 \text{ pH}, \quad (4)$$

$$C_2: E = 1.377 - 0.137 \text{ pH}, \quad (5)$$

$$C_3: E = 1.531 - 0.098 \text{ pH}. \quad (6)$$

The maximums of resistance corresponding to R_1 are observed in all the curves of Fig. 9 but the second maximums of resistance, which are designated R_2 , exist in the potential region of secondary passivation only in the curves for the solutions having pH values lower than 2.6. The relations between the potentials of R_1 and R_2 and the pH of solutions are shown in Fig. 13 and the following linear relation is obtained for R_1 .

$$R_1: E = 0.875 - 0.048 \text{ pH}. \quad (7)$$

Fig. 13. Relations between the pH of solutions and the potentials of R_1 and R_2 for Type 304 stainless steel.

4. Discussion

4.1 Electrode reactions which are responsible for the characteristic changes in the C-E and R-E curves

The experimental results obtained for C_1 , C_2 and C_3 in the C-E curve and R_1 in the R-E curve

of Type 304 stainless steel are summarized as follows.

C_1 : (1) The minimum capacitances which correspond to C_1 are observed in metals and alloys, such as pure chromium, Fe–Cr alloys (20–70% Cr) and Fe–40%Ni alloy, which exhibit a transition from the passive to the transpassive state. The potentials and capacitances of $C_{(\text{Fe}-\text{Cr})1}$ and $C_{(\text{Fe}-\text{Ni})1}$ are nearly equal to those of C_1 . (2) The pH dependence of the potential of C_1 is in approximate agreement with that of the transpassive potential E_1 ; that is, the slopes of the straight lines C -pH (Fig. 12) and E -pH (Fig. 11) give nearly equal values.

C_2 : (1) The maximum capacitances which correspond to C_2 are observed in alloys, such as Fe–Cr alloys containing 20 to 40% chromium, which show secondary passivation after transpassive dissolution. (2) The pH dependence of the potential of C_2 agrees fairly well with that of the secondary passivation potential E_2 .

C_3 : (1) The minimum capacitances which correspond to C_3 are observed in metals and alloys, such as pure nickel and Fe–Cr alloys containing 20 to 40% chromium, which show the oxygen evolution reaction after the secondary passivation. (2) The pH dependence of the potential of C_3 agrees fairly well with that of the oxygen evolution potential E_3 .

R_1 : (1) The maximum resistances which correspond to R_1 are observed in metals and alloys which show the minimum capacitance corresponding to C_1 in the C - E curve and the transition from the passive to the transpassive state in the anodic polarization curve. The potentials of $R_{(\text{Fe}-\text{Cr})1}$ and $R_{(\text{Fe}-\text{Ni})1}$ are nearly equal to that of R_1 . (2) The pH dependence of the potential of R_1 agrees fairly well with that of C_1 .

Consequently, C_1 and R_1 are related to the changes caused by the same origin, which is assumed to be the start of a transpassivation reaction. Since it can be considered that both C_1 and R_1 are influenced by the transpassivation reaction of chromium and/or nickel in Type 304 stainless steel, some electrode reaction presumed for the transpassivation and their equilibrium potentials, which have similar potentials and coefficients of pH terms to those in Eq. (4), are given by Eqs. (8) to (13). The values of standard free energy of formation used here are employed from the works of Latimer⁷⁾ and Pourbaix.⁸⁾

$$E = 1.0451 - 0.0592\text{pH} + 0.0197 \log a_{\text{CrO}_3-\text{Ox}} \quad (8)$$

$$E = 1.1197 - 0.0592\text{pH} + 0.0197 \log a_{\text{CrO}_3-\text{Ox}} \quad (9)$$

$$E = 0.9781 - 0.0592\text{pH} + 0.0197 \log a_{\text{CrO}_3-\text{Ox}} \quad (10)$$

$$E = 1.1197 - 0.0592\text{pH} + 0.0197 \log a_{\text{CrO}_3-\text{Ox}} \quad (11)$$

$$E = 0.7868 - 0.0592\text{pH} + 0.0296 \log a_{\text{Ni}_2\text{O}_3-\text{Ox}} \quad (12)$$

$$E = 1.059 - 0.0592\text{pH} + 0.0888 \log a_{\text{Ni}_2\text{O}_3-\text{Ox}} \quad (13)$$

$a_{\text{CrO}_3-\text{Ox}}$ and $a_{\text{Ni}_2\text{O}_3-\text{Ox}}$ in those equations represent the activities of CrO_3 and Ni_2O_3 in the passive film, respectively. Although a detailed knowledge of the chemical composition and structure of the passive and transpassive films is essential to determine the most reasonable reaction for the transpassivation of Type 304 stainless steel, the transpassivation of the steel seems to result from oxidation of a lower oxide containing species of Cr^{3+} and Ni^{2+} , such as $\text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3 \cdot \text{NiO}$, to a higher oxide containing species of Cr^{6+} and Ni^{3+} , such as $\text{Fe}_2\text{O}_3 \cdot \text{CrO}_3 \cdot \text{Ni}_2\text{O}_3$.

The transpassive dissolution of Type 304 stainless steel seems to arise from the chemical dissolution of CrO_3 formed in the passive film into aqueous solutions as follows:

The same dissolution mechanism for transpassivity is also thought for pure chromium^{9,10)} and binary Fe–Cr alloys.¹¹⁾

The activities of CrO_3 in oxide films, $a_{\text{CrO}_3-\text{Ox}}$, at the potentials of E_1 or C_1 can be calculated by solving the simultaneous equations of Eq. (1) and one of Eqs. (8)–(11) or Eq. (4) and one of Eqs. (8)–(11), respectively. Calculated values of $a_{\text{CrO}_3-\text{Ox}}$ at the potentials of E_1 and C_1 for a solution of pH 0 are listed in Table 2, where the potential of E_1 is more noble than that of C_1 .

Table 2. Calculated values of $a_{\text{CrO}_3-\text{Ox}}$.

Equations of the reaction	$a_{\text{CrO}_3-\text{Ox}}$ at the potential of C_1	$a_{\text{CrO}_3-\text{Ox}}$ at the potential of E_1
Eq. (8)	10^{-16}	10^{-7}
Eq. (9)	10^{-20}	10^{-11}
Eq. (10)	10^{-13}	10^{-4}
Eq. (11)	10^{-20}	10^{-11}

Table 2 shows that the activity of CrO_3 in the passive film is so small at the potential of C_1 that the beginning of chemical reaction according to Eq. (14) can hardly be recognized by polarization measurements. However, according to the calculations from Eq. (8) or Eq. (10), the activity of CrO_3 at the potential E_1 is large enough to distinguish the initiation of transpassive dissolution on the basis of the increase of current in the anodic polarization curve.

The change in capacitance at C_2 may be related to the secondary passivation of Type 304 stainless steel. Although the potential and capacitance of C_2 depend on the pH of the solutions, the electrochemical reactions of which equilibrium potentials have the same pH dependence as that of Eq. (5) cannot be found in the possible chemical reactions in which chromium compounds participate. Therefore, the secondary passivation of Type 304 stainless steel can be related not to a specific electrode reaction but to the increase of anodic polarization resulting from the decrease in chromium content and the enrichment of iron and nickel on the electrode surface with progress of the transpassive dissolution.

The minimum capacitance which corresponds to C_3 is assumed to be related to the oxygen evolution reaction because the pH dependence of the potential of C_3 agrees well with that of E_3 .

4.2 Relations between the variations in the oxide film and in the interfacial impedance

As mentioned already, there are differences in the characteristic potentials between the C - E curve and the anodic polarization curve. For example, by comparing Eq. (1) with Eq. (4) at an equal pH, the potential of C_1 in the C - E curve is less noble by about 170 mV than the transpassive potential E_1 on the anodic polarization curve. Although the participation of Faradaic components in the impedance should be taken into account when the dissolution current of transpassivation is large,⁴¹ Faradaic components may be neglected up to the potential E_1 because the anodic polarization curves in this region show extremely small current densities corresponding to the passivity of Type 304 stainless steel.

Therefore, it is assumed that some changes related to the transpassivation may occur in the passive film even at the potential of C_1 which is more negative by about 170 mV than the initial potential of the transpassive dissolution, E_1 . With regard to the cause of these changes, the variations in thickness, composition or structure

of the surface film may be considered. As for the variations in film thickness, it is difficult to attribute the increase of capacitance at a potential more positive than C_1 to the decrease in thickness of the surface film, since a continuous growth in thickness of the surface film at a potential more negative than the oxygen evolution potential has been shown by ellipsometric measurements^{8,12,14)} and coulometric measurements.^{11,13)} Although the film is considered to be porous at a potential more noble than E_1 by the transpassive dissolution,^{1,2)} it can hardly be expected that there is a remarkable change in the structure of the film, such as the formation of a porous solid structure, at a potential between C_1 and E_1 , because the dissolution current is very small below the potential E_1 . Consequently, the variation in the dielectric constant of the film with film composition should cause the increase of capacitance above the potential C_1 . According to the variation in film composition based on the mechanism of transpassivation stated before, it may be assumed that the amounts of Cr^{3+} and Ni^{2+} species decrease, and, on the contrary, those of Cr^{6+} and Ni^{8+} species increase in the surface film with increasing potential in the range more positive than the potential of C_1 . The possibility of formation of a mixed oxide such as $\text{Cr}_2\text{O}_3/\text{CrO}_3$ has been discussed by Vetter *et al.*⁹⁾ for a pure chromium electrode in the transpassive region.

5. Conclusions

The following conclusions were obtained by measuring interfacial impedances of Type 304 stainless steel under anodic polarization in the solution of 1 M- Na_2SO_4 .

The capacitive component-potential curve (C - E curve) obtained in the solution at pH 6.4 shows two minimums C_1 and C_3 at +0.40 and +0.95 V (vs. SCE), respectively, and one maximum C_2 at +0.75 V. The resistive component-potential curve (R - E curve) has a maximum R_1 at +0.60 V only. The minimums in capacitance corresponding to C_1 are also recognized in the C - E curves for pure metal and binary alloys which exhibit the transition from passivation to transpassivation in the anodic polarization curves. The maximums in capacitance corresponding to C_2 are seen only for the alloys which show the transition from transpassivation to secondary passivation. The minimums in capacitance corresponding to C_3 are observed in the C - E curves for pure metals and alloys which exhibit oxygen evolution reactions.

The potentials at which C_1 , C_2 and C_3 appear in the C - E curve are dependent on the pH of the solutions and the pH dependence agrees fairly well with that of the potentials at which the variation in current is observed in the anodic polarization curve. Accordingly, it may be concluded that the changes in capacitance which correspond to C_1 , C_2 and C_3 are related to the electrode reactions of transpassivation, secondary passivation and oxygen evolution, respectively.

As the potential C_1 is always more negative by about 170 mV than the initial potential of transpassive dissolution in the polarization curve, it is presumed that the variation in chemical composition of the passive film arising from the transpassive reaction begins at a lower potential than the potential at which an increase of current caused by the transpassive dissolution is observed.

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