Chronoamperometric Evaluation of Sensitization of SUS 316 Stainless Steel

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ABSTRACT

The extent of sensitization of austenitic stainless steel, SUS316, was evaluated by both conventional cyclic voltammetry and potential step chronoamperometry (PSCA). The test solution used for the test was $0.5\mathrm{kmol \cdot m^{-3}} H_2SO_4$ – $0.01\mathrm{kmol \cdot m^{-3}}$ potassium thiocyanate solution. First, the ratio of peak currents in cathodic and anodic scanning (reactivation ratio) using the Electrochemical Potentiokinetic Reactivation method (EPR) based on conventional cyclic voltammetry was measured. Second, the modification reactivation ratio by PSCA was measured and both data were compared and discussed to determine the extent of sensitization. The modified reactivation ratio had a better correlation with sensitization time than the conventional reactivation ratio. However, the correlation ratio was not so high as a whole for SUS316. The reason for this could be attributable to the complication involved in the anodic reaction.

1. INTRODUCTION

Austenitic stainless steels become sensitive to intergranular fracture when they are heated to temperatures within 923K to 1123K. Such temperatures cause some chromium carbides to precipitate along the grain boundaries during the heating process. The phenomenon is called sensitization and is significant for practical application, since it can lead to the destruction of structures. Therefore, rapid and precise evaluation techniques are important. Conventionally, the degree of sensitization has been measured by hardness, optical microscopy, electron microscopy, X-ray, etc. /1-3/. However, an electrochemical measurement technique based on cyclic voltammetry in aqueous solutions, Electrochemical Potentiokinetic Reactivation (EPR) has been devised /4-11/ and has become established in Japanese Industrial Standard (JIS G-0580-1986) /12/. However, the result of this method does not always correspond with the results of other methods and in addition /13/, it requires a relatively long time to evaluate the sensitization. As an electrochemical method, potential fluctuation in aqueous solutions is also being applied /14/, but requires expensive apparatus. For the electrochemical evaluation of the sensitization of SUS 304 steel, we have applied Potential Step Chronoamperometry (PSCA) /15/. This does not require expensive apparatus or a long test period. We have confirmed that the reactivation ratio based on EPR has a relatively good correlation with that based on PSCA. Therefore, we investigated the applicability of this method to another austenitic stainless steel, SUS316, in this study.

2. EXPERIMENTAL

The specimen used was a cold-worked sheet of austenitic stainless steel readily available commercially, SUS 316 (thickness: 2mm). The standard chemical

Table 1

Chemical composition of the SUS316 steel used in this experiment

C	Si	Mn	P	S	Ni	Cr	Mo
<0.08	<1.00	<2.00	<0.045	<0.030	10.00 ~14.00	16.00 ~18.00	2.00 ~3.00

composition is shown in Table 1. The stainless steel was cut into smaller rectangular pieces (1 cm × 1 cm) and heat treated. First, specimens were solution treated in a vacuum at 1323K for 2.4 ks. After cooling in water, they were heated again to 923K and maintained at that temperature for a pre-determined time (sensitization). The specimens were cooled rapidly in water immediately after treatment, then connected by a lead wire, embedded in epoxy resin, hand-polished by abrasive papers, buffed and subjected to electrochemical measurements.

Fig. 1 shows the block diagram of the experimental apparatus used in the present investigation. Specimens were used as the working electrode. Platinum in a helical form was used as the counter electrode with a silver/silver chloride electrode (Ag/AgCl/3.3kmo·m^{-3} KCl) as the reference electrode. (All potentials in the present paper are described on the basis of the reference electrode.) The cell was constituted by the three electrodes connected to a potentiostat (Hokuto Denko, HA303). 0.5kmol·m^{-3}H_2SO_4 – 0.01kmol·m^{-3} potassium thiocyanate solution without deaeration was used as the test solution. Conventional Electrochemical Potentiostatic Reactivation (EPR) and Potential Step Chronoamperometry (PSCA) were performed. In the former, the potential was scanned by a function generator (Hokuto Denko, HB104) at a constant rate and the current-potential curves were recorded by X-Y recorder (Yokogawa Denki 3025). The procedure of changing potentials was carried out according to Japanese Industrial Standard G-0580-1986. The specimens were immersed in the solution. After 300 seconds, the potentials were measured as rest potentials (RP) and scanned up to 0.3V at 100mV/60s. The scanning direction was then reversed and the potential was scanned back to RP which was measured in advance. In the latter, the potentials of the specimen were set up to pre-determined values instantaneously by a digitizing oscilloscope (Tektroniks TDS-420), the current-time curves (chronoamperograms) were recorded and printed out via GP-IB to X-Y plotter (Epson HI-80).

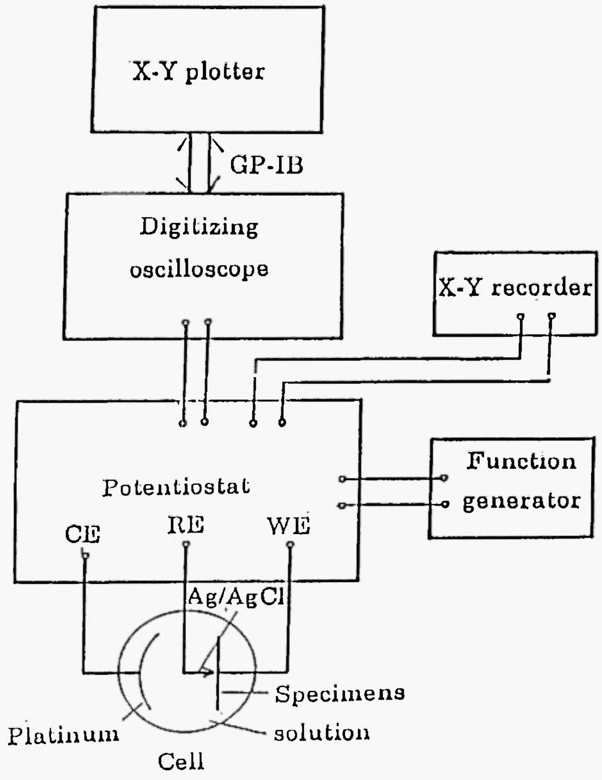

Fig. 1: Block diagram of experimental apparatus.

3. RESULTS AND DISCUSSION

Figs. 2, 3 and 4 show the results of conventional EPR based on cyclic voltammetry. Fig. 2 shows the result for the solution treated specimen. When the specimen was scanned in the anodic direction, the anodic current peak was observed at –0.05V. The anodic dissolution could be attributed to the active dissolution of iron matrices. After anodic dissolution, the current decreased with potential gradually and the specimen passivated again. When the potential scanned back to the less noble direction, the current increased

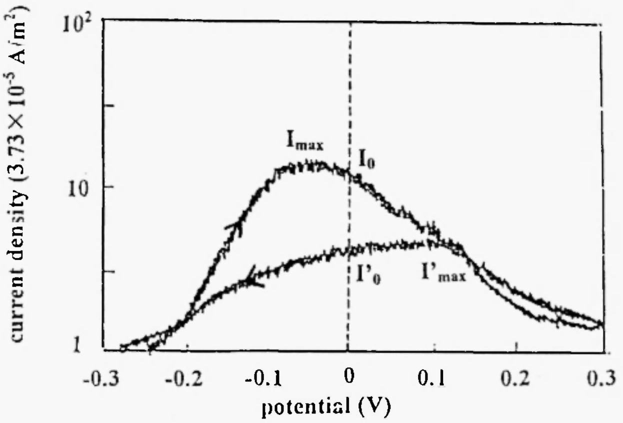

Fig. 2: Cyclic voltammograms of solution treated SUS316 steel.

and reached peak value at about 0.1V. The current peak corresponded to the anodic dissolution of the parts near the grain boundaries where passivation had not occurred enough due to the depletion of chromium (reactivation). The peak potential for cathodic scanning differed from that of anodic scanning.

Fig. 3 shows the result for the specimen sensitized for 61.2ks. In this case, the peak currents could also be observed for both anodic and cathodic scanning, as in the solution-treated specimen. However, a new peak current was observed in a nobler potential region, at about 0.1V, in addition to the peak recognized between –0.05V and 0V. In contrast, only one peak was observed in cathodic scanning. However, the peak potential moved in the less noble direction in comparison with the solution-treated specimen. That is. the peak potential of the former was about 0.007V, and that of the latter was about 0.12V.

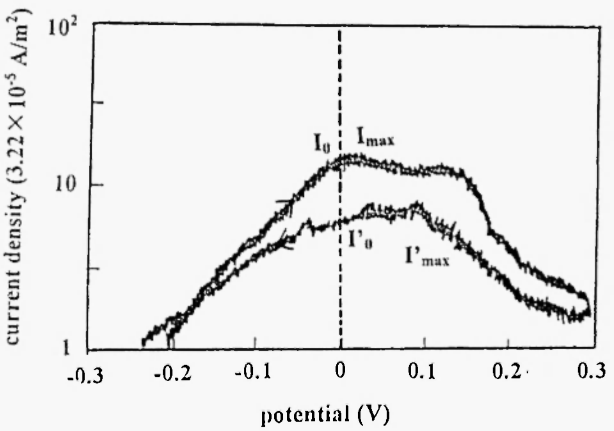

Fig. 3: Cyclic voltammograms of SUS316 steel sensitized for 61.2ks.

Fig. 4 shows the result for the specimen sensitized for 158.4ks. The current peak in the nobler potential became more remarkable than the one observed at the less noble potential. In addition, the peak potential for cathodic scanning moved in the less noble direction, further, compared with the result shown in Fig. 4. For SUS304 stainless steel, only one current peak was observed for both anodic and cathodic scanning, and both were almost at the same potential. Although the precise details in the redox reactions are not discussed, the differences in electrochemical behavior between the two kinds of stainless steel could be attributed to that of added elements. For SUS316 steels, molybdenum is usually added to enhance the anti-pitting characteristics (Table 1). Therefore, the thin oxide film formed on SUS316 steels must also contain molybdenum to some extent and is inevitably involved with the redox reactions on the surface. Also, application of cyclic voltammetry to the evaluation of the extent of sensitization is considered to be very difficult for SUS316, since plural current peaks were observed and the peak for anodic scanning did not quite correspond to that in cathodic scanning.

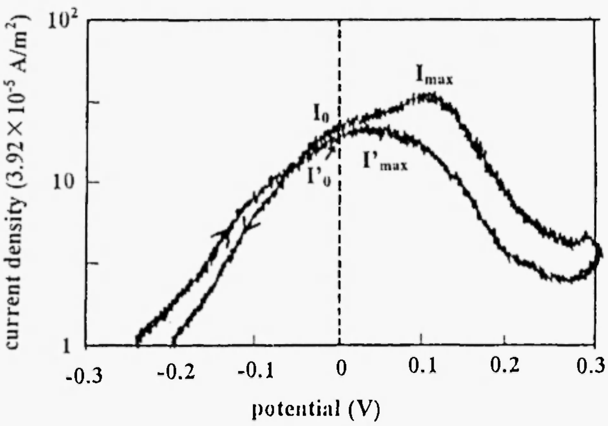

Fig. 4: Cyclic voltammograms of SUS316 steel sensitized for 158.4ks.

Firstly, the ratio of the maximum current density for cathodic scanning to that for anodic scanning was calculated (reactivation ratio, I'_{max}/I_{max}) and plotted versus the sensitization time. The result is shown in Fig. 5. Sensitization was expected to proceed with

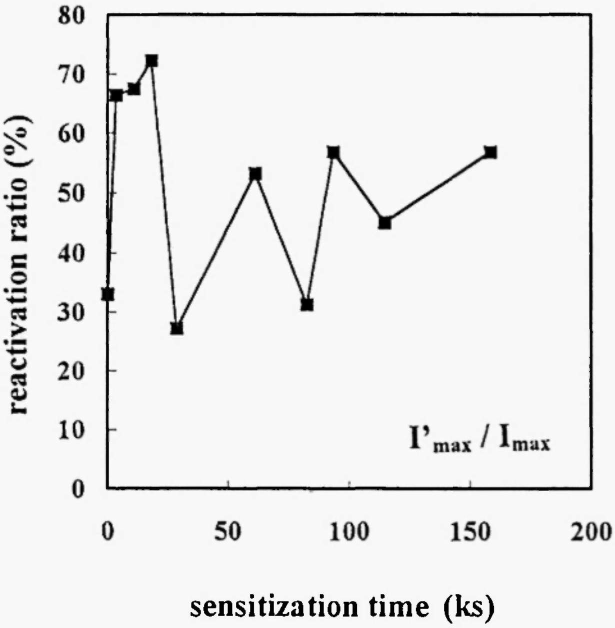

Fig. 5: Reactivation ratio of each maximum value from cyclic voltammograms for SUS316.

increasing treatment time at the original temperature /12/. If this had happened, the reactivation ratio should have increased with time. However, the result did not come up to our anticipation and on the contrary, the plots seemed to scatter at random. As an indicator of the correlation, the product-moment coefficient of correlation by Pearson (r) was calculated and is shown in the figure. The Pearson correlation coefficient /16/, r, can be obtained by the following equation (1) generally:

$$r = S_{xy} / (S_x S_y) \quad (1)$$

where S_x and S_y are standard deviations for the two variables, x and y, respectively. S_{xy} is known as the covariance of variables, x and y, and defined as the equation (2):

$$S_{xy} = \Sigma (x - x_{av})(y - y_{av}) / (n-1) \quad (2)$$

where x and y are raw scores, x_{av} and y_{av} are the means for variables, x and y, and n is the number of the measuring points.

The value r in Fig. 5 was negative and extremely small (r = –0.096), which suggests a low correlation and decreasing reactivation ratio with the increase in time. This result can be attributed to the complicated anodic reactions in SUS316 steel.

Secondly, the reactivation ratio was redefined as a ratio of the current density of cathodic scanning to that of anodic scanning at a certain potential and calculated. Fig. 6 shows the correlation between the reactivation ratio at 0V (I'_0/I_0) and treatment time. The result does not show a good correlation (r = 0.4). However, the correlation in Fig. 6 was higher than that in Fig. 5. Although the correlation coefficient was increased by redefining the reactivation coefficient as mentioned above, several problems remained concerning the practical evaluation of the extent of sensitization. One particular problem was how to decide the potential for the calculation of the reactivation ratio.

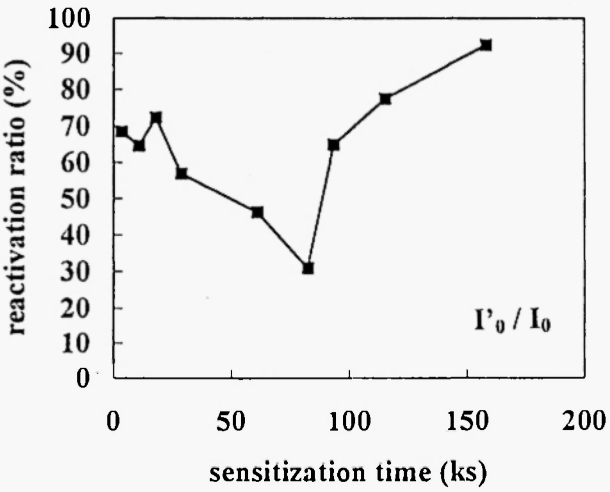

Fig. 6: Reactivation ratio of current densities at 0V from cyclic voltammograms for SUS316.

Therefore, we tried to apply the electrochemical transient by using an oscilloscope, i.e., chronoamperometry, to the evaluation of sensitization for SUS316 steel. The modified reactivation ratio calculated from the potential step chronoamperometry (PSCA) corresponded to the extent of sensitization for SUS304 steel /15/. Before the application of this method to the evaluation of sensitization for SUS316 steels, the current-time behavior by potential step electrolysis (chronoamperometric behavior) was investigated in the test solution. The potential was imposed to three potentials, 0V, +0.2V, +0.4V from the rest potential,

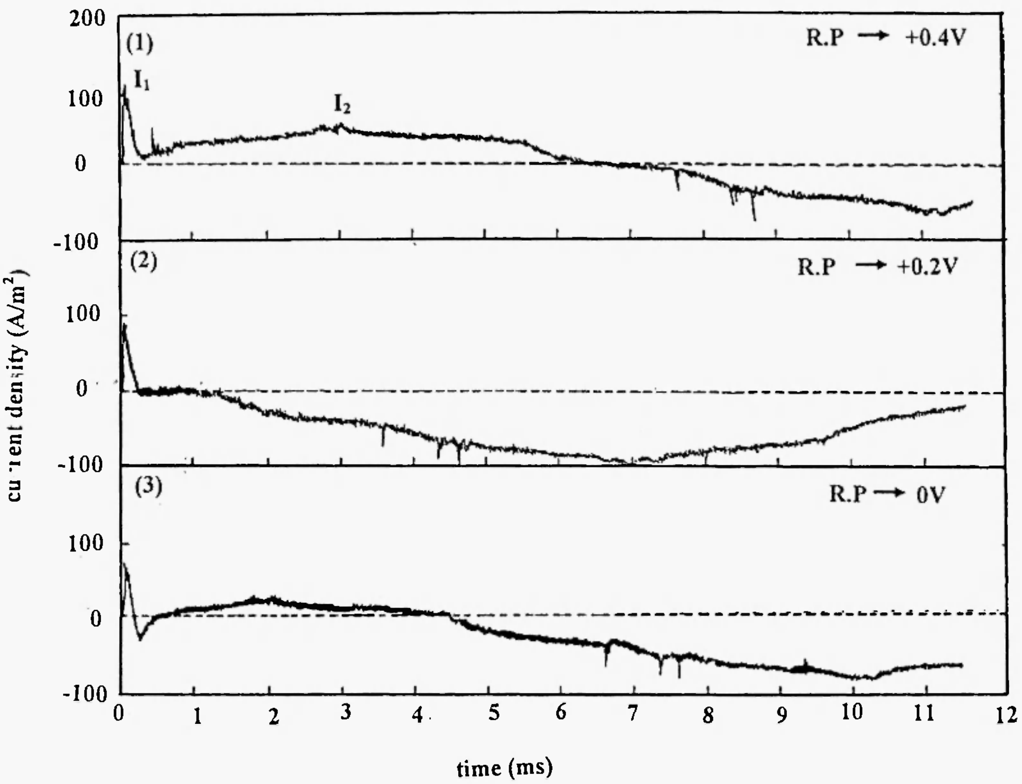

Fig. 7: Chronoamperograms of SUS316 steel sensitized for 158.4ks by potential step from rest potentials to nobler potentials.

respectively. The chronoamperograms are shown in Fig. 7. In all potential steps in the anodic direction, the sharp peak corresponding to sudden increases of the current was observed first. However, the current decreased almost immediately. In the step to +0.4V (Fig. 7-(1)), a broad current peak was observed after the first peak, while no significant peak was observed except for the first one for both 0V (Fig. 7-(3)) and +0.2V (Fig. 7-(2)). The first peak in each chronoamperogram corresponded to the formation of the electric double layer and the second peak in Fig. 7-(1) to the active dissolution. In the potential step to both 0V and 0.2V, the active dissolution was too suppressed to be observed and, in addition, the reduction reaction like hydrogen evolution and the reduction of dissolved oxygen were detected at the same time. Therefore, the total faradaic current observed after the first peaks tended to be negative as a whole. Regarding the application of potential step electrolysis to the evaluation of sensitization, the active dissolution must be detected. Therefore, the peak current values at the potential step to +0.4V, I_1 and I_2, were adopted for the calculation of the modified reactivation ratio (Fig. 7-(1)).

The current-time behavior by potential step electrolysis in the less noble direction was investigated according to the following procedure. First, the potential was imposed on 0.4V from the rest potential instantaneously, held in 1.8ks and then imposed on 0.2V, 0V and –0.2V, respectively. The results are shown in Fig. 8. For the potential step electrolysis in the cathodic direction, the sharp current peak due to the formation of electric double layers was also observed immediately after the beginning of electrolysis. For the step electrolysis to –0.2V (Fig. 8-(3)), the faradaic current peak following the first peak was cathodic, since the reduction of dissolved oxygen and the evolution of hydrogen were included, and the anodic reactivation was not detected as a whole. The faradaic current peak became remarkable with moving the step potential in the noble direction (Fig. 8-(3) → Fig. 8-(1)), since the cathodic currents for both reactions (the reduction of dissolved oxygen and the hydrogen

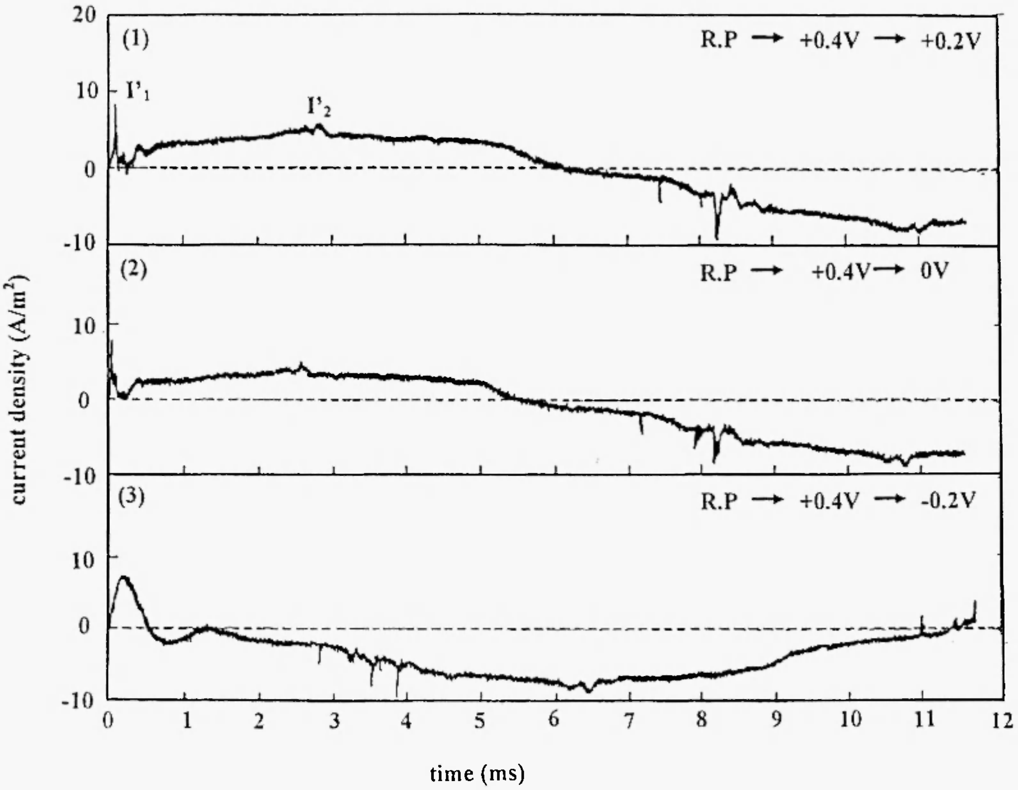

Fig. 8: Chronoamperograms of solution treated SUS316 steel by potential step from +0.4V to less noble potentials.

evolution) decreased gradually with the change in the step potential, and the reactivation dissolution became remarkable. Therefore, the peak current values at the potential step to 0.2V from 0.4V, I'_1 and I'_2, were adopted for the calculation of the modified reactivation ratio by PSCA (Fig. 8-(1)).

The potential was imposed on 0.4V from the rest potentials at first and the chronoamperograms were recorded by the oscilloscope. The current values of both the first and the second anodic current peaks, I_1 and I_2, were measured from the results. Being maintained in 1.8ks, the potential was imposed on 0.2V and the chronoamperograms were recorded again by the oscilloscope. The current values of the two peaks for each specimen, I'_1 and I'_2, were also measured. Finally, each ratio of the value for the second step to that of the first step (I'_1/I_1 for Fig. 9 and I'_2/I_2 for Fig. 10) was calculated as the modified reactivation ratio for both peaks and was compared among all specimens aged at different times. Fig. 9 and Fig. 10 show the correlation between the modified reactivation ratios and the sensitization times. Fig. 9 shows the result for the first non-faradaic peaks. The reactivation ratio seems to increase gradually with the sensitization time. In addition, the correlation coefficient was 0.7, the highest value among all of the coefficients in this study. As already

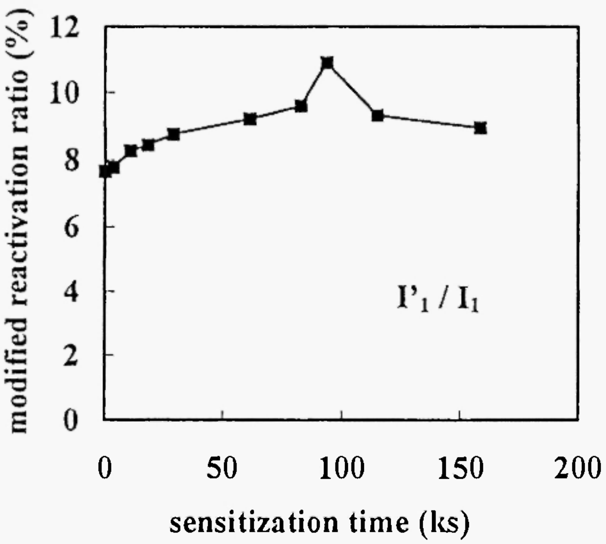

Fig. 9: Modified reaction ratio of each first peak from chronoamperograms for SUS316.

described, the first peak was supposed to correspond with the formation of the electric double layer. However, the reactivation ratio calculated from the first peak has a relatively higher correlation with sensitization time for SUS316. The same tendency was observed for SUS304 steel. The reason can be attributed to the incompleteness of separation for the two peaks. That is, the first peak contained the faradaic components to some extent and led to the good correlation with sensitization time. Fig. 10 shows the result for the second peak. Although the data were scattered to some extent, the correlation coefficient was 0.5 and slightly higher than that in Fig. 6. The extent of scattering was almost the same as in the cyclic voltammetry. The second peak in chronoamperograms may contain anodic current for some anode reactions at the same time as cyclic voltammograms also showed for SUS316 steels and the correlation coefficient would not correspond to the activation-reactivation behavior. As a result, the modified reactivation coefficient calculated from the first peaks in the chronoamperograms had a good correlation with sensitization time as in SUS304 steels /15/. To increase the correlation coefficient and its reliability further, the most appropriate combination of imposing potentials must be determined, and for this multiple experiments are required. However, the results by chronoamperometry indicate that the proposed modified method has better correlation and higher rapidity than the conventional JIS method based on cyclic voltammetry. Further investigation is required for practical application.

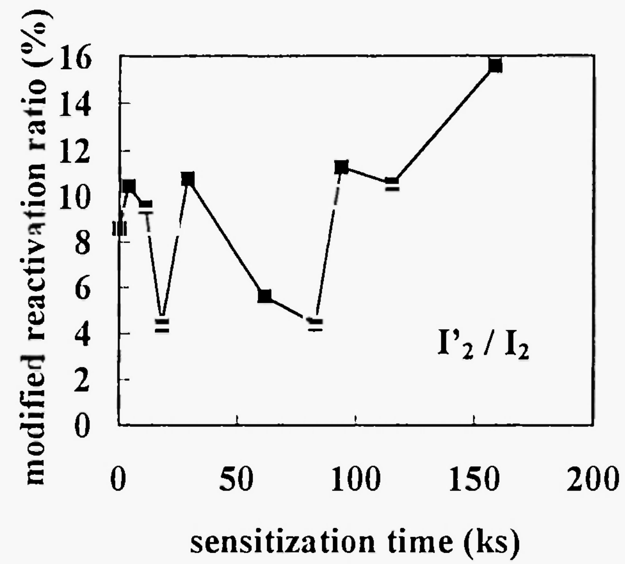

Fig. 10: Modified reactivation ratio of each second peak from chronoamperograms for SUS316.

4. CONCLUSION

We investigated the electrochemical evaluation of sensitization for SUS316 steel in this study. Sensitized SUS316 steel was examined in dilute sulfuric acid containing potassium thiocyanate by both conventional cyclic voltammetry and chronoamperometry, and the following results were obtained:

1) Both activation and reactivation processes were much more complicated for SUS316 steel than for SUS304 steel. The results indicate that the steel has more than two anodic reaction processes.
2) Reactivation ratio was calculated from the results of cyclic voltammetry. The correlation between the ratio and sensitization time was relatively low, although several calculation methods were devised. The low correlation between them can be attributed to the complicated behavior of cyclic voltammetry.
3) Chronoamperometry was introduced to evaluate the extent of sensitization more thoroughly. In the chronoamperograms, two peaks were observed, when the imposing potentials were set up correctly.
4) The modified reactivation coefficients were calculated from the results obtained by chronoamperometry. The ratio from the first peak in the chronoamperograms had the highest correlation with the sensitization time.
5) Chronoamperometry can be expected to be applied to obtain more rapid and precise electrochemical evaluation of the sensitization.

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