Title	Stress Corrosion Cracking of SUS304 Stainless Steel in High Temperature Water : Effects of Solution Treatment Temperature and Sensitization Treatment(Materials, Metallurgy & Weldability)
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Stress Corrosion Cracking of SUS304 Stainless Steel in High Temperature Water†

– Effects of Solution Treatment Temperature and Sensitization Treatment –

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Abstract

Effects of solution treatment temperature and sensitization time on stress corrosion cracking (SCC) have been studied on SUS304 stainless steel in high temperature water at 562K containing dissolved oxygen of 8 ppm using a slow strain rate testing (SSRT) technique at $4.17 \times 10^{-6}\ s^{-1}$.

For the specimen solution-treated at 1373K, the SCC drastically occurred by the sensitization treatment at 923K for 7.2 ks, but the SCC hardly occurred even at 72 ks of sensitization time for the specimens solution-treated at 1473K and at 1573K.

For the specimen solution-treated at 1373K, the size of grain boundary carbides and the width of attacked grain boundaries after sensitization treatment for 7.2 ks are larger than those solution-treated at 1473K and at 1573K by means of transmission electron microscopy and Strauss test. The corrosion rates of grain boundary attack by Huey test increased with increasing holding time during solution treatment at 1373K for the solution-treated specimen and the sensitized specimen.

The results suggest that impurity elements segregate to the grain boundaries during solution treatment at 1373K and impurity elements accelerate the precipitation of grain boundary carbides during sensitization.

The SCC occurred under the presence of both the Cr depleted zone by the sensitization and impurity elements at grain boundary.

KEY WORDS: (Intergranular Corrosion) (Intergranular Stress Corrosion Cracking) (Sensitization) (Solution Treatment Temperature) (Grain Boundary Segregation) (Transmission Electron Microscopy)

1. Introduction

In Boiling Water Reactor (BWR) environment, the intergranular stress corrosion cracking (IGSCC) has been occurred at weld heat affected zones (HAZ) of SUS304 stainless steel. The stress corrosion cracking (SCC) in the high temperature water has been correlated with sensitization, residual stress and dissolved oxygen[1]. Since the sensitization is associated with intergranular corrosion, the SCC in high temperature water has been studied with the correlation of the behavior of intergranular corrosion[2-4].

Recently, intergranular corrosion has been considered to be correlated with the segregation of impurities as well as the Cr depleted zones. That is, Briant[5] and Danyluk[6] reported that the intergranular corrosion was correlated with the Cr depleted zones resulting from the sensitization and with the grain boundary segregation of P and S.

Armijo[7] also found that the intergranular corrosion greatly occurred for the specimens solution-treated at 1373K, but for the specimens solution-treated at the temperature over 1373K, intergranular corrosion hardly occurred. He proposed that the phenomena was correlated with the behavior of grain boundary segregation of impurities. For high strength steel, furthermore, Briant et al[8] showed that the segregation of P and S at grain boundaries was small for the specimens solution-treated at the temperature over 1473K using Auger electron sepctroscopy.

It is considered that the solution treatment temperature affects the grain boundary segregation of impurities and intergranular corrosion.

In previous report[9], for the specimens sensitized after solution-treated at 1373K, the width of intergranular

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corrosion by grain boundary carbides ($M_{23}C_6$) were larger than those of 1573K, and intergranular corrosion and SCC easily occurred. Grain boundary segregation of impurities as well as Cr depleted zones have an important effect on intergranular corrosion and SCC susceptibilities.

In this study, it was investigated the effects of solution treatment temperature on grain boundary segregation of impurities and segregation. And the relationships between SCC susceptibilities in high temperature water, intergranular corrosion and grain boundary segregation were studied.

2. Experiments

Commercial SUS304 stainless steel was employed in this investigation. The chemical compositions of the alloy were shown in **Table 1**. Samples were solution-treated at 1373, 1473 and 1573K in vacuum for 1.8 ks, and then water-quenched. The mean grain sizes were 55 μm (ASTM No.5), 115 μm (ASTM No.3) and 220 μm (ASTM No.1) respectively. Solution-treated samples were sensitized at 923K for various times between 1.08 ks and 360 ks. SCC test was carried out using a slow strain rate testing apparatus. Autoclave system and specimen size were as same as those of the previous report[9]. SCC tests were carried out at the crosshead speed of 4.17×10^{-6} s^{-1} in high temperature water dissolved oxygen of 8 ppm at 562K under 8 MPa. The dissolved oxygen content in the water was automatically controlled by introducing N_2 and O_2 gas. The fracture surfaces of specimens were examined using scanning electron microscopy.

Table 1 Chemical composition of SUS 304 steel.

Material	C	Si	Mn	P	S	Ni	Cr
SUS 304	0.04	0.60	1.06	0.031	0.008	9.01	18.26

SCC susceptibilities were evaluated by means of the fracture strain and reduction of area (R.A.). Transmission electron microscopy was used to observe the carbides at grain boundaries. The degrees of sensitization were evaluated using the 10% oxalic acid test (ASTM A262A), the Strauss test (ASTM A262E), the Huey test (ASTM A262C) and pitting potential in 3.5% NaCl solution.

3. Results and Discussions

3.1 Effects of solution treatment temperature and sensitization times on SCC susceptibilities.

Figure 1 shows the effect of sensitization times on SCC susceptibilities. In the case of the specimens sensitized after solution-treated at 1373K, the R.A. drastically decreased at 7.2 ks. On the other hand, for the specimens sensitized after solution-treated at 1473 and 1573K, the R.A. hardly decreased at the sensitization times longer than 7.2 ks. This tendency was same as the results of the fracture strain.

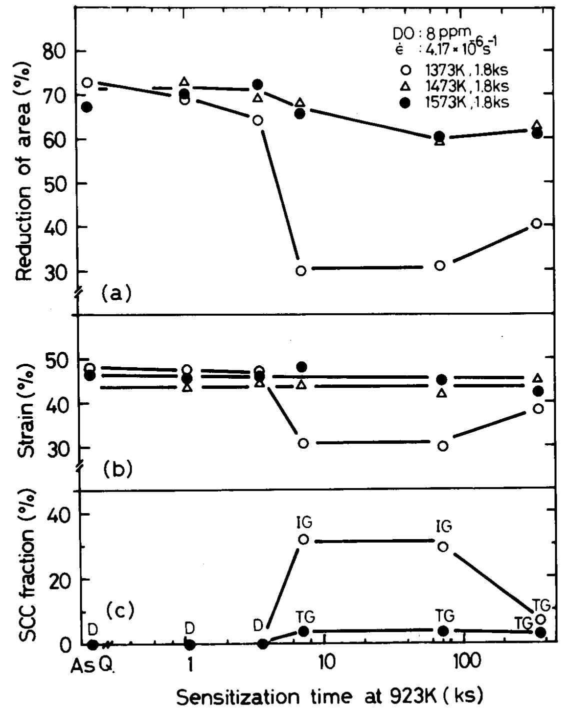

Fig. 1 Effect of sensitization time on SCC susceptibility.

As shown in Figure 1, there were intergranular fracture surfaces in the specimens sensitized after solution-treated at 1373K, while the specimens sensitized after solution-treated at 1473 and 1573K were occupied in terms of transgranular fracture surfaces. From these results, it was concluded that the SCC susceptibilities decreased with increasing the solution treatment temperature.

In order to study the initiation behavior of SCC crack, the corrosion appearance in high temperature water was observed. **Figure 2** shows scanning electron micrographs of the specimen surfaces, as the specimen sensitized after solution-treated at 1373 and 1573K was exposed for 108 ks in high temperature water. In the case of the specimens solution-treated at 1373K, pits occurred at the triple point of grain boundaries. On the other hand, for the specimens solution-treated at 1573K, pits randomly occurred in matrix and grain boundaries.

It is concluded that the initiation and growth behavior of pitting varied with the solution treatment temperature and SCC is considered to be initiated by pits. Effects of pit initiation on SCC susceptibilities were investigated in present study.

Figure 3 shows micrographs of the surface and cross sectional area after SCC test for sensitized specimens. In

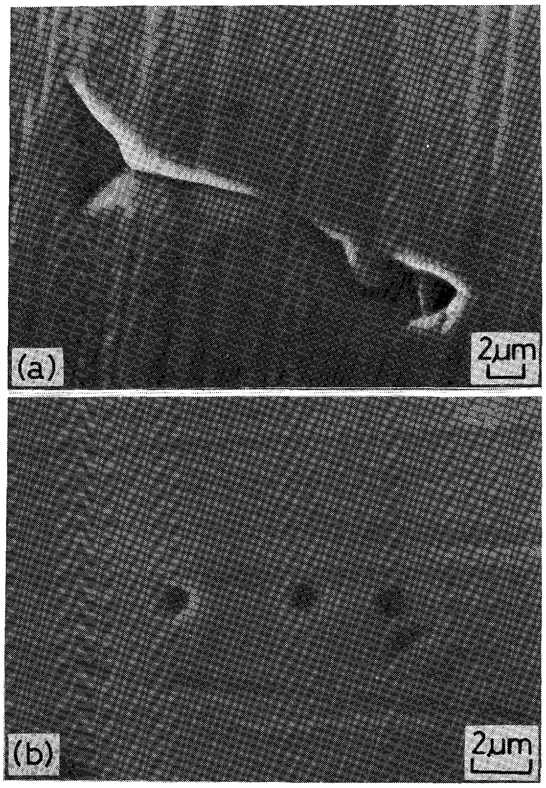

Fig. 2 Pits and intergranular corrosion as the samples sensitized at 923K for 72 ks were immersed in high temperature water at 562K for 108 ks.
(a): Solutionized at 1373K for 1.8 ks.
(b): Solutionized at 1573K for 1.8 ks.

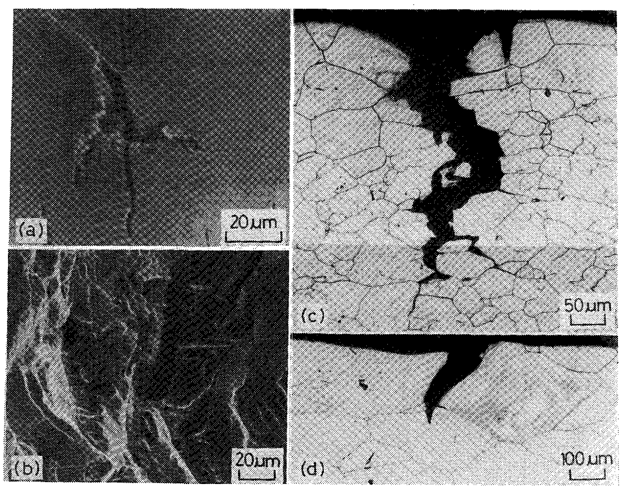

Fig. 3 Pits and intergranular cracks on side surfaces (a) and (b), and cross sectional area (c) and (d) after SSRT tests for the specimens sensitized at 923K for 72 ks.
(a) and (c): Solutionized at 1373K.
(b) and (d): Solutionized at 1573K.

the case of the specimen solution-treated at 1373K, as shown in Figure 3(a) cracks seem to have grown from the pits. Also, as shown in Figure 3(c), cracks propagated along grain boundaries. On the other hand, as shown in Figure 3(b), in the case of the specimen solution-treated at 1573K, crack did not propagate from these pits. As can be seen in Figure 3(d), crack initiated at grain boundaries and grew toward in grain. The length of crack, as shown in Figure 3(c), is shorter than that of specimen solution-treated at 1373K. This tendency was consistant with that of the previous report[9].

3.2 Effects of solution treatment temperature and sensitization time on intergranular corrosion and pitting potential

Figure 4 shows the results of the 10% oxalic acid test for the specimens sensitized at 923K after solution-treated at 1373K and 1573K. The degree of sensitization owing to intergranular corrosion rate was determined by means of the Solomon's method[10,11]. The method is similar to that of the previous report[9]. At any case of solution treatment temperatures, the degree of sensitization increased with increasing the sensitization time. However, the sensitization of the specimens after solution-treated at 1373K is considered to be accelerated comparing with those solution-treated at 1573K. These intergranular corrosions are correlated with the precipitation of intergranular carbides[1]. Therefore, it is considered that the precipitations of intergranular carbides of the specimens solution-treated at 1373K and sensitized are accelerated than those of the specimens solution-treated at 1573K and sensitized.

Figure 5 shows the results of Strauss test. The widths of attacked grain boundaries increased with increasing the sensitization time. The widths of attacked grain boundaries are different by the solution treatment temperature for the sensitization time over 7.2 ks. That is, the widths of attacked grain boundaries in the sensitized specimens after solution-treated at 1373K are broader than those of 1573K. It has been reported that the Strauss test was correlated with Cr depleted zone below 12% Cr[1].

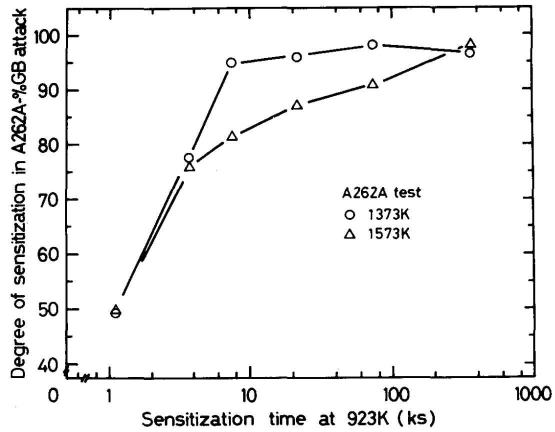

Fig. 4 Effect of sensitization time on degree of sensitization by A262A test.

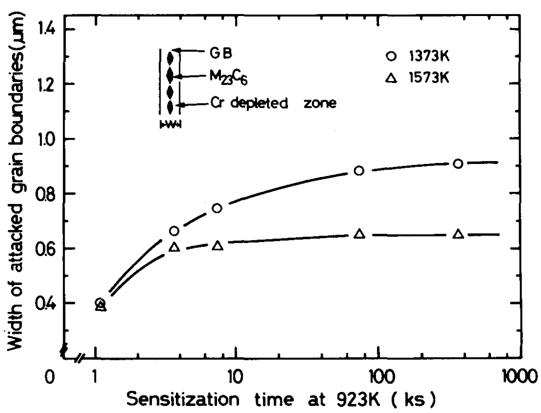

Fig. 5 Effect of sensitization time on the width of attacked grain boundaries by Strauss test.

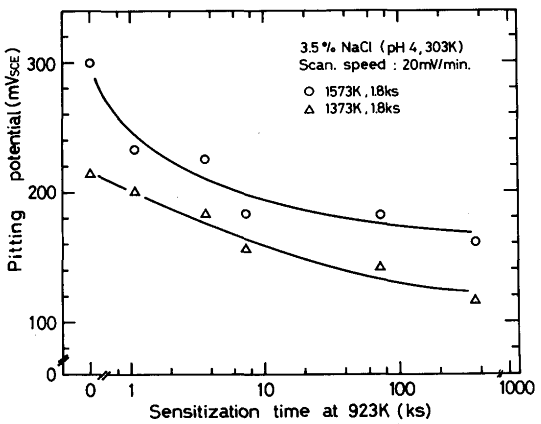

Fig. 6 Effect of sensitization time on pitting potential of anodic polarization.

It is considered that the difference of the width of attacked grain boundaries resulting from solution treatment temperature is correlated with the difference of precipitation behavior of Cr carbides as shown in Figure 4. The behavior of pitting in high temperature water during SCC test was phenomenally similiar to that of anode polarization in 3.5% NaCl solution[9]. Therefore, the relationships between pitting potential and the sensitization for the specimen heat-treated at various solution treatment temperatures were investigated.

Figure 6 shows the relation between the pitting potential in 3.5% NaCl solution and sensitization time for the specimens after solution-treated at 1373 and 1573K. For as solution-treated specimens at 1373K, the pitting potential is lower comparing with that of 1573K. At any solution treatment temperature, pitting potential decreased with increasing sensitization time. However, up to sensitization time of 360 ks, the pitting potential of sensitized specimens after solution-treated at 1373K were lower than those of 1573K.

3.3 Relationship between intergranular corrosion and SCC susceptibilities

Figure 7 shows the relationship between the width of attacked grain boundaries and the reduction of area for SCC test. At any case of solution treatment temperature, SCC did not occur up to 0.6 μm of the width of attacked grain boundaries. However, SCC susceptibilities greatly increased over 0.6 μm.

Figure 8 shows the relationship between pitting potential in 3.5% NaCl solution and reduction of area for SCC in high temperature water. SCC did not occur at the range

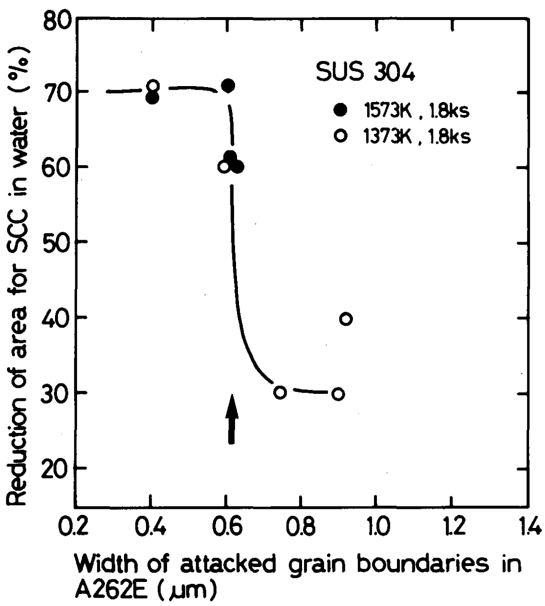

Fig. 7 Relation between the width of attacked grain boundaries by Strauss test and the reduction of area for SCC test in high temperature water.

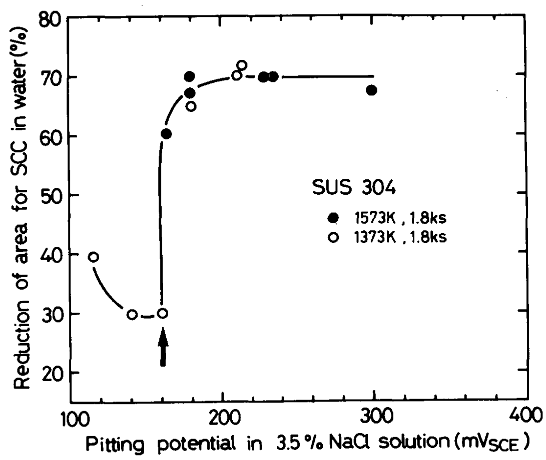

Fig. 8 Relation between pitting potential and reduction of area for SCC test in high temperature water.

of pitting potential from 300 mV_{SCE} to 200 mV_{SCE}. However, SCC susceptibilities greatly increased at 160 mV_{SCE}. On the base of these results, it is concluded that SCC occur under 0.6 μm of the width of attacked grain boundaries and under 160 mV_{SCE} of pitting potential.

3.4 Effect of step solution treatment on intergranular corrosion

In this part, it was investigated the effect of the segregation of impurities during solution treatment on sensitization.

Generally, as received materials were solution treated at 1373K, so that it is considered that the impurities had already segregated at grain boundaries. Therefore, it is considered that the segregation of impurities decreases by solution treating at 1573K[7]. It has been reported that the segregation of impurities could not be detected in Strauss test, but could be detected in the Huey test[5,6,12,13]. Therefore, the segregation behavior of impurities was investigated by means of the Huey test in this study.

Figure 9 shows corrosion rates of the specimens holded at 1373K after solution-treated at 1573K. In the case of solutionized specimens, the corrosion rates increased with holding times at 1373K. These corrosion rates were correlated with intergranular corrosion. From these results, it is suggested that the grain boundary segregation of impurities occur during solution treatment at 1373K and the amounts of grain boundary segregation of impurities increase with holding time at 1373K. It has been reported that these impurities were P, S, Si and N[12,14]. In this study, it is considered that the grain boundary impurities mainly may be phosphorus. In the sensitized specimens, corrosion rates are 10 times larger than those of the solutionized specimens. It is considered that the corrosion rates are correlated with both Cr depleted zone and the segregation of impurities for the sensitized specimen.

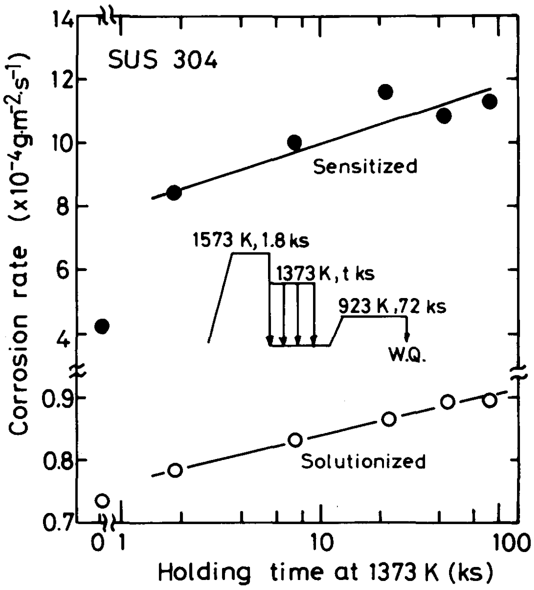

Fig. 9 Effect of holding time at 1373K on corrosion rate by Huey test.

Figure 10 shows the cross sectional microstructure after Huey test. The depth of intergranular corrosion was increased with holding time at 1373K. From these results, it is considered that the impurities segregated during solution treatment at 1373K accelerate the precipitation of Cr carbides during sensitization.

Furthermore, the widths of intergranular corrosion also were increased with increasing holding time at 1373K. The widths of integranular corrosion in the Huey test were greatly broader than those in the Strauss test[1] which attacks the regions under 12% Cr.

Figure 11 shows transmission electron micrographs as the specimens holded at 1373K for various times after solution-treatment at 1573K, were sensitized at 923K for 72 ks. In the case without holding at 1373K after solution-treated at 1573K(a), the grain boundary carbides were small, however the grain boundary carbides were coarsened in terms of holding at 1373K for 21.6 ks(b) and for 72 ks(c). From these results, it is considered that the

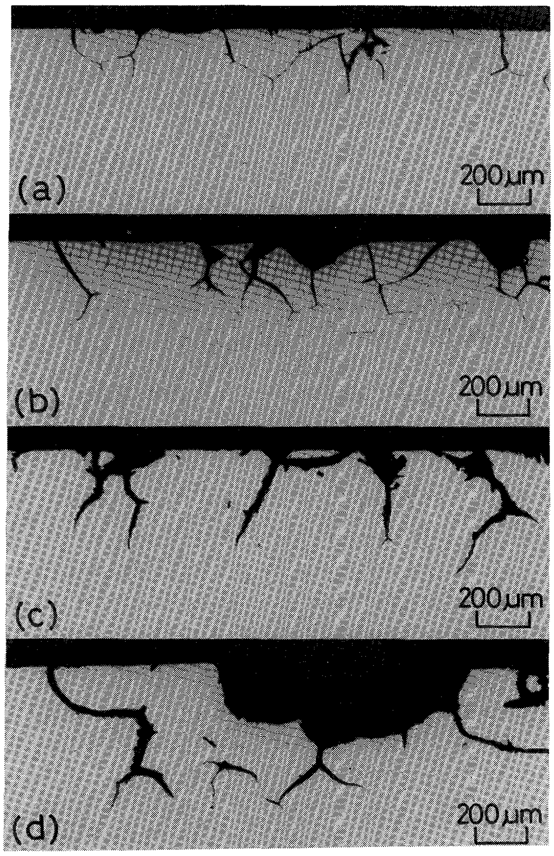

Fig. 10 Micrographs of cross sectional area after Huey test of the specimens solutionized at 1573K for 1.8 ks and solutionized at 1373K for 1.8 ks (a), 7.2 ks (b), 36 ks (c) and 72 ks (d), and then sensitized at 923K for 72 ks.

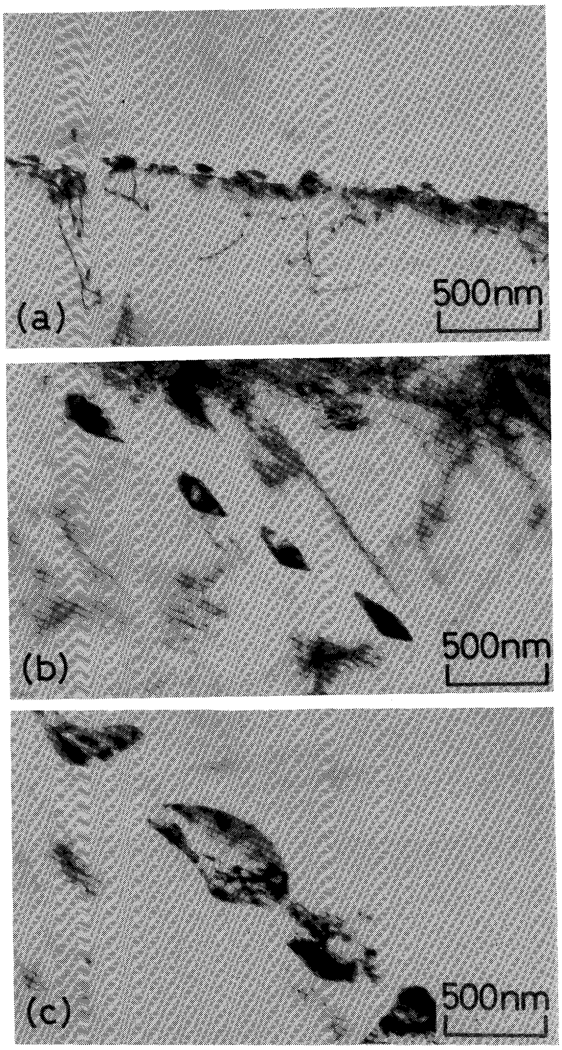

Fig. 11 Transmission electron micrographs as the specimens were solutionized at 1573K for 1.8 ks, then held at 1373K for 0 ks (a), 21.6 ks (b) and 72 ks (c) and then sensitized at 923K for 72 ks.

impurities segregate at grain boundaries during holding at 1373K and accelerate the precipitation of grain boundary carbides.

Also, it is believed that the impurities segregate at grain boundaries during the sensitization for long times. That is, it is considered that the impurities segregate at grain boundaries not only during solution treatment at 1373K but also during sensitization treatment at 923K. But, as shown in Figure 1, SCC hardly occurred in sensitized specimens after solution-treated at 1573K. It is considered that the impurities segregated during sensitization hardly accelerate the precipitation of carbides.

3.5 Effect of step solution treatment on pitting potential and SCC susceptibilities

Figure 12 shows the pitting potential of the specimens

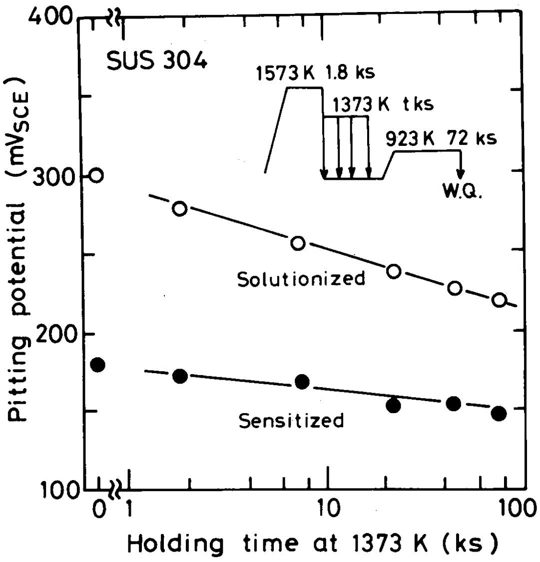

Fig. 12 Effect of holding time at 1373K on pitting potential.

holded at 1373K after solution-treated at 1573K and those sensitized at 923K for 72 ks. In the solutionized specimens, the pitting potentials were decreased with increasing holding time at 1373K. This is consistent with the corrosion rates of Figure 9. Therefore, it is considered that the pitting potential detects the segregation of impurities at grain boundaries. In the sensitized specimens, the pitting potentials were also decreased with increasing holding time at 1373K. The decrease of pitting potentials in sensitized specimens was small comparing with that of solution-treated specimens.

Therefore, it is suggested that the grain boundary impurities segregated during sensitization are included in Cr carbides[14] and then the amounts of impurities in Cr depleted zone decrease.

It is considered that the pitting potential in 3.5% NaCl solution detects both Cr depleted zone and grain boundary segregation of impurities. Also, the test was interrupted at pitting potential during anode polarization and the behavior of initiation and growth of pitting was observed. As the results, pitting was mainly initiated at grain boundaries, furthermore grew along grain boundaries as reported in the previous report.[9]

As can be seen in Figure 8, SCC occurred at 160 mV$_{SCE}$. Therefore, in the case of solution treated and sensitized specimen as shown in Figure 12, pitting potentials were decreased in terms of the increase of holding time at 1373K. But, it is considered that SCC hardly occurs at the pitting potential over 160 mV$_{SCE}$.

Also, in the case of the specimens heat treated at 1573K, the pitting potentials of sensitized specimen were decreased comparing with those of solution-treated specimens. These trends were correlated with the results

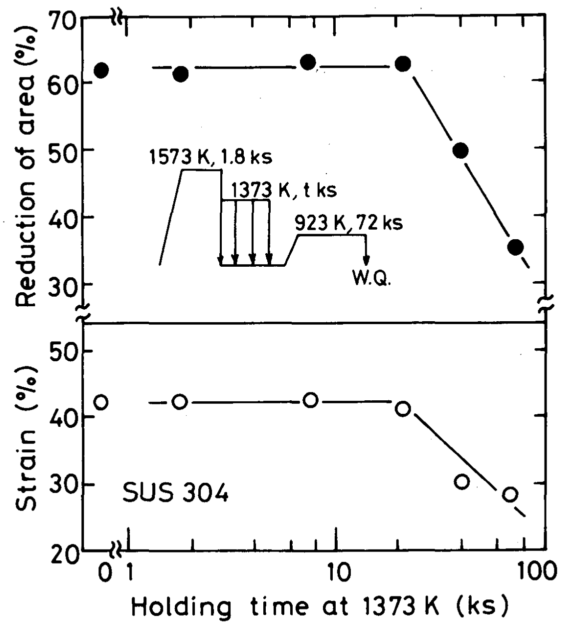

Fig. 13 Effect of holding time at 1373K on SCC susceptibility in high temperature water.

of the Huey test as shown in Figure 9. However, these pitting potentials are higher than 160 mV_{SCE} which SCC occurs. Therefore, SCC did not occur in terms of sensitization treatment alone. It is considered that the pitting potential decreases in terms of the impurity segregation with increasing holding time at 1373K, and then SCC occurs in terms of the decrease of pitting potential to 160 mV_{SCE}.

Figure 13 shows SCC results of the specimens holded at 1373K after heat treated at 1573K for 1.8 ks. SCC susceptibilities increased with holding time at 1373K. These were correlated with the results of Figure 8. That is, the impurities were segregated at grain boundaries during solution treatment at 1373K, but SCC did not occur in terms of the segregation of impurities alone. Also, SCC did not occur by means of the segregation treatment alone, without the grain boundary segregation of impurities during holding over 20 ks at 1373K for SUS304 steel used in this investigation.

On the base of the results, the grain boundary segregation of impurities affects on Cr-C equilibrium at grain boundaries and then have an important effect on the kinetics of Cr carbide precipitation.

SCC occurred in sensitized specimens after heat treated at 1373K and in the specimens holded over 20 ks at 1373K after heat treated at 1573K, as shown in Figure 1 and Figure 13 respectively. It is considered that the grain boundary segregation of impurities mainly accelerates the precipitation of grain boundary Cr carbides, $(MP)_{23}C_6$ [14] and then SCC susceptibilities increase. Also, the impurities segregated at grain boundaries may affect on SCC susceptibilities in high temperature water.

4. Conclusions

In this study, it was investigated the effect of solution treatment temperature on SCC susceptibilities of SUS304 stainless steel in high temperature water. Also, it was investigated of the effects of solution treatment temperature and its holding time on the grain boundaries segregation of impurities and sensitization phenomenon by means of intergranular corrosion test and pitting potential. And these were compared with SCC results in high temperature water.

The results obtained in this study are summarized as follows.

(1) In sensitized specimens after heat treated at 1373K, SCC drastically occurred at the sensitization time of 7.2 ks. On the other hand, in the specimens sensitized after solution-treated at 1473 and 1573K, SCC did not occur even at the sensitization time of 360 ks.

(2) In the 10% oxalic acid test, the degrees of sensitization for the specimen sensitized after solution-treated at 1373K were higher than those of the specimen sensitized after solution-treated at 1573K. In the Strauss test, the widths of attacked grain boundaries for the specimens sensitized after solution-treated at 1373K were broader than those of the specimen sensitized after solution-treated at 1573K. Pitting potential in 3.5% NaCl solution was decreased with increasing sensitization time. Also, pitting potentials of the specimens solution-treated at 1373K were lower than those of the specimens solution-treated at 1573K. Therefore, the solution treatment temperature affects on sensitization.

(3) In the Huey test, the corrosion rates of the specimens holded at 1373K after solution-treated at 1573K were increased with increasing holding time at 1373K. This means that the impurities segregate at grain boundaries during solution treating at 1373K.

(4) In the sensitized specimens holded at 1373K after solution-treated at 1573K, the grain boundary carbides were enlarged with increasing holding time at 1373K. That is, it means that the impurities segregated at grain boundaries accelerate the precipitation of carbides at grain boundaries.

(5) The tendency of decrease of pitting potential for sensitized specimens in 3.5% NaCl solution was correlated with the increase of corrosion rates in the Huey test. SCC occurred under 160 mV_{SCE}, at which it was necessary to solution treatment at 1373K as well as sensitization. That is, both grain boundary segregation of impurities and sensitization was neces-

sary to occur the SCC in high temperature water.

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