研 究

Evaluation of Pitting Corrosion Behavior of Sintered SUS444 Stainless Steel in MgCl_2 SolutionSatoshi Sunada^{☆1}, Kazuhiko Majima^{☆1}, Yusuke Miyazaki^{☆1} and Takeshi Hasegawa^{☆2}^{☆1}Department of Materials Systems Engineering and Life Science, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555.^{☆2}Metal Powder Division, Daido Steel Co., Ltd., 10 Ryugu-cho Minato-ku, Nagoya 455-0022.

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SYNOPSIS

Three kinds of sintered SUS444 stainless steels (P/M stainless steels) whose porosity ratios were 6.9, 9.1 and 13.3 were used in this experiment, and their pitting corrosion behaviors in MgCl_2 solution were investigated by means of electrochemical measurement and SEM observation compared with normal type SUS444 stainless steel (I/M stainless steel) produced by conventional method. The pitting corrosion resistance of P/M stainless steel decreased with the increasing porosity ratio, and it was lower compared with the I/M stainless steel. The potential of pitting corrosion decreased with an increase in porosity, and the pitting corrosion rate increased as the anodic potential and the porosity ratio increased.

KEY WORDS

pitting corrosion, SUS444 steel, porosity ratio, electrochemical measurement, pitting potential

1 Introduction

Ferritic stainless steel SUS444, which has superior corrosion resistance, especially to stress corrosion cracking, is applied to relatively low pressure vessels such as warm or hot water tanks¹⁾. Recently, since sintered stainless steels using powder metallurgy process have the advantage of better formability, they have been studied to produce complex shape products without machining or welding.

On the other hand, since passivation film of the stainless steel surface becomes unstable in the solution containing halogen ions even under the neutral corrosive environment, pitting corrosion which is one type of local corrosion occurs. Because the occurrence of pits increases the surface roughness and they grow to the perpendicular direction to the surface, they sometimes become the through-holes in spite of small weight loss and, as a result, they cause an accidental leakage of the media.

In this study, the quantitative investigation on initiation

and growth of the pit using electrochemical measurement and surface and cross sectional observation were carried to clarify the pitting corrosion behavior of sintered SUS444 stainless steel in neutral MgCl_2 solution.

2 Experimental procedures

2.1 Experimental material

Materials used for the experiment were SUS444 stainless steels: one was made by conventionally processed steel and another was sintered one using powder metallurgy process. These compositions are shown in Table 1 and 2, respectively. Sintered materials were formed by 3 different compacting pressures. Conventionally processed SUS444, marked as I/M material in the figures, was sampled from the cast and wrought commercial plate in 2 mm thickness, and the plate was cut into a specimen of 12 mm in width and 60 mm in length. Sintered SUS444 was produced using water-atomized powder of approximately 60×10^{-6} mm in average diameter

Table 1 Chemical composition (wt%) of SUS444 stainless steel.

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Nb	N	Ti
0.004	0.26	0.13	0.02	0.001	0.10	18.30	1.92	0.02	0.337	0.011	0.01

Table 2 Chemical composition (wt%) of SUS444 stainless steel powder.

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Nb	N	O
0.012	0.84	0.22	0.025	0.005	0.12	17.70	1.86	0.04	0.01	0.028	0.28

made by Daido Special Steel Co. Ltd. The appropriate amount of the powder was compressed to the size of $2.2 \times 12 \times 60$ mm at different applied pressures of 392, 588, and 784 Mpa. 1 mass% of ACRAWAX was mixed with the powder as a lubricant for compaction. After forming at the room temperature with different pressures, the compressed specimens were dewaxed at 673 K for 3.6 ks in air and subsequently sintered at 1473 K for 3.6 ks in vacuum. These specimens are marked as P/M material in the figures. For pitting potential measurement, reactive side of the specimen for the electrode was polished with a No. 2000 grit water-proofed abrasive paper followed by ultrasonic rinsing in acetone. Electrodes were made by coating with silicon rubber with uncoated area of $1 \times 10^{-4} \text{ m}^2$ for as the exposed surface.

2.2 Test solution

MgCl_2 solution concentrations of which were 0.1, 0.2, 0.5, 1.0, and 2.0 kmol/m^3 was used in this experiment. Before being used for the experiment, specimens were treated by 0.5 kmol/m^3 MgSO_4 solution for the formation of the passivation film. Those solutions were adjusted by deionized water whose specific electric conductivity was less than $2.0 \times 10^{-5} \text{ S} \cdot \text{m}$.

2.3 Measuring apparatus

Fig. 1 shows the diagram of measuring apparatus for pitting corrosion behavior of SUS444 stainless steels. It consists of thermostatic bath, H-type electrolytic cell with anodic and cathodic chambers of $2 \times 10^{-4} \text{ m}^3$ in volume, intermediate cell Ag-AgCl (3.33 kmol/m^3 KCl) as a reference electrode, potentiostat, coulomb meter and a personal computer for the measurement control. All of the potential values were shown based on the Ag-AgCl reference electrode.

2.4 Pitting potential measurement

Before pitting potential measurement, specimens were treated in 0.5 kmol/m^3 MgSO_4 solution of 298 K for 1.8 ks with the potential of 0.2 V by potentiostat. As soon after pre-treatment, an anodic polarization curve was measured by potentiodynamic polarization method in MgCl_2 solutions with a potential sweeping rate of $dE/dt = 5 \times 10^{-4} \text{ V/s}$. Pitting potential, E_{pit} , was determined using anodic polarization curve: the potential at which anodic current density rapidly increased from the passivation area in which the current

density curve are constantly linear. High purity nitrogen gas was introduced for 1.8 ks into the test solution to deoxidize, and the solution surface was covered with the same gas during potential measurement.

2.5 Static potential corrosion test

Static potential test was carried out in order to investigate quantitatively the effect of MgCl_2 concentration and potential on the initiation and growth of the pit. First, for the formation of the constant passivation film, specimens were treated in 0.5 kmol/m^3 MgSO_4 solution at 298 K for 1.8 ks with the potential of 0.2 V. Potentiostatic measurement was conducted in MgCl_2 solution at the constant potentials of 0.257, 0.357, and 0.457 V. During the test, anodic current was recorded until the total current reached $3.0 \times 10^5 \text{ C/m}^2$. Apparent rate constant, dI/dt , was calculated from the automatically recorded anodic current (I) variation for the pit initiation and growth. The effect of corrosion potential and porosity on dI/dt was also discussed by using the experimental results.

2.6 Observation of corroded surface

The number and the diameter of the pit on the surface and the cross sectional area after corrosion test were measured

Fig.1 Experimental apparatus for pitting corrosion.

by SEM observation at both initiation and growth stages of the pit.

3 Results and discussion

3.1 Effect of forming pressure on porosity ratio

As previously mentioned, the one of materials used in this study was produced using SUS444 water atomized powder by compressing them at the pressures of 392, 588 and 784 MPa at the room temperature followed by dewaxing and vacuum sintering. The porosity ratio of sintered stainless steels must be an important factor for corrosion resistance since the oxides originated from powder surface and the impurities may remain in the pore and they may affect corrosion properties due to the formation of micro cells. Therefore, the porosity ratios of sintered SUS444 specimens were measured by the porosity area ratios using computerized image processing of optical microscopy images. According to this measurement, the porosity ratios of the specimens were 13.3%, 9.11%, and 6.88% for the compression pressure of 392, 588, and 784 MPa, respectively. For the case of conventionally processed SUS444, porosity ratio was presumed to be 0%.

3.2 Determination of pitting potential

Pitting potential is often used for the evaluation of pit generation²⁾. Fig. 2 shows a typical polarization curve in 0.2 kmol/m^3 MgCl_2 solution at 298 K for the P/M specimen compressed at 392 MPa. Cathodic current density gradually decreased with increasing potential from -0.8 V in cathodic region. Natural electrode potential E_{corr} was indicated at

Fig. 2 Procedure for determining pitting corrosion in $0.2 \text{ kmol} \cdot \text{m}^{-3}$ MgCl_2 solution for the specimen compressed at 392 MPa.

-0.035 V . Although anodic current density increased with increasing potential in anodic region over the potential of -0.035 V , anodic current density abruptly rose at certain potential shown by E_{corr} . This polarization behavior was different from the one for the typical stainless steel, which shows activation-passivation behavior with increasing potential. Pit was observed at specimen surface by increasing current density. By considering these phenomena, that point of abrupt increase was defined as pitting potential.

3.3 Effect of MgCl_2 activity on pitting potential

Fig. 3 shows the effect of the activity of Cl^- ion on pitting potential. Because Cl^- was considered to affect on the stability of passivation film in passive region, the activity of Cl^- ion which directly affects the pitting potential was chosen as a variable. The activities of MgCl_2 test solutions were obtained from the reference³⁾.

Wrought SUS444 showed the highest pitting potential under the same Cl^- activity conditions. In the case of sintered steels, pitting potential of the one compressed at 784 MPa was the second highest, and it was indicated that pitting potential became low with decreasing the compressing pressure. For each specimen, the pitting potential tended to be lower with increasing the activity of Cl^- . Pitting potential of the test specimen indicated linear relationship to the logarithm of Cl^- activity, and slope of approximately -0.17 V was obtained at 10 times increase of the Cl^- activity, however, the reason of this relationship was unclear.

Fig. 3 Effect of $[\text{Cl}^-]$ on pitting corrosion potential.

Considering these results, it suggests that an increase of the Cl^- activity declines pitting corrosion resistance and causes the initiation of the pit under the investigated corrosive environment.

3.4 Effect of vacant ratio on pitting potential

It suggests that the conventionally processed material has better pitting corrosion resistance than sintered one from previous results. Since the sintered steel with higher compressed pressure exhibits better pitting resistance, it is implied that pores in the sintered steel significantly affects the pitting resistance. With thinking this results, the effect of porosity ratio on pitting potential was shown in Fig. 4. As previously mentioned, porosity ratio of conventionally processed steel was considered to be 0%. The results for the Cl^- activity of 0.145 and 3.59 were shown as the typical results. It indicated that pitting potential showed the tendency to linearly decrease with the increase of porosity ratio and it decreased approximately 26 mV per 1% of porosity ratio. It is suggested from the result that pitting corrosion resistance of SUS444 has closely related to the porosity ratio and the stability of passivation film depends on the amount of pore.

3.5 Effect of porosity ratio on morphology of the pit

Although the effects of Cl^- activity and porosity ratio on conventional and sintered SUS444 steels are effective as the evaluation parameters of pitting corrosion resistance of different production processes and the variation of porosity

ratio, it is difficult to obtain the information of dynamic behavior for an initiation and growth of the pit. Therefore, the effect of porosity ratio on morphology of the pit was quantitatively examined by using potentiostatical anodic polarization method and SEM observation on the electrode surface.

Fig. 5 shows the SEM photographs after anodic polarization testing at the potential of 0.357 V for total current of 30 C with a histogram of the diameter of pits at a left side. Many of the observed pits in the specimen of 13.3% porosity ratio were smaller than 5×10^{-5} m. The number of the pits bigger than 5×10^{-5} m gradually decreased and no pits over 2.5×10^{-4} m could not be observed. In the specimen of 9.11% porosity ratio, the pits of smaller than 5×10^{-5} m were observed while the number of them was less than half compared with 13.3% specimen. Moreover, the bigger pits up to 4.5×10^{-4} m were observed with decreasing the number of the pits compared with 13.3% specimen. The tendency was emphasized in the specimen of 6.87% specimen, and only 41 pits were smaller than 5×10^{-5} m. The bigger pits up to 4.0×10^{-4} m were observed while the number of them were less than that of 9.11% specimen. In the conventionally processed steel, only 7 pits were smaller than 5×10^{-5} m and only each one of 3×10^{-4} m, 4.5×10^{-4} m, and over 5.0×10^{-4} m were observed.

The shape of the pits relates with the porosity ratio. The number of pits smaller than 5×10^{-5} m decreased as porosity ratio lowered. Although the number of pits bigger than 5×10^{-5} m also decreased as porosity ratio lowered, their size distribution shifted to be bigger. The number of pits decreased while their size became bigger in the conventionally processed steel.

Considering these results, the vacancy is considered to act as the initiation of pits. In the case of the specimen with higher porosity ratio, more initiation of pits occurred. In the case of less pore specimen, less number of initiation occurred, but they might grow bigger and deeper.

3.6 Effect of porosity ratio on initiation and growth of pit

Fig. 6 shows typical time-dependent variations of anodic current density at constant potential of 0.357 V of conventional and differently compressed/sintered SUS444 steels. Variation of the current density divided into 2 regions. The first is incubation region in which the current density is independent on time and indicates nearly 0 and at which nuclear of the pit is generated on the passivation film⁵⁾. In the second region, the current density linearly increases with depending on time, and an initiation and growth of the pit. As indicated in Fig. 6, the region is found at which anodic current density I tends to increase with

Fig. 4 Effect of porosity ratio on pitting corrosion potential.

Fig.5 Histogram showing relationship between the number of pits and the diameter of pits, and SEM photographs showing pitting corrosion type corresponding to each specimen.

Fig. 6 Procedure for determining growth rate of pitting corrosion.

Fig. 7 Effect of porosity ratio on growth rate of pitting corrosion for I/M and P/M specimens.

constant slope. Therefore, the effect of an apparent rate dI/dt calculated from the slope on the initiation and growth of the pit was examined.

Fig. 7 shows the effect of porosity ratio on the apparent rate dI/dt . The potential used was constant at 0.257 V, 0.357 V and 0.457 V. The apparent rate exponentially increased with increasing porosity ratio, which indicates the pore works as an accelerating factor for the growth of the pit.

3.7 Effect of potential on initiation and growth of pit

The effect of potential on apparent rate was examined to evaluate the quantitative effect of the potential on initiation and growth of pit for conventionally processed and differently compressed/sintered SUS444 steels.

Fig. 8 shows the effect of the potential on apparent rate. The apparent rate increased almost linearly with increasing the potential. The specimen which was formed at 392 MPa and had the largest porosity ratio took the greatest influence of the potential, which suggests that the tiny increase of potential leads to the initiation and growth of the pit.

4 Summary

In this study, the pitting corrosion behavior in neutral $MgCl_2$ solution was examined for conventionally processed and sintered SUS444 stainless steels. The main results obtained are as follows.

Fig. 8 Effect of potential on growth rate for I/M and P/M specimens.

- (1) The pitting potential of conventional material indicated the highest pitting potential than any other sintered materials. The conventional material has better pitting corrosion resistance.
- (2) The pitting potential of in neutral MgCl_2 solution decreased almost linearly as porosity ratio increased. The decreasing amount of the potential was 26 mV per 1 % of porosity ratio.
- (3) Regarding the effect of potential on the corrosive manner of the pit, more small pits were observed in the specimen with larger porosity ratio while less number but larger diameter pits were observed in the specimen with smaller porosity ratio.
- (4) The apparent rate in the stage of the pit initiation and growth exponentially increased as porosity ratio increased.
- (5) The apparent rate in the stage of the pit initiation and growth increased almost linearly with potential increase, irrespective of porosity ratio. The specimen which was formed at 392 MPa and had the largest porosity ratio took the greatest influence of the potential, which

suggests that the tiny increase of potential leads to the initiation and growth of the pit.

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