

Corrosion Behavior of Ni base alloys and 316 stainless steel in Supercritical Water under Alkaline conditions

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ABSTRACT

Supercritical water (SCW) process is an attractive method for decomposition of hazardous organic wastes and for upgrading of low-quality hydrocarbon resources. However, the corrosion of a reactor or a heat exchanger is known as the major difficulty to put the SCW processes into industrial applications. It is important to select suitable structural materials, which are compatible with the SCW environment of each particular process, to ensure long term integrity of the reactor components.

The objectives of this study are to evaluate the corrosion behavior of candidate corrosion-resistant alloys in SCW environments under reducing atmosphere and to understand the corrosion mechanisms. Four kinds of Ni base alloys, Alloy 625, Alloy C-276, Ni-45Cr-1Mo (MC alloy) and Ni-19Cr-19Mo (MAT 21) and a Type 316 stainless steel were used in this study. Corrosion experiments were carried out to investigate the influences of environmental variables such as temperature, anion, pH and the hydrogen partial pressure, on corrosion rate and corrosion morphology of the alloys. A static autoclave was used for the corrosion study. Exposure time was 50 hours. Applied pressure was 25 MPa and testing temperature was 400°C. Susceptibility of the alloys to stress corrosion cracking (SCC) was also evaluated by slow strain rate technique (SSRT).

Corrosion rate of type 316 stainless steel was always higher than that of any of the Ni base alloys in SCW containing NaOH. While weight change of type 316 stainless steel was small in deionized water, weight gain was significantly increased with increasing NaOH concentrations. In reducing atmosphere containing NaOH, the weight loss was increased with increasing hydrogen partial pressure. In SCW under reducing atmosphere containing NaOH, Ni base alloys containing both Cr and Mo, such as Alloy C-276 and MAT21, would be more resistant to corrosion than Ni-Cr binary alloys.

SCC did not occur in the deionized water at 400°C/25MPa. With 0.001mol/L HCl or 0.01 mol/l NaOH, cracking occurred in type 316 stainless steel at 400°C/25MPa. With 0.001mol/L HCl or NaOH, cracking occurred in Alloy C-276 at 400°C/25MPa. With 0.01mol/L HCl or NaOH, cracking occurred on Alloy 625 at 400°C/25MPa. Cracking susceptibility of Ni base alloys decreased with increased Cr content of alloys in SCW either containing HCl or NaOH.

Keywords : supercritical water, alkaline, corrosion rate, stress corrosion cracking, stainless steel, Ni base alloy,

INTRODUCTION

Supercritical water (SCW) process is an attractive method for decomposition of hazardous organic wastes and for upgrading of low-quality hydrocarbon resources. However, the corrosion of a reactor or a heat exchanger is known as the major difficulty to put the SCW processes into industrial applications. It is important to select suitable structural materials, which are compatible with the SCW environments of each particular process, to ensure long term integrity of the reactor components. The almost study for corrosion in SCW has ever been made in oxidizing environment. On the other hands, in this reducing SCW environment, the study of corrosion has been not yet made enough. The environment is reducing in the process for upgrading of low-quality hydrocarbon resources. The hydrogen, carbon oxide, carbon dioxide and methane is generated by the pyrolysis and hydrolysis of hydrocarbon resources [1]. In this reducing environments, the oxide film, which is most important factor to determine the corrosion resistance, seemed to have different behavior as compared with oxidizing environments. The objectives of this study are to evaluate the corrosion rate of candidate corrosion-resistant alloys in SCW environments under reducing atmosphere and to understand the corrosion mechanisms. We have studied the corrosion behavior in neutral and acidic supercritical water environments [2]. In alkaline condition, the study of corrosion behavior has been very limited [3]. So in this study we reported mainly the corrosion behavior of type 316 stainless steel and Ni base alloys in SCW containing NaOH.

2. EXPERIMENTAL

2.1 Materials

Five kinds of materials were selected out of existing commercially used materials, type 316 stainless steel (SUS316) and four Ni base alloys (Alloy 625, Alloy C-276(HC-276), Ni-45Cr-1Mo (MC alloy) and Ni-19Cr-19Mo (MAT 21)). The chemical compositions of these materials are shown in Table 1. The size of specimens for corrosion experiment was 15mm × 30mm × 3mm. Surfaces of the specimens were polished with up #1200 emery grade and degreased ultrasonically in acetone, and dried. The size of specimens for SCC test was round bar type specimen, which have gauge section of 3mm in diameter and 20mm in length. The gauge section were polished with up #1200 emery grade and degreased ultrasonically in acetone, and dried.

2.2 Corrosion Experiments

The apparatus was an Alloy 625 static autoclave having a capacity of 1600 cm³. Firstly, the weight of test solution was calculated with density of water at test condition. For example, the test solution was put in it about 266g at 400C/25MPa, because the density of water is 0.1663 g/cm³ at this condition. Then the specimen and test solution were put in the autoclave. The specimens were located above the water line at room temperature. And autoclave was heated up to the test temperatures, but pressure was a little below test pressure. Then pressure increased up to the test pressure with a help of high pressure pump. The test solution was deionized water and NaOH solutions. The test temperature and pressure were fixed at 400C and 25MPa. The exposure time was 50 hours including heating time of about 2 hours. So, corrosion damages occurred during heating-up and cooling-down processes are reflected in the results. The reducing environment was made by decomposition of HCOOH. HCOOH was decomposed to hydrogen and carbon dioxide at 160°C. The hydrogen partial pressure was changed with

the additive mass of HCOOH in water. The test solution and hydrogen partial pressure are summarized in Table 2.

Weight changes were measured by weighing specimens to a precision of 0.1mg before and after the test. The surface and cross section of specimens was observed by scanning electron microscopes (SEM). And the chemical composition of thin film cross section was analyzed by Electron Probe Micro-Analysis (EPMA).

2.3 Cracking Experiments

The slow strain rate test (SSRT) was adopted to evaluate SCC susceptibilities of the materials in supercritical water. Fig.1 shows a schematic of the apparatus. The specimens were uniaxially pulled at constant strain rate of $2.78 \times 10^{-6} \text{ s}^{-1}$. Testing temperature was 400°C , testing pressure was 25MPa. The test solutions were deionized water, HCl solutions (0.001, 0.01 mol/l) and NaOH solutions (0.001 mol/l, 0.001mol/l + 50 ppm NaCl, 0.01 mol/l) were taken as a parameter to investigate effects of pH and anion on SCC susceptibilities of the materials. The test conditions were summarized in Table 3.

3. RESULTS AND DISCUSSION

3.1 Corrosion Behavior

Fig.2 shows the weight change per hour as a function of NaOH concentration at 400C/25MPa. Type 316 stainless steel gained weight. The weight gain increased approximately with increasing NaOH concentration. Type 316 stainless steel specimens were cover with uniform black films after test. EPMA analysis revealed the film of the specimen in 0.2 mol/l NaOH was about $8 \mu\text{m}$ thick, porous film, and composed of Fe, Ni, Cr, and O. It is suggested that this porous film was not very protective, because the specimen had large weight gain in supercritical water containing 0.2 mol/l NaOH. Ni base alloy, Alloy C-276 and MAT21, lost weight. The weight loss increased with increasing NaOH concentration. MC alloy showed little weight change in this test condition. Fig.3 shows the weight change per hour of Fig.2 as a function of Cr content in Ni base alloys. From this figure, one can see that the weight change per hour decrease with increased Cr content in Ni base alloy in SCW environment containing NaOH. This result was similar to that obtained in sulfuric acid and NaCl solutions [4, 5]. In low oxidizing conditions, Cr seemed the most important element to corrosion resistance in supercritical water at wide range of pH. The effect of addition NaCl was little on the weight change in supercritical water containing NaOH.

In reducing atmosphere, Fig.4 shows the weight change per hour as a function of hydrogen partial pressure at 400/25MPa in 0.5 mol/l NaOH solution. Type 316 stainless steel shows weight loss, which decrease with increasing hydrogen partial pressure. Ni base alloy, Alloy 625, Alloy C-276 and MAT21 show small weight change with increasing hydrogen partial pressure. But, MC alloy, which contains only 1 mass % Mo in contrast to other Ni base alloys, showed large weight loss, which decrease with increasing hydrogen partial pressure. This result is similar to that in SCW containing HCl [2]. The results would suggest importance of Mo in corrosion resistance in the reducing conditions, and the possible role of Mo would be stabilizer of Cr oxide film [6].

3.2 Cracking Susceptibility

Strain-stress curves of Alloy C-276 obtained by the SSRTs in the SCW containing NaOH are shown in Fig.6. In the deionized water at 400°C/25MPa, no crack was found. In the 0.01 mol/l NaOH solutions at 400C/25MPa, the specimen failed in intergranular mode with failure strain of about 5-8%. This result indicated high susceptibility of Alloy C-276 to SCC in the SCW containing NaOH. Fracture surfaces of the specimens are shown in Fig.7. In 0.01 mol/l NaOH, failure mode was almost fully intergranular and the large cracks were observed at the side of the specimens. Alloy 625 was susceptible to SCC above 0.01 mol/l NaOH concentration. Watanabe have mentioned dissolution mechanism would not be very likely for the cracking in gas-like supercritical conditions, like 400°C/25MPa, and the grain boundary oxidation might contribute to the cracking [7]. These results of SSRTs for Ni base alloys are summarized in Fig.8. MC alloy, which have 45 mass% Cr, have high resistance to SCC in SCW containing NaOH. The effect of Cr was similar to the results of corrosion test (Fig. 3). The almost same results were obtained in SCW containing HCl (Fig.9).

4. CONCLUSITON

Corrosion properties were investigated on stainless steel and Ni base alloys in supercritical water containing NaOH.

(1) In supercritical water containing NaOH, corrosion rate of type 316 stainless steel was always higher than that of the Ni base alloys, Alloy625, HC-276, MC Alloy and MAT21.

(2) In reducing supercritical water containing NaOH, Ni base alloys containing both Cr and Mo, such as Alloy C-276 and MAT21, had better corrosion resistance than Ni-Cr binary alloys.

Cracking susceptibility of the materials was investigated by SSRT in supercritical water containing NaOH or HCl.

(3) With 0.001mol/l HCl or 0.01 mol/l NaOH, cracking occured in type 316 stainless steel.

(4) Cracking susceptibility of Ni base alloys decreased with increased Cr content of alloys in SCW either containing HCl or NaOH.

5. ACKNOWLEDGMENT

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Table 1 Chemical composition of specimens

	Ni	Cr	Mo	W	Fe	C	Mn	Si	Nb,Ta
SUS 316	12	18	2.5		Bal.	<0.08	<2	<1	
Alloy 625	Bal.	21.5	9		2.5				3.7
HC- 276	Bal.	16	16	4	5	<0.1		<0.1	
MC Alloy	Bal.	45	1						
MAT21	Bal.	19	19						2

Table 2 Testing solution of corrosion test

NaOH concentration (mol/l)	NaOH	NaOH + 1000ppm NaCl	NaOH + 3.6MPa H ₂	NaOH + 6.3MPa H ₂
0.05	○	○	○	○
0.1	○	○	—	—
0.2	○	○	○	○
0.5	—	—	○	○

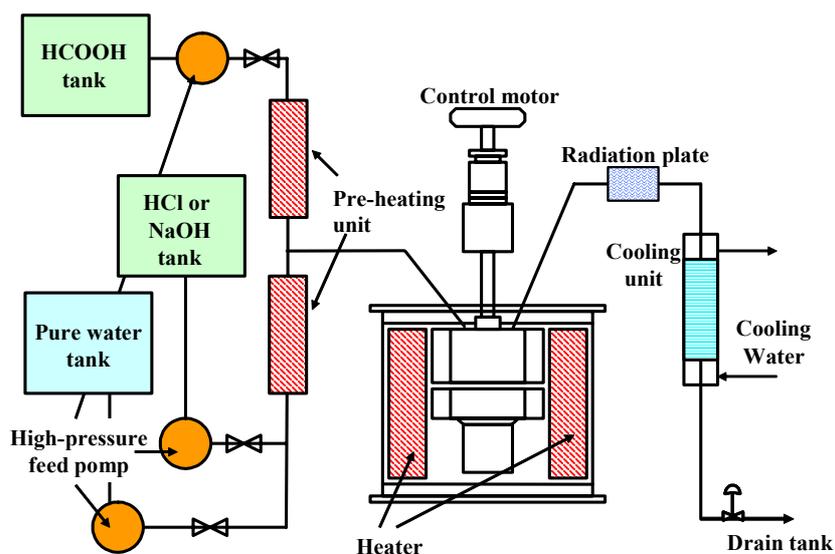


Fig. 1 Schematic diagram for SSRT apparatus.

Table 3 Test solution for SSRT

	HCl		NaOH		
	0.001mol/l	0.01 mol/l	0.001mol/l	0.001mol/l 50ppm NaCl	0.01 mol/l
SUS316	○	○	○	○	○
Alloy 625	○	○	○	○	○
HC- 276	○	○	○	○	○
MC Alloy	○	○		○	

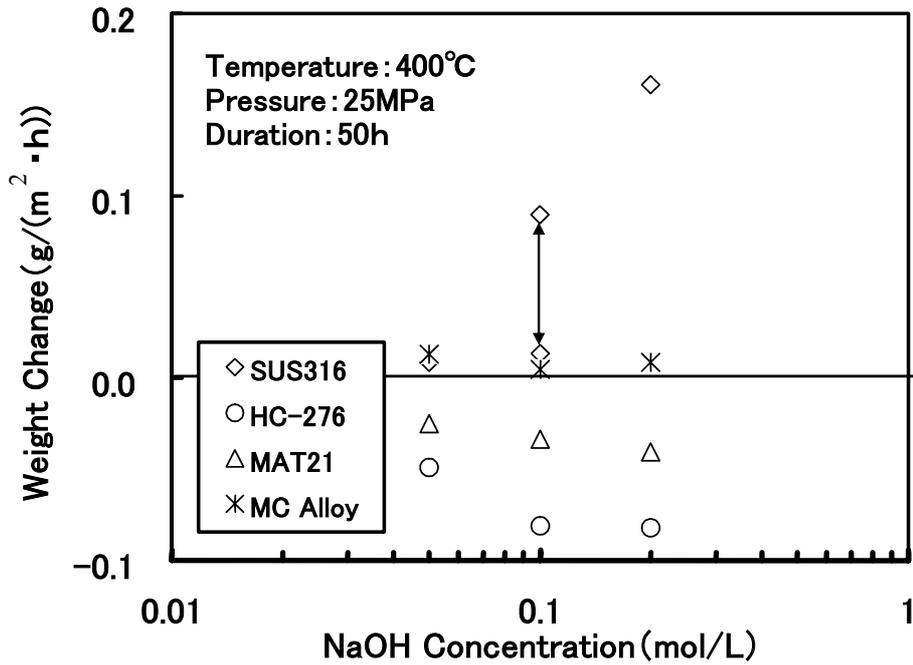


Fig.2 Weight change per hour of SUS316 stainless steel and Ni base alloys in supercritical water with different NaOH concentration at 400C/25MPa.

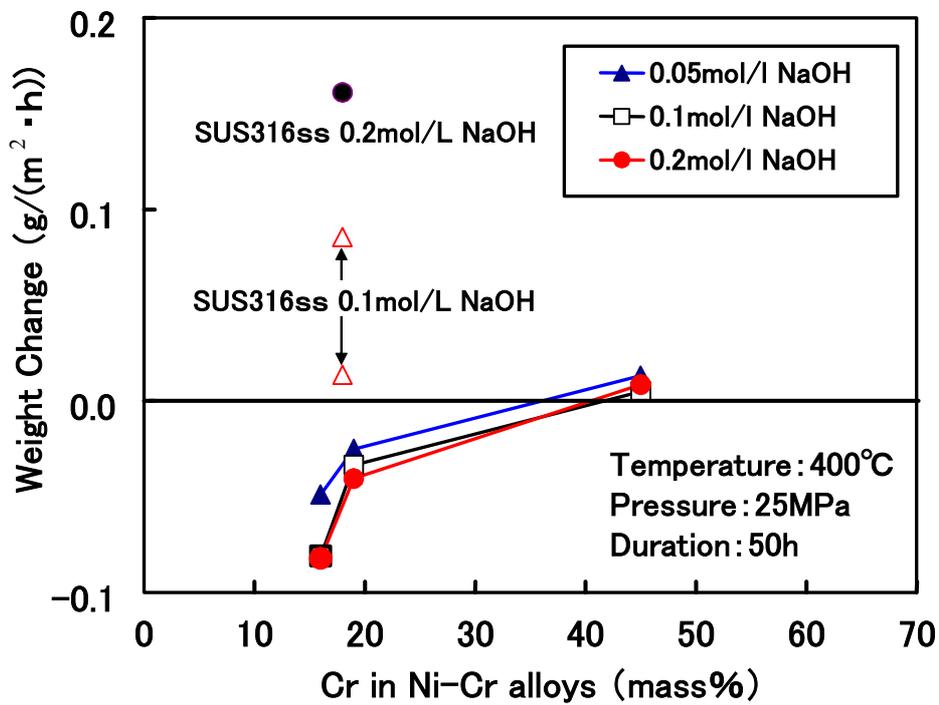


Fig.3 Effect of Cr(mass %) content on the weight change per hour of Ni base alloy.

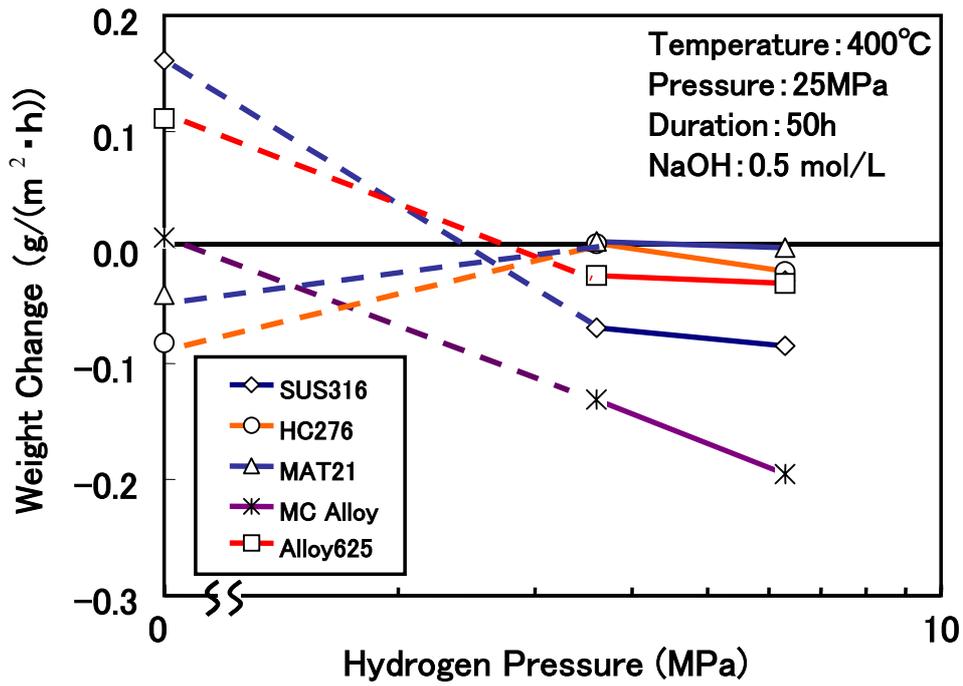


Fig.4 Weight change per hour of type 316 stainless steel and Ni base alloys in supercritical water with 0.5 mol/l NaOH at different hydrogen partial pressure.

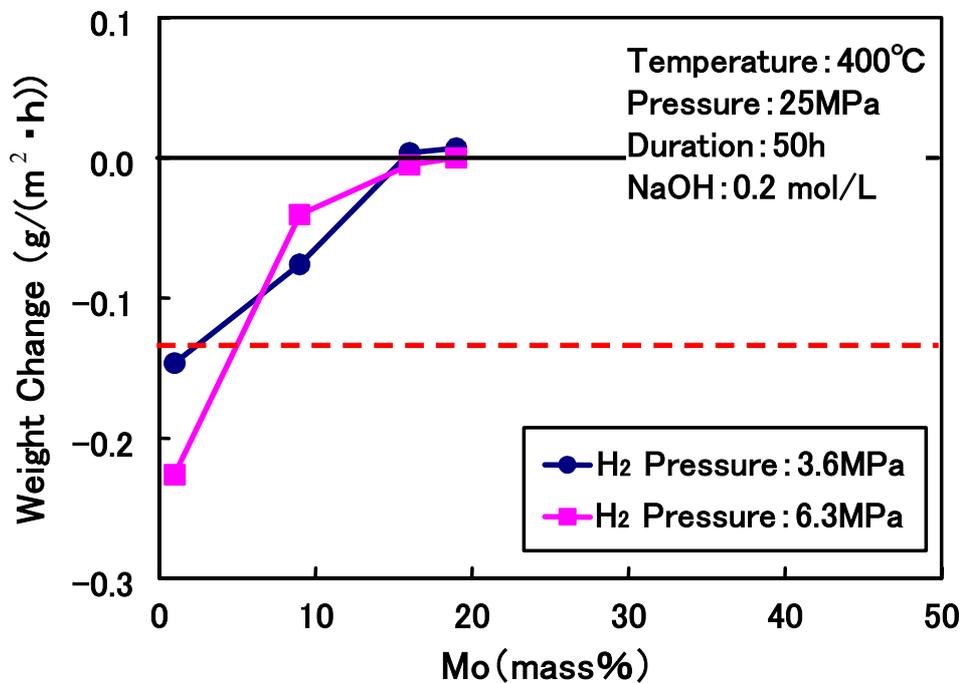


Fig.5 Effect of Mo(mass %) content of Ni-Cr-Mo alloys on the weight change per hour in reducing atmosphere.

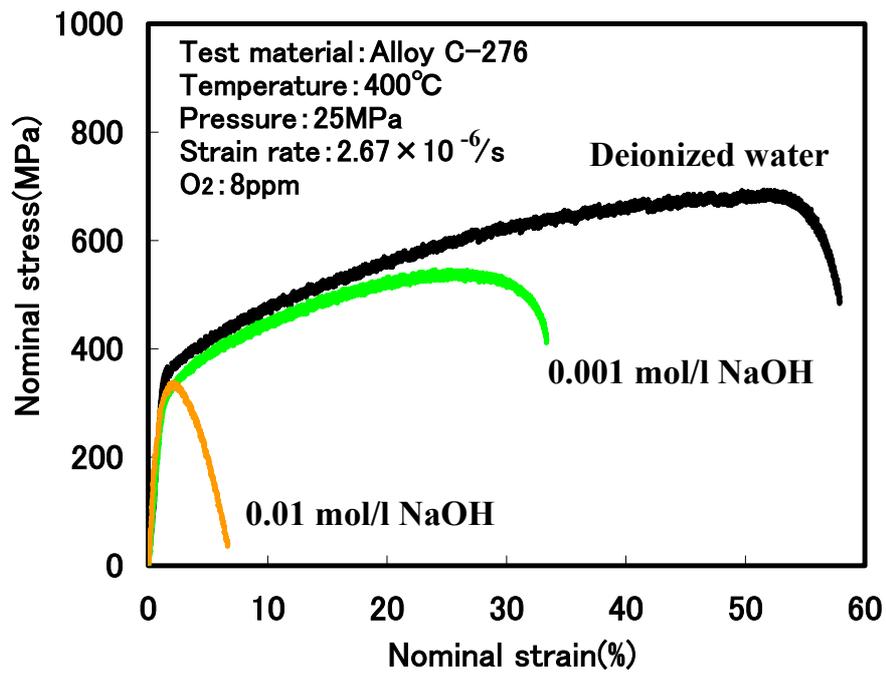
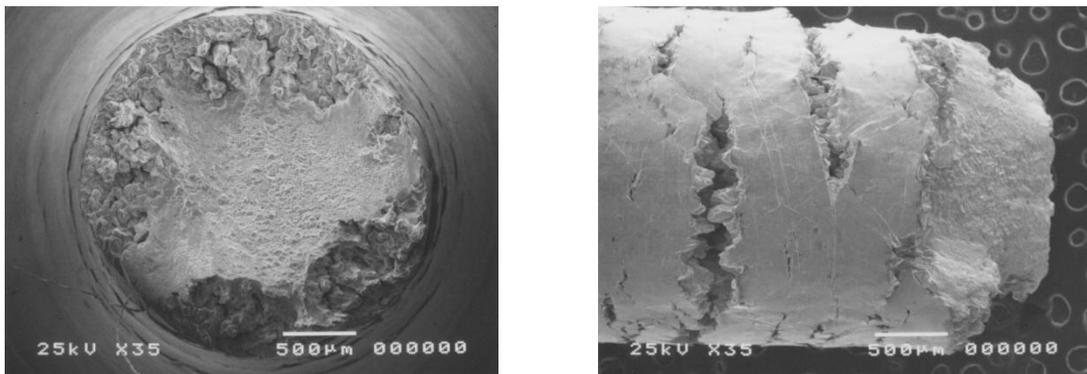
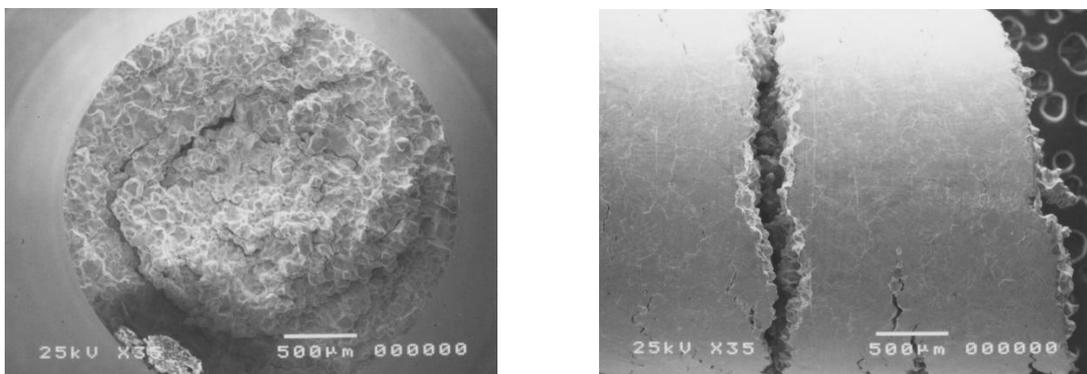


Fig.6 Stress-strain curves of Alloy C-276 in supercritical water with HCl at 400°C /25MPa.



(a) 0.001 mol/l NaOH at 400°C/25MPa (Alloy C-276)



(b) 0.01 mol/l NaOH at 400°C/25MPa (Alloy C-276)

Fig.7 Cracking appearances of Alloy C-276 in supercritical water with NaOH at 400°C/25MPa

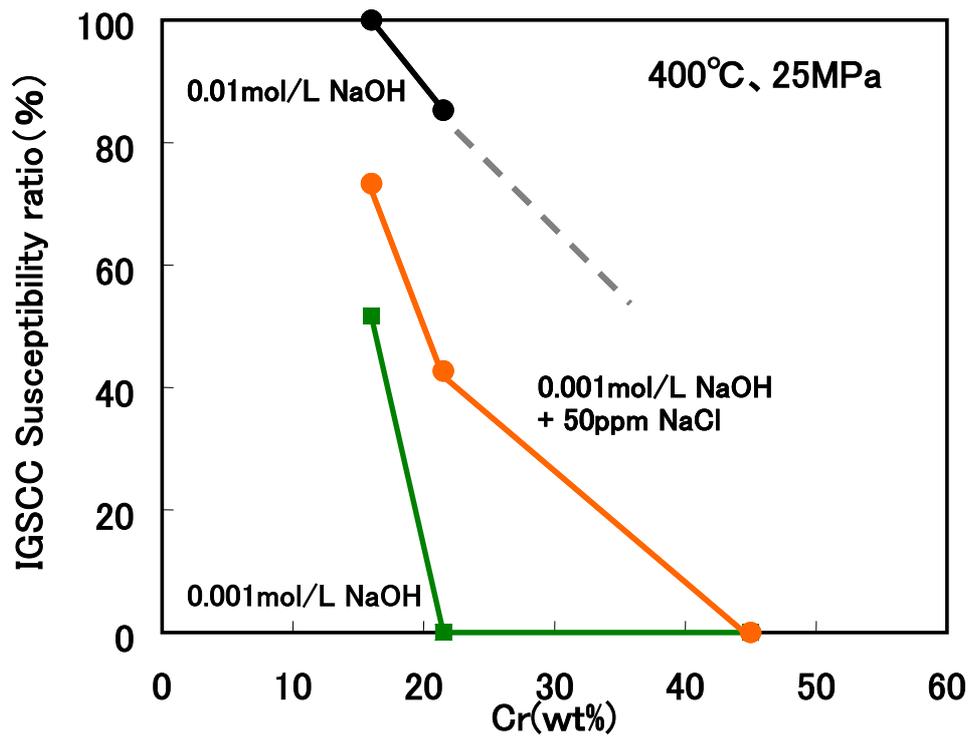


Fig.8 Susceptibilities of Ni base alloys to IGSCC in supercritical water containing NaOH.

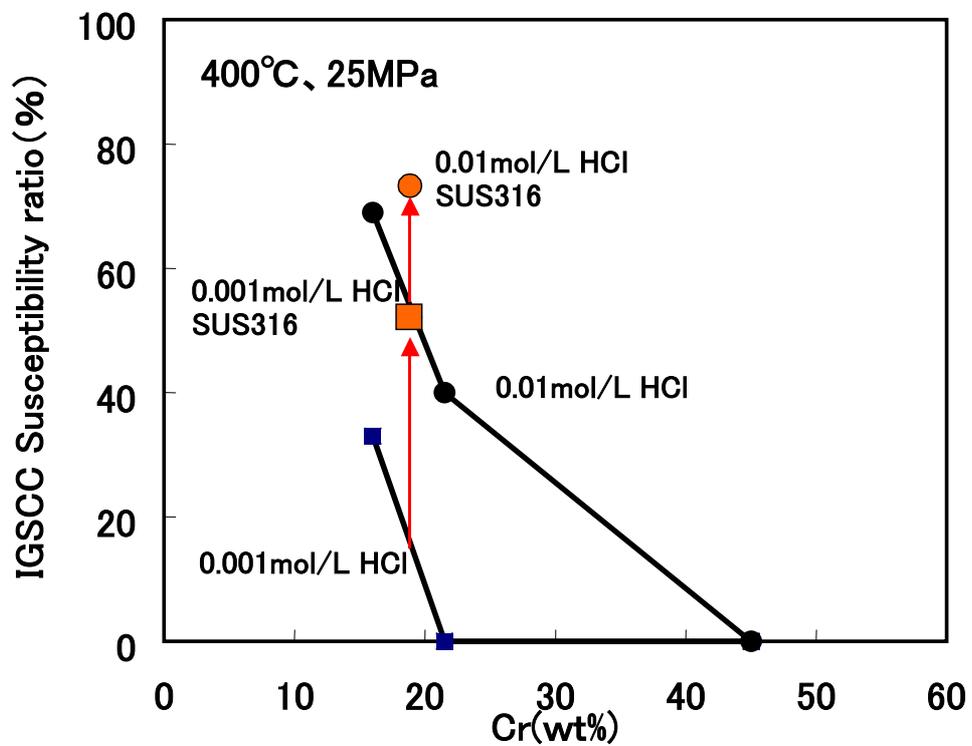


Fig.9 Susceptibilities of type 316 stainless steel and Ni base alloys to IGSCC in supercritical water containing HCl.