Environmentally Assisted Cracking of Alloys at Temperatures near and above the Critical Temperature of Water

Yutaka Watanabe

Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Physical properties of water, such as dielectric constant and ionic product, significantly vary with the density of water. In the supercritical conditions, since density of water widely varies with pressure, pressure has a strong influence on physical properties of water. Dielectric constant represents a character of water as a solvent, which determines solubility of an inorganic compound including metal oxides. Dissociation equilibrium of an acid is also strongly dependent on water density. Dissociation constant of acid rises with increased density of water, resulting in drop of pH. Density of water and the density-related physical properties of water, therefore, are the major governing factors of corrosion and environmentally assisted cracking of metals in supercritical aqueous solutions. This paper discusses importance of "physical properties of water" in understanding corrosion and cracking behavior of alloys in supercritical water environments, based on experimental data and estimated solubility of metal oxides. It has been pointed out that the water density can have significant effects on stress corrosion cracking (SCC) susceptibility of metals in supercritical water, when dissolution of metal plays the key role in the cracking phenomena.

Keywords : *corrosion, stress corrosion cracking, supercritical water, sub-critical water, dielectric constant, oxide solubility, density of water, slip-dissolution model*

1. Introduction

The fourth state of water, supercritical water (SCW), holds great potential of industrial applications as a reaction solvent for chemical industries and also as a coolant for energy conversion industries. One of the most difficult challenges to put the supercritical water to practical use is mitigation of corrosion and environmentally assisted cracking of containment materials. Difficulty in understanding corrosion in supercritical water over that in liquid water is diversity and complexity of environmental factors, in particular, effects of physical properties of water. Fig. 1[1] is corrosion depth profiles of Alloy 625 tubes as a function of temperature, which were exposed to oxygenated water containing 0.05 mol/kg-HCl under fixed pressures, 24 MPa and 38 MPa. This complicated temperature dependence of corrosion depth represents complexity in effects of the temperature/pressure combination on aqueous corrosion near and above the critical temperature.

A number of mechanisms have been proposed to understand stress corrosion cracking (SCC) of metals, e.g. (1) slip dissolution and active pass corrosion based on anodic dissolution of metals, (2) tarnish rupture and internal oxi-
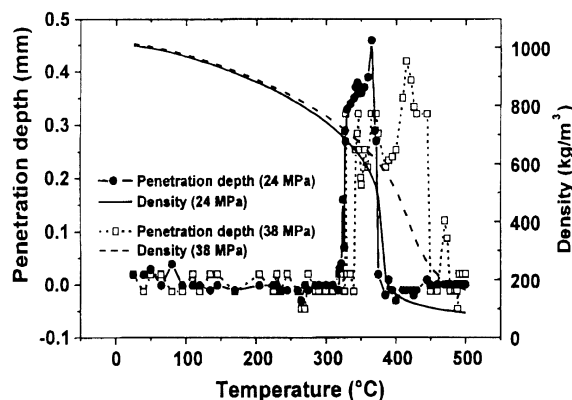

Fig. 1. Corrosion depth profiles of Alloy 625 tubes as a function of temperature. The tubes were exposed to oxygenated water containing 0.05 mol/kg-HCl under fixed pressures, 24 MPa and 38 MPa.[1]

dation based on oxidation ahead the crack tip and cracking of the oxides, and (3) hydrogen cracking, etc. If dissolution of metals takes the essential role in the stress corrosion cracking concerned, cracking susceptibility is expected be significantly affected by dielectric constant of water. In this paper, we also look into cracking behavior of sensitized stainless steels in water under various pressures and at fixed temperature above and below the critical point

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by using Slow Strain Rate Tests (SSRT), and discuss its correlation to dielectric constant of water.

2. Dielectric constant of water as a major controlling factor of corrosion near and above the critical temperature of water

Important environmental factors governing corrosion rate in an aqueous solution are, in general, anion and its concentration, pH, oxygen concentration, and temperature. In case of corrosion near and above the critical temperature of water, solvent properties of water, e.g. dielectric constant, is another key parameter. The particular characteristic of supercritical water is that physical properties widely vary depending on applied pressure as well as on temperature. Fig. 2 shows how widely the density of water varies above the critical temperature by applied pressure.[2] Since the properties of water, such as dielectric constant[3] and ionic product,[4] are strong function of density, those properties are also very sensitive to applied pressure. When dielectric constant of water is high, dissociation of acid, alkalis, and salt is enhanced. Hence, concentrations

of anion and hydrogen ion are also strongly affected by pressure. Water density has significant effect on solubility of metal oxide, too.

Fig. 3[5] is a good example showing the effect of pressure and of resultant water property on corrosion rate in sub-critical and supercritical water environments. A few kinds of Ni base alloys, including B-2, C-276, MAT21, and MC alloy, were exposed to high-temperature water containing 0.01 mol/kg-H_2SO_4 and 0.025 mol/kg-O_2 either at sub-critical 360°C/25 MPa or at supercritical 400°C with various pressures from 25 MPa to 60 MPa. When we compare the data at the fixed pressure, 25 MPa, corrosion rates are much higher under the sub-critical condition (360°C) than those in the supercritical condition (400°C). The corrosion rates at 400°C, however, significantly increased and reached almost the same values as those at 360°C, when pressure was increased to 60 MPa. When we plot the same data as a function of dielectric constant, Fig. 4,[5] it is recognized that the corrosion rates of each Ni-base alloy are uniquely correlated to dielectric constant of water including both the supercritical conditions and the sub-critical condition. This data set demonstrates the importance of
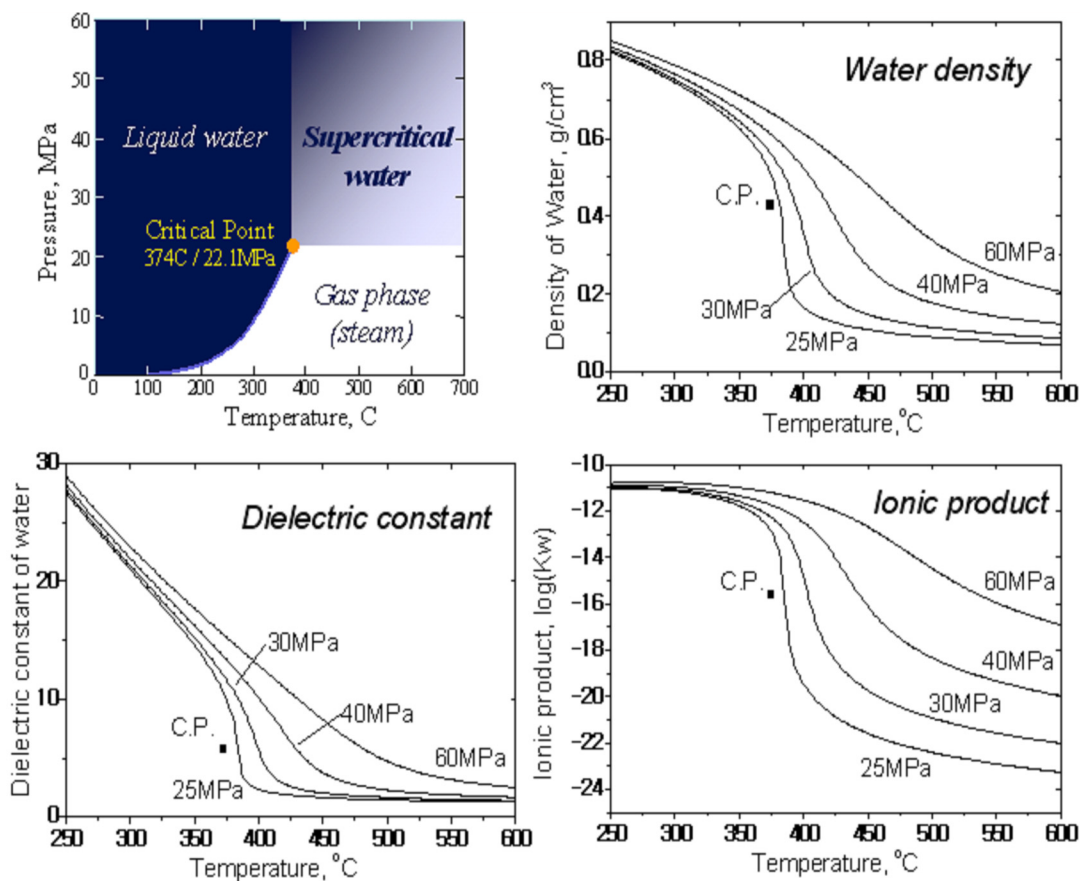

Fig. 2. Density and physical properties of water as functions of temperature and pressure.
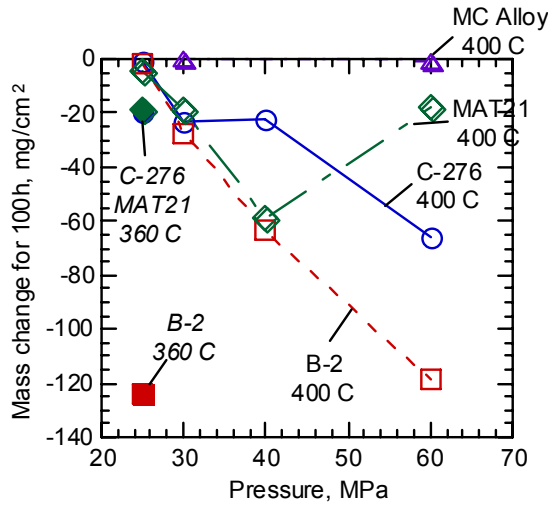
Fig. 3. Pressure dependence of corrosion rate of Ni base alloys in water containing 0.01 mol/kg-H_2SO_4 and 0.025 mol/kg-O_2 either at sub-critical condition or supercritical conditions.[5]
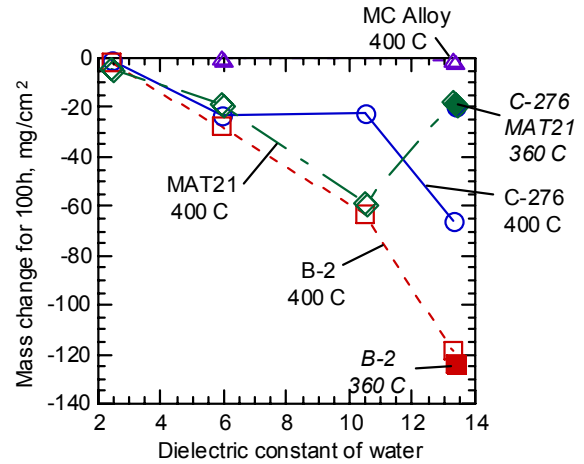

Fig. 4. The same data in Fig. 3 are plotted as a function of dielectric constant of water, indicating the importance of dielectric constant of water for understanding SCW corrosion.[5]

dielectric constant of water for understanding corrosion in sub-critical and supercritical water environments. The overall picture of major controlling factors of corrosion in supercritical and sub-critical water may be drawn as Fig. 5, where corrosion property is eventually attributed to properties of oxide layers formed on alloys in the environment at the elevated temperature and pressure.

3. Importance of water property for understanding cracking of alloys in supercritical and sub-critical water

SCC susceptibility of alloys is also strongly dependent on physical properties of water. The series of SCC experiments[6] done under various pressures at fixed temperature above and below the critical temperature give us good demonstration about importance of water properties for SCC of alloys.
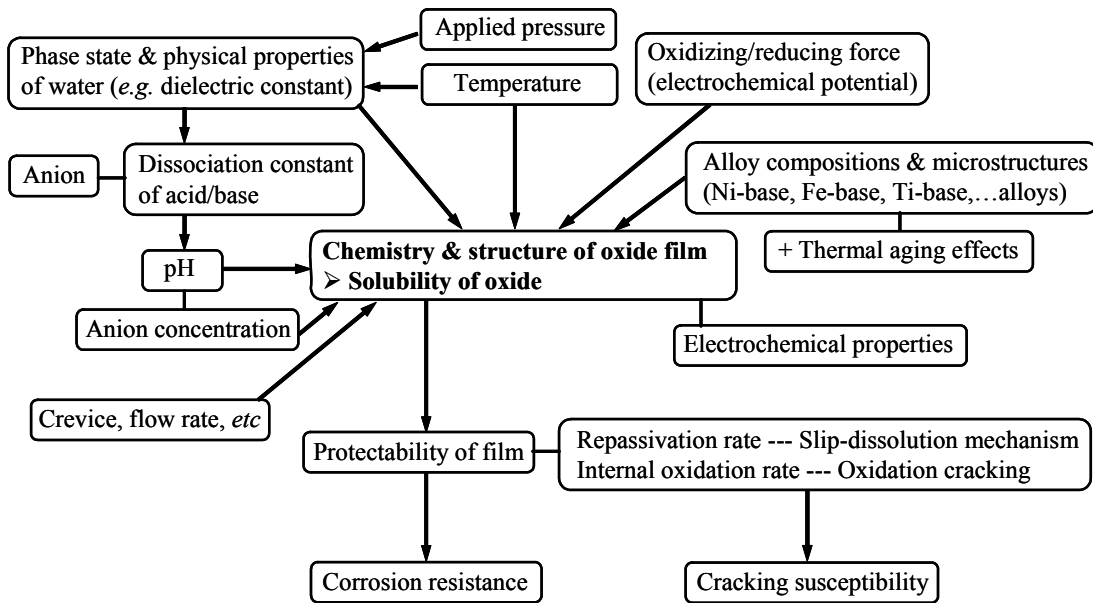
Type 316 stainless steel was used in this study. The

Fig. 5. Whole picture of major controlling factors of corrosion in supercritical and sub-critical water.

chemical compositions are shown in Table 1. The 316 stainless steels was solution treated (1050°C/30 min, water cooled) and then sensitized (650°C/24 h, air cooled). The degree of sensitization was evaluated by the electro-chemical potentiokinetic reactivation method and re-activation ratio of the material was 15.4%, which indicates that the material was well sensitized. The material was machined to round bar type specimens, which have gauge section of 3 mm in diameter and 20 mm in length. The slow strain rate test (SSRT) was adopted to evaluate SCC susceptibility of the materials in sub-critical and super-critical pure water environments. The specimens were uni-axially pulled at a constant strain rate of $2.78 \times 10^{-6} s^{-1}$. The testing environment was distilled and then deionized high-purity water with 8 ppm dissolved oxygen. Testing temperature/pressure combinations were 400°C/25 MPa, 400°C/30 MPa, 400°C/40 MPa, 400°C/60 MPa for super-critical conditions, and 360°C/25 MPa for sub-critical condition. The testing conditions are summarized in Table 2. Changing pressure from 25 MPa to 60 MPa at fixed temperature at 400°C gives variation in dielectric constant of water from 2.4 to 13.3. Dielectric constant of water at 360°C/25 MPa is 13.4.

Stress-strain curves obtained in the SSRTs are shown in Fig. 6. In the sub-critical liquid water at 360°C/25 MPa, the sensitized steel failed at 12% of strain. The failure mode was fully intergranular. This result indicated high susceptibility of the sensitized stainless steel to SCC in the oxygenated sub-critical liquid water at 360°C. It is well known from extensive researches[7] on boiling water reactor (BWR) components that sensitized stainless steels are highly susceptible to intergranular stress corrosion cracking (IGSCC) in high-temperature water, when water contains a few ten ppb or higher level of oxygen. The SSRT result in the sub-critical condition is consistent with the previous BWR studies. As for supercritical water con-
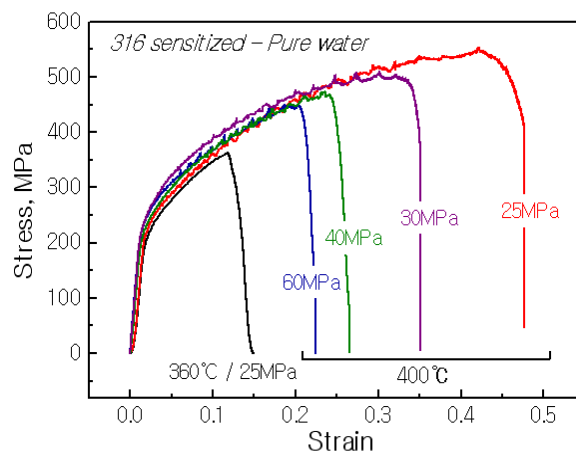

Fig. 6. Stress-strain curves of sensitized 316 SS in high-purity water under supercritical and sub-critical conditions.

ditions at 400°C, cracking susceptibility was strongly affected by applied pressure. Although the specimen failed in ductile mode with elongation of about 45% and no crack was found in the "gas-like" condition at 400°C/25 MPa, failure strain monotonically decreased as the pressure was increased. Failure strain was as low as 21% at 60 MPa of applied pressure. Under supercritical conditions at 400°C, fracture morphologies were also strongly dependent on pressure. Although only transgranular cracks were found under relatively low pressure, e.g. 30 MPa, where reduction in failure strain was not significant, intergranular cracking was more enhanced with increased pressure and failure mode was almost fully intregranular at 60 MPa, Fig. 7.

The failure strain, which represent SCC susceptibility, is plotted against the temperature/pressure combination of each experiment, together with estimated solubility of hematite, Fig. 9. These results indicate that cracking is more enhanced under higher dielectric constant condition, whether sub-critical or supercritical water. Under high density conditions, namely high dielectric constant conditions, ionization of metal is easier and solubility of metal oxide is higher, anodic dissolution of metal would be more enhanced. Electric conductivity of water is also higher for higher density condition, since ionic product is higher. The result shown in Fig. 9, therefore, clearly indicates that dis-solution of metal holds the essential role in the cracking phenomena of a sensitized stainless steel in high-purity water both in sub-critical and supercritical conditions. The slip-dissolution mechanism, which is one of the dis-solution-driven cracking mechanisms, was proposed for cracking of sensitized stainless steels in BWR coolant en-vironment and widely accepted. However, sufficient ex-perimental evidence has not been obtained. The result in

Table 1. Chemical composition of 316 stainless steels used. (wt%)

Fe	Cr	Ni	C	Si	Mn	P	S	Mo
Bal.	17.46	12.35	0.03	0.58	0.82	0.032	0.002	2.07

Table 2. Conditions for slow strain rate tests.

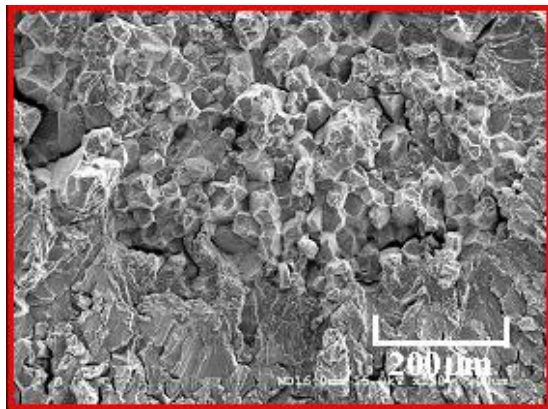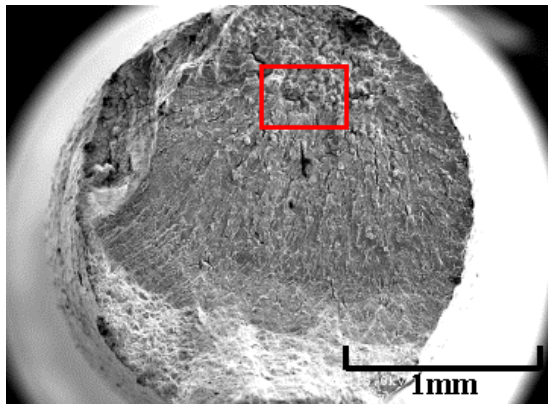| Temperature °C	Pressure MPa	Phase of water	Dielectric constant	Oxygen ppm
360	25	Liquid	13.4	8
400	25	Supercritical	2.4	8
400	30	Supercritical	5.9	8
400	40	Supercritical	10.5	8
400	60	Supercritical	13.3	8

Fig. 7. Cracking morphology of the sensitized 316 stainless steel in oxygenated high-purity water at 400˚C/60 MPa
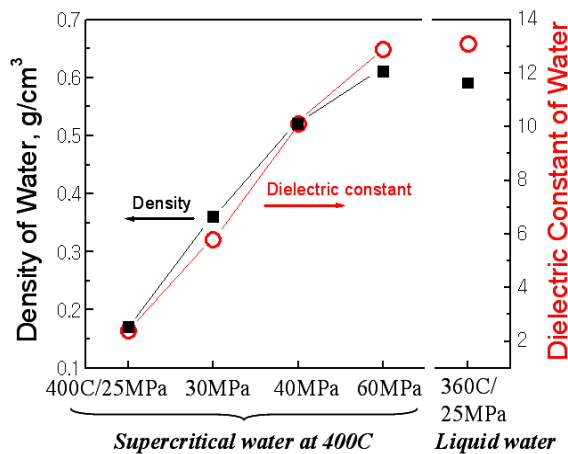

Fig. 8. Density and dielectric constant of water for the temperature/pressure conditions for the SSRT.

this study would give a clear evidence of the dissolution mechanism. Cracking susceptibility seems somewhat higher for sub-critical 360°C/25 MPa condition compared with supercritical 400°C/60 MPa condition, although dielectric constant is almost same for the two. Besides direct effect
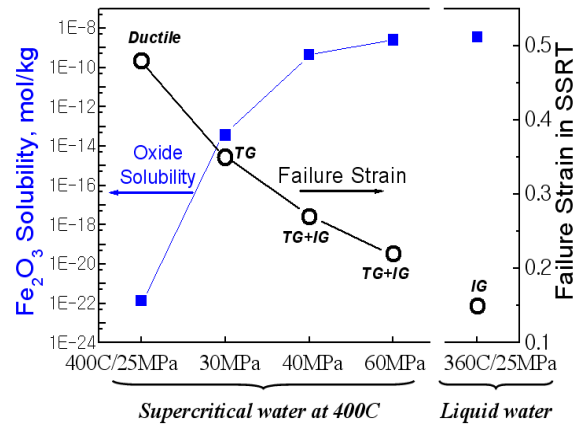

Fig. 9. Failure strain in SSRT plotted together with estimated solubility of hematite for each testing conditions.

of temperature on kinetics, difference in diffusivity of ionic species between sub-critical and supercritical water might have some effect.

4. Summary

This paper discusses importance of "water density" in understanding corrosion and environmentally assisted cracking of alloys in supercritical water environments, based on physical properties of water and experimental data of corrosion rate of Ni base alloys and of cracking susceptibility of a sensitized 316 stainless steel. It has been well demonstrated that the water density has significant effects on SCC susceptibility of the alloy in supercritical water. While no SCC formed in the oxygenated "gas-like" supercritical water at 400°C/25 MPa, cracking occurred at 400°C/30 MPa and the cracking severity was more pronounced as applied pressure was increased up to 60 MPa at the same temperature. This variation in cracking susceptibility being dependent on pressure was understood from dielectric constant of water. The results give a strong evidence of the "dissolution mechanism".

Acknowledgments

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