Corrosion Behavior in Subcritical and Supercritical Water Containing Sodium Chloride

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Immersion tests have been examined in subcritical and supercritical water containing sodium chloride. Crevice corrosion is confirmed SUS316L specimens in supercritical water and subcritical water containing 0.6-kmol/m^3 NaCl solutions (Equivalent to sea water). Electrochemical measurement is also examined in subcritical water containing 0.6-kmol/m^3 NaCl solutions.

Keywords : *supercritical water, subcritical water, corrosion in supercritical water, crevice corrosion, and decomposition processes of wastes*

1. Introduction

Treatment processes of hazardous materials and persistency waste materials have been gathering attention recently. Therefore various processes for decomposition wastes have been investigated. One of these processes is utilizing subcritical or supercritical water process. Characteristics of supercritical water above critical state (374 °C, 22MPa, for pure water) have strange differences from characteristics of ordinary water at room temperature. Characteristics of subcritical water less than critical state also have differences form ordinary water. So subcritical and supercritical water processes are very effective for decomposition of such wastes. Many of these waste materials contain certain amounts of chloride compounds, and no past practical experience exists on the behavior of existing materials in water environments containing high concentration of chloride compounds under subcritical and supercritical states. Many kinds of corrosion incidents like crevice corrosion and stress-corrosion cracking (SCC) are expected to be induced in water environments containing high concentrations of chloride compounds at high temperature as shown in Figs. 1 and 2.

Our test program is selecting appropriate materials to be exposed to disposal conditions of animal and plant wastes (300 °C, 1000 ppm [Cl-], equilibrium with ambient atmosphere) confirmed no SCC to be induced in SUS316 stainless steel, and some pitting corrosion to be induced in mild steel samples. Thus, we have recommended SUS316 stainless steel as the main structural alloy for constructing the processing plant. Parallel tests conducted for

ascertaining behavior of an oxidation equipment (under air saturated environments at 200 °C how no severe corrosion incidents to be induced under the experimental conditions employed.

The present investigation are aimed to clarify the following tasks:

1) Corrosion maps are to be developed for various alloys in subcritical and supercritical water reaction environments in immersion tests.

2) The further knowledge in subcritical and supercritical water environments is acquired by carrying out electrochemical measurements.
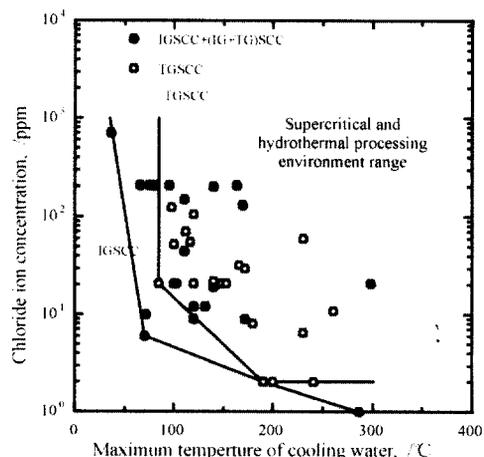

Fig. 1. SCC map of SUS304 stainless steel under various heat exchanger environments.

2. Experimental

2.1 Immersion tests

Alloys tested: SUS316L and Hastelloy series alloys
Test environments: temperature; 200 300, and 400 °C
pH: not adjusted
Specimens: Welded specimens

The tests are conducted by immersing the specimens in test solutions in a static type autoclave. The equilibrium pressure increases with increasing the solution temperature with the test pressure being about 9.0-MPa at the test temperature of 300 °C and about 27 to 28-MPa at 400 °C. The volume expansion of the test solution in the autoclave is accommodated by restricting the initial volume of the solution to about 40 to 60 % of the autoclave volume.

Welded specimens are prepared by spot welding two sheets of flat plates placed on each other of the sizes of 20×50×2 mm and 20×20×2 mm at the centers as shown in Fig. 3. The diameters of the nuggets are kept to be 4.5 mm. The welding surfaces are machined to smooth finish, and are polished by #600 polishing paper before welding. The nugget is drilled by a tool of 3.5 to
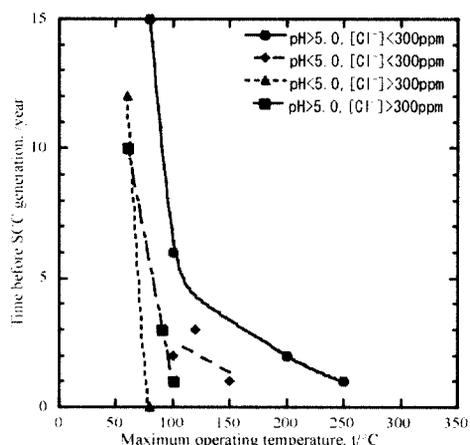
4.0 mm diameters for separating, the welded plates into two separate plates for evaluating the corrosion behavior after being immersed in test solutions. Corrosion damages like corrosion pits and SCC tend to be generated in crevices near welded parts, and thus, evaluation of corrosion damages is difficult to be accomplished quantitatively. However, the evaluation is easily conducted, as the specimen size is relatively small. The corrosion conditions in the tests conducted are rather severe because many crevices are found to exist in a test specimen. Thus, the test specimen is thought to be appropriate in conducting the corrosion tests for screening potential alloys.

The crevices and free surfaces of the specimens tested are inspected by naked eyes and microscopically. The welded zones are also observed microscopically.

2.2 Electrochemical measurements (anodic polarization measurements)

Alloys tested: SUS316L
Test environments: temperature; 200 300, and 350 °C
pH: not adjusted
Specimens: Flag type specimens
Sweep late: 20 mv/min
Starting point: 1000mV vs. Ag/AgCl electrode in 0.1-kmol/m^3 KCl solutions

Flag type specimens shown in Fig. 4 are polished by #600 polishing paper, and degreased with acetone, and carried out ultrasonic washing with ion exchanged water before measurements. The tests are conducted by immersing the specimens of flag area into test solutions in a static type autoclave.

3. Results and Discussion

3.1 Immersion tests

Fig. 5 shows the corrosion map of the alloys based on immersion test results of the alloys in subcritical and supercritical water environments that contain various concentrations of chloride ions.

Fig. 2. Environmental condition dependency of the time before SCC generation of SUS316 series stainless steel.

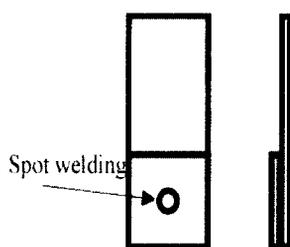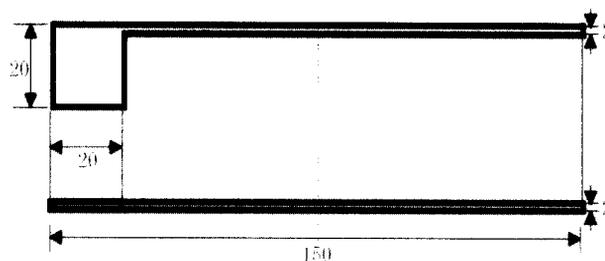**Fig. 3.** Schematic diagram of spot welded specimen.

Fig. 4. Schematic diagram flag type specimen.

The transgranular type SCC is observed in SUS316L specimens tested at 200 °C in the test solution containing 0.6-kmol/m³ NaCl solutions after 150 hours as shown in Fig. 6. The figure shows that these stress corrosion cracks are originated at spot welded parts. No existence of the
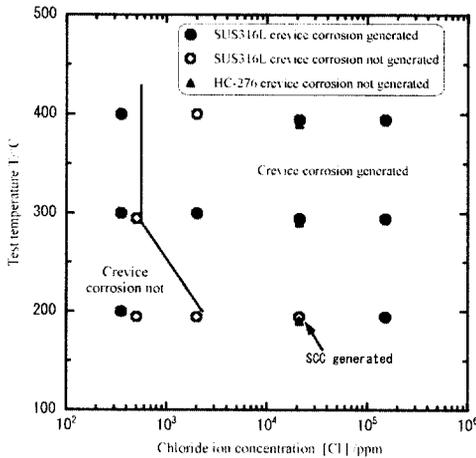

Fig. 5. Crevice corrosion map in sub-critical and supercritical water environments containing various concentrations of chloride ions.

(1)

(2)

Fig. 6. Stress corrosion cracks generated in a spot welded specimen after immersed in NaCl solution of 0.6 M at 200 °C for 150 hours (1) Surface (2) Cross section.

SCC originated from any local corrosion is confirmed in the present study although the existence is believed to be possible in the environments tested. The reason is that the origins of the cracks may be lost during drilling operations for separating two welded plates.

No existence of crevice corrosion, pitting corrosion, and SCC are confirmed to exist in SUS316L specimens tested at 200 and 300 °C in solutions containing 5000 ppm of [Cl-], and at 200 and 400 °C in 2000 ppm [Cl-] solutions all for 150 hours.

The SCC generation is not confirmed to exist in specimens tested under other experimental conditions, although the pitting corrosion type crevice corrosion is confirmed to exist inside crevices. No pitting corrosion is observed on free surfaces. The pitting corrosion type crevice corrosion is generated in crevices where test solutions can be penetrated. These crevice corrosion incidents are observed not only in the stainless steel samples, but also in the Hastelloy samples when tested in the test solution containing 0.6-kmol/m³ NaCl solutions.

Fig. 7 shows the relationship between the crack propagation rate and the chloride concentration of the sensitized stainless steel samples of SUS304 and SUS316L tested in NaCl solution at 300 °C. The crack propagation rate for SUS316L specimens are plotted based on the threshold to be less than 10 μm. Generation of SCC is confirmed only at one test conducted at 200 °C in a NaCl solution with the crack propagation rate of 20 mm/year. Crevice corrosion incidents are always detected to exist in most of the experimental conditions that are simulating subcritical water treatment environments of waste materials. Thus, the crevice corrosion type SCC may be generated in environments in which crevice corrosion can be induced in SUS316L with the presence of residual stresses.
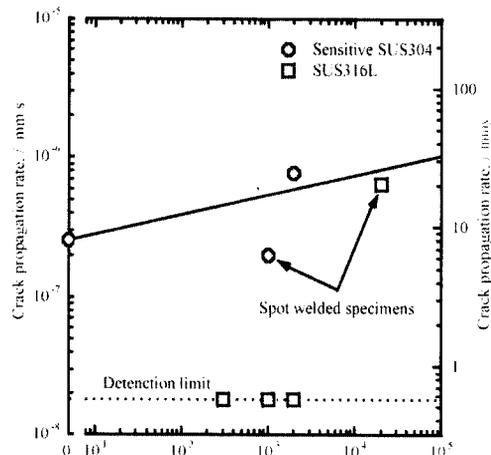

Fig. 7. Relationship between chloride ion concentration and crack propagation rate.
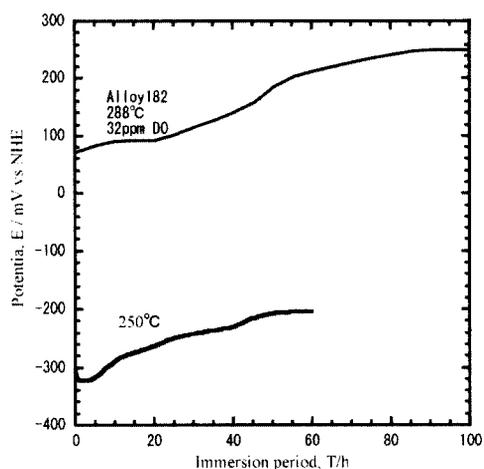
Fig. 8. Measured natural potential of SUS316L flat plates immersed in 1000 ppm [Cl-] solutions.

Fig. 9. Anodic polarization curves of SUS316L steel in subcritical water environment.

3.2 Electrochemical measurements

Fig. 8 shows measured results of the natural potential of flat plate test specimens of SUS316L being immersed in a 0.6-kmolm^{-3} NaCl solution. The ennoblement of the potential is believed to be brought by the growth of oxidation films of SUS316L by dissolved oxygen in the test solution. The measured potential is less noble than the measured values obtained in a flowing type autoclave at 288 °C with 32 ppm of the dissolved oxygen content. The reason for this phenomenon is that although the initial dissolved oxygen content is low in the present study, the dissolved oxygen initially present in a static type autoclave like the one employed in this study is consumed easily during an immersion test of test specimens. Thus, the immersion environment of a static type autoclave becomes a reducing environment during conducting immersion tests, and therefore, any measure as adding an oxidizer to the test solution during a test is needed for conducting an immersion test in a simulated oxidation environment.

Fig. 9 shows measured results of the anodic polarization curves of flat plate test specimens of SUS316L being immersed in test solutions. Although the passivation film protects SUS316L by the system that does not contain a chloride, it is considered that the passivation film is destroyed by the system containing a chloride.

In oxidizer (H_2O_2) addition environment, corrosion potential is nobler and cathodic current density is lager than existing no oxidizer. The difference in anodic current was not looked at by the existence of oxidizer addition. It is
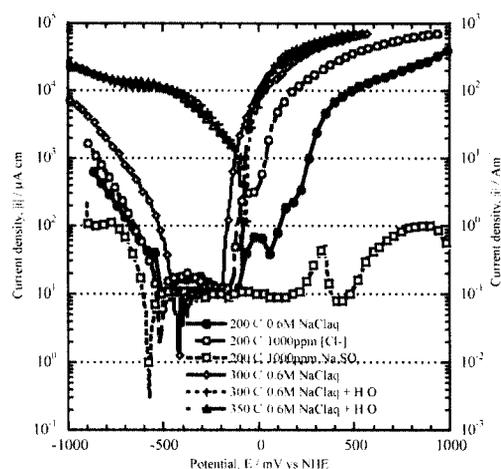
thought that oxidizing environment was able to be imitated in a static type autoclave by H_2O_2 addition.

4. Conclusions

1) Crevice corrosion incidents are observed under a wide range of temperature and chloride concentration conditions on the various alloy specimens when tested in a static type autoclave. Only one incident is observed to be SCC generation. However, a large-scale generation of SCC can be possible under oxidation conditions.

2) By the system containing H_2O_2, it turns out that it becomes severe oxidizing environment compared with the system that is not included.

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