

# EFFECTS OF A SMALL QUANTITY OF METAL IONS ON THE STRESS CORROSION CREAKING OF AUSTENITIC STAINLESS STEEL IN SIMULATED CONCENTRATED-BRINE

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## 1. Introduction

Conventional austenitic stainless steel (SS) such as type-304SS and type-316SS are widely used for the structural materials of salt production facilities. The austenitic stainless steel shows an excellent resistance to uniform corrosion even in highly-concentrated chloride solutions, if their pH are kept within near-neutral or alkaline range. However, it has a weakness that rather susceptible to localized corrosion such as pitting, stress corrosion creaking (SCC) and crevice corrosion in the chloride solutions. Among these variety forms of localized corrosion, SCC might be the most concerned form for practicing plant engineers, because in general, SCC propagates at higher rate than the other forms of localized corrosion, and easily cause a leakage of a process solution.

The susceptibility of the austenitic SS to SCC in the chloride solutions is affected by several environmental factors such as chlorides concentrations, dissolved oxygen, pH, and temperature [1]. The chloride concentrations, pH and temperature would directly relate to the process factors for facilitating the production, so it is difficult to modify them for the sake of corrosion control. A decrease in dissolved oxygen concentration has been regarded as the most feasible way for controlling the SCC of the salt production facilities. A team at Sumitomo Metal Industries comprehensively investigated the

effect of dissolved oxygen to the SCC of solution annealed type-304SS and type-316SS in the MgCl<sub>2</sub> solutions whose concentration were 20 to 45mass% at a variety of temperatures up to the solution's boiling point [2]. Their result revealed that when the solutions were fully deaerated, the type-304SS was almost immune to SCC even in 25 and 35 mass% MgCl<sub>2</sub> solutions up to 100°C, while in the oxygen saturated solutions, the SCC reproducibly developed at a temperature as low as 80°C. As shown in this result, it would be clear that the increase in the concentration of dissolved-oxygen increases the SCC susceptibility of the austenitic SS in concentrated-chloride solutions, however, it might be questionable if the dissolved-oxygen is the only factor for greatly promoting the SCC under the given chlorides concentrations, pH and temperature. The level of the dissolved oxygen concentration in the actual salt production facilities should be close to that in the fully deaerated conditions, because all the modern salt-production facilities employ vacuum evaporation processes. However, in actuality, the SCC of the type-304 SS or higher grade austenitic SS are frequently seen anywhere in the facilities.

The concentrated brine in salt manufacturing processes potentially would contain a small quantity of copper and other metal ions, because copper-nickel and copper-zinc alloys such as Monel, cupronickel, aluminum-brass

and naval-brass are widely used for the materials of the heater tubes and the linings of evaporator in salt production facilities; these materials have a fairly good corrosion resistance in a concentrated chloride solution, however, they are not passivated in the concentrated chloride solution unlike austenitic SS or titanium alloys, so it is considered that they are gradually dissolved into the process solutions at certain rates. The existence of small amount of copper ions in concentrated brines should not be a risk for the production safety, because even in the tap water, which is apparently taken much more than salt, World Health Organization (WHO) admitted to be contained 2mg/L of copper ions. However, the copper ions are active species with a high reduction potential, so there is a possibility that the copper ions dissolved from copper-nickel or copper-zinc alloys would promote the corrosion of austenitic SS and other passivated materials of salt production facilities. In fact, for dilute solutions such as circulating water in nuclear power reactor [3] and heated tap water for domestic use [4], there are some evidences that the existence of a small amount of copper ions makes the SCC susceptibility of the austenitic SS considerably increase. However, for concentrated chloride solutions, the effect of copper ion as well as other metal ions to the SCC susceptibility has not been investigated yet.

In the present study, the change in the SCC susceptibility of type-304 SS with the existence of 10mg/L of cupric or cuprous ions was evaluated in a chloride solution that simulates the composition of a concentrated-brine in an actual salt production process, by using the slow strain rate test (SSRT). The effect of nickel and zinc ions, which are also potentially dissolved from the copper-nickel and the copper-zinc materials, was evaluated in the chloride solution to which 10mg/L of nickel or zinc ions were added. The combination effect was also examined using the chloride solution that contained 10mg/L of cupric and nickel ions or the same concentration of cupric and zinc ions.

## 2. Experimental procedure

Type-304 stainless steel for standard corrosion-test specimen (304-78) from Japan stainless steel association was used for the material. It was provided as 2mm thickness

sheet after being applied a solution annealing. Table 1, which was attached to the provided sheet, shows the material's chemical composition. A flat tensile specimen with 2x4mm cross-section and 20mm gage length was machined from the sheet. The specimen was heat-treated in a furnace at 1050°C for 600s and quenched in air, in order to remove a residual stress induced by the machining. The surfaces of the gage-length part of the specimen were finished up to #2000 with emery papers. Leaving the exposed part of 10mm long (80mm<sup>2</sup> in area) in the midsection of the gage-length, the entire surfaces of the specimen were covered with silicone sealant.

Table 2 shows the composition of the simulated concentrated-brine used in the present work. The solution that was added the 10mg/L of Cu<sup>2+</sup>, Cu<sup>+</sup>, Ni<sup>2+</sup> or Zn<sup>2+</sup> as well as the 10mg/L of Cu<sup>2+</sup> and Ni<sup>2+</sup>, or the same concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup> to the above concentrated-brine was examined. The prepared solutions were shortly brought to a boil to remove the dissolved oxygen, and smoothly poured into the test cell in which the specimen had been set. The solution was exposed to pure-Ar gas stream during the experiments. In some cases, pure-O<sub>2</sub> or 10vol%O<sub>2</sub>-Ar gas was used instead of the pure-Ar, in order to evaluate the effect of the dissolved oxygen to the SCC susceptibility. The solution temperature was kept at 100±0.5°C throughout the experiment.

The change in the SCC susceptibility of the specimen with the environmental conditions was assessed by a slow strain rate test (SSRT). The test was initiated after the specimen being immersed in the solutions for 2 hours. The dynamic extension was applied to the specimen strain, at a strain rate of 2.0 x 10<sup>-6</sup> s<sup>-1</sup>. The changes in the elongation and the apparent stress of the specimen were measured every 60s, and determined the fracture elongation,  $\delta f$  under each environmental condition. From the obtained fracture elongation data, the index to the SCC susceptibility, ISCC was calculated as follow:

$$ISCC = \delta f_{SCC} / \delta f_{immune} \quad (1)$$

$\delta f_{SCC}$  and  $\delta f_{immune}$  are the fracture elongations in the solution and a dry-air, respectively.  $\delta f_{immune}$  was measured at a



strain rate of  $2.0 \times 10^{-6} \text{ s}^{-1}$ , in the dry-air whose temperature was controlled at  $100 \pm 2^\circ\text{C}$ . The dry-air is regarded as an immune environment for the SCC of type-304 SS. All the specimens used for the present study are considered as equivalent, so the obtained ISCC would indicate how the tested solution is immune to the SCC of type-304 stainless steel, and decreases with increasing the specimen's SCC susceptibility.

After finishing the SSRT, the fracture surfaces of the tested specimens were ultrasonically cleaned in acetone and then examined with a FE-SEM.

### 3. Results and discussion

Table 2 shows the summary of the SSRT results. Fig 1 and 2 display the stress-elongation curves for the test no.1, 2 and 3, and the test no.5, 8 and 9, respectively, of which fracture elongations are listed in Table 2. The  $\delta f_{\text{immune}}$ , the fracture elongation in the dry-air measured 16.9mm. All the fracture surfaces of the tested specimens, except those in the dry-air, show a transgranular creaking feature. Each Iscc in Table 2 was calculated from the  $\delta f_{\text{SCC}}$  and the  $\delta f_{\text{immune}}$  according to the equation (1). As clearly shown in Fig.1, the fracture elongation,  $\delta f_{\text{SCC}}$  was decreased with the increase in the oxygen partial-pressure of the gas that had been introduced in the cell.

As listed in Table 2, the  $\delta f_{\text{SCC}}$  as well as the ISCC for the test no.4 and 5 are smaller than those for test no.1. These results indicate the presence of the copper ions, regardless of cuprous or cupric, markedly increase the specimen's SCC susceptibility. It is worth of note that the ISCC for the test no.4 and 5 is smaller than that for the test no.2. The vacuum evaporation process is wholly employed for modern salt production systems, so that the dissolved-oxygen concentration in the actual process solutions is estimated much lower than those being exposed to the 10vol%O<sub>2</sub>-Ar mixture gas. These results suggest that the existence of the copper ions, of which concentration is as low as 10mg/L, might give a considerable effect to the SCC susceptibility of austenitic SS used in the salt production facilities.

The ISCC for the test no.6 and 8 are greater than those for the test no.1, as shown in Table

2. The results indicate the addition of nickel or zinc ions decreases the SCC susceptibility, so their existence in the solutions causes a preferable effect to prevent SCC. However, when the cupric ions were simultaneously added with the nickel or the zinc ions, for the test no.7 and 9 in Table 2, the preferable effects that were seen in the nickel or the zinc ions solely added were greatly inhibited. ISCC of test No.7, added 10mg/L of cupric and nickel ions simultaneously, was as low as 11.3. The value is less than that for test No.3, which was carried out in the solution exposed to pure-oxygen gas, or equivalently, the coexistence of cupric and nickel ions would significantly promotes the SCC susceptibility of austenitic SS in the concentrated-brine.

### 4. Conclusion

The effect of a small amount of copper ions as well as nickel and zinc ions to the SCC susceptibility of austenitic SS was evaluated in a simulated concentrated-brine at  $100^\circ\text{C}$ . Solution-annealed type-304 SS was employed for the specimen. The SCC susceptibility of the specimen in each environment was evaluated from the fracture elongation obtained by SSRT.

- (1) It was confirmed that the existence of a small concentration of copper ions as low as 10mg/L, regardless of cupric or cuprous, greatly increased the SCC susceptibility.
- (2) The SCC susceptibility was reduced when 10mg/L of nickel or zinc ions were solely added to the base solution.
- (3) The coexistence of 10mg/L of cupric and nickel ions greatly increased the SCC susceptibility. The degree of the susceptibility was higher than that for the solution being exposed pure-oxygen gas.

### Acknowledgement

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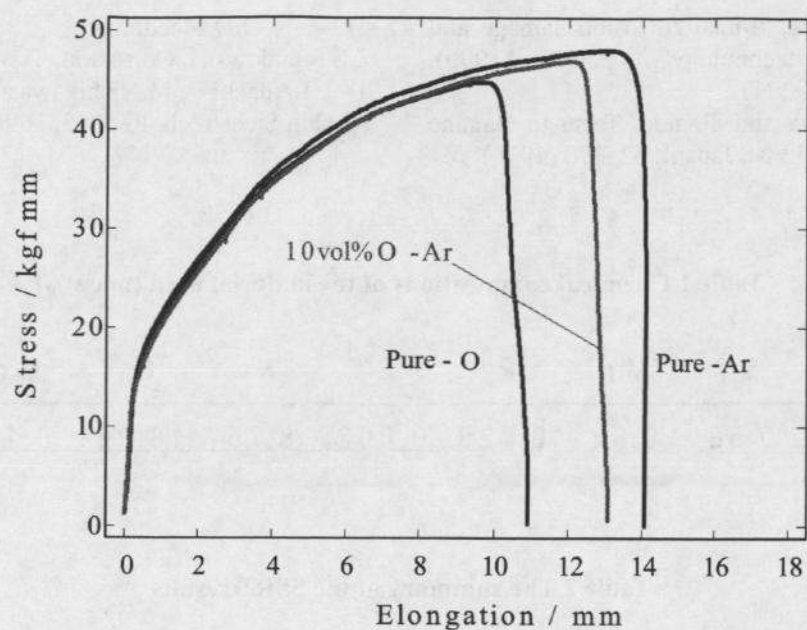
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**Table 1 Chemical compositions of the material used (mass%)**

C	Si	Mn	P	S	Ni	Cr	Mo	Cu
0.066	0.58	0.82	0.029	0.002	8.75	18.29	0.14	0.14

**Table 2 The summary of the SSRT results**

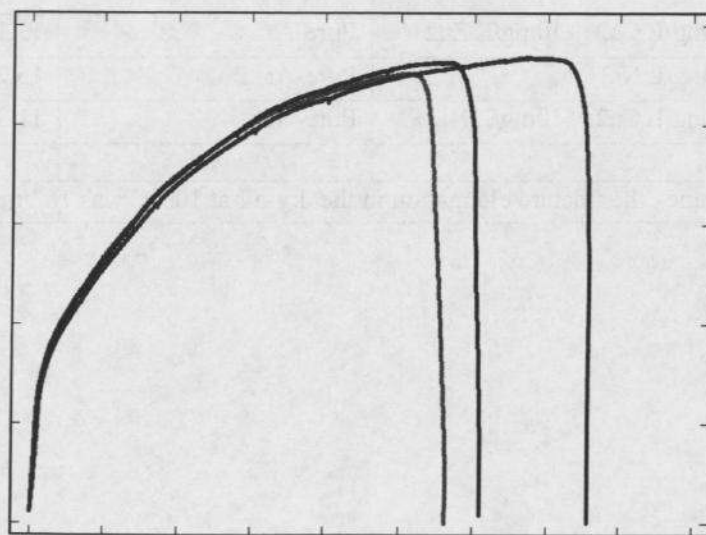
test No.	Added metal ions	gas exposed to the solution	$\delta f, SCC$ / mm	ISCC
1	-	Pure-Ar	14.1	0.83
2	-	10%O <sub>2</sub> -Ar	13.1	0.78
3	-	Pure-O <sub>2</sub>	10.9	0.64
4	10mg/L Cu <sup>+</sup>	Pure-Ar	12.8	0.76
5	10mg/L Cu <sup>2+</sup>	Pure-Ar	12.3	0.73
6	10mg/L Zn <sup>2+</sup>	Pure-Ar	15.3	0.91
7	10mg/L Cu <sup>2+</sup> +10mg/L Zn <sup>2+</sup>	Pure-Ar	13.1	0.78
8	10mg/L Ni <sup>2+</sup>	Pure-Ar	15.2	0.90
9	10mg/L Cu <sup>2+</sup> +10mg/L Ni <sup>2+</sup>	Pure-Ar	11.3	0.67
The $\delta f, immune$ , the fracture elongation in the dry-air at 100°C was 16.9mm.				



**Fig.1 Change in the stress-elongation curves with the oxygen partial**

pressure of the gases that were exposed to the solution. The simulated concentrated-brine was used for the solution and its temperature

was controlled at 100°C through the experiments.



**Fig.2 Effect of the cupric and the nickel ions to the stress-elongation curves, which were added to the simulated concentrated-brine.**

The solution was exposed pure-Ar gas and its temperature was kept at 100°C through the experiments.