Stress Corrosion Cracking of Type 304 Stainless Steel in Sulfuric Acid Solutions Containing Cyanide or Thiocyanate*

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Behavior of stressed Type 304 steel in H₂SO₄ solutions with addition of cyanide or thiocyanate has been studied in view of the reported strong adsorption characteristics of these species. Annealed Type 304 wire was examined at 353 K in 1 to 4 kmol/m³ H₂SO₄ solutions with additions of different quantities of KCN, NH₄SCN, or NaN₃ (pseudohalides) mainly under open circuit conditions at a stress of 275 MPa.

With increased additions of KCN or NH₄SCN the attack morphology changed from heavy general corrosion to cracking or localized attack and the time or fracture was prolonged. KCN was a cathodic and anodic inhibitor and NH₄SCN was a cathodic inhibitor. The latter was also an anodic inhibitor at and near the open circuit potential. In the solutions containing NaN₃ Type 304 did not fail due to passivation resulting from the cathodic reaction stimulated by NaN₃ or fractured by general corrosion at the small addition of NaN₃.

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I. Introduction

In cyanide solutions, stress corrosion cracking (SCC) occurs in mild steel¹(²) and in a NH₄SCN solution, SCC also occurs in high carbon steel³, high manganese steel³, and austenitic stainless steels (Type 304 and 316 aged at 773 K)⁴. It was also reported⁵ that H₂SO₄ solutions containing NH₄SCN caused (transgranular) SCC in 25Cr-14Ni stainless steel.

Cyanide and NH₄SCN are pseudohalides, the chemical behavior of which is generally like that of halides as is well known. CN⁻ ion is very strongly adsorbed at active sites of the steel surface in its solutions⁶ and SCN⁻ ion or NCS⁻ ligands of various isothiocyanatochromium (III) complex ions are also adsorbed on the Hg surface from their solutions⁷.

The relative adsorptivity of anions on the Pt surface from their potassium salt solutions increases in increasing order of Cl⁻ < Br⁻ < I⁻ < SCN⁻ (⁸) and when these anions are characterized as the bases in the hard and soft acids and bases principle, the above order is the same as that⁹ of their softness. CN⁻ ion is softer than SCN⁻ ion⁹ and this may account for the reported strong adsorption of CN⁻ on the steel surface. Halide ions, which have also adsorptivity, cause SCC in Type 304 steel corroding in H₂SO₄ solutions¹⁰; hence, the reported SCC of 25Cr-14Ni steel may be similar to that of Type 304 steel in H₂SO₄-halide solutions in mechanism.

This paper deals the effects of additions of cyanide, thiocyanate, or azide (which is also a pseudohalide) on the behavior of Type 304 steel stressed in H₂SO₄ solutions. Cracks or localized attack under applied stress were observed when corrosion of Type 304 steel was suppressed by cyanide or thiocyanate additions.

II. Experimental

Type 304 wires of 1 mm diameter from different charges (charge marks, DR81 and 5H) were used. Their chemical compositions

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and mechanical properties are given in Table 1. The specimens were solution annealed at 1373 K for 900 s in argon gas and quenched in flowing argon at room temperature. The solutions used were 1 to 4 kmol/m$^3$ H$_2$SO$_4$ with additions of KCN, NH$_4$SCN, or NaN$_3$ in amounts of 10 to 50 moles, 1 to 50 moles, or 10 to 100 moles per 1 m$^3$ H$_2$SO$_4$ solution, respectively. Although part of KCN was consumed as HCN gas and part of NH$_4$SCN decomposed into NH$_3$, SCO, CO$_2$, and H$_2$S because of its hydrolysis$^{(11)}$$^{(12)}$, the effects of the pseudohalides on SCC were evaluated in terms of their quantities added to solutions (for example, 10 mol/m$^3$ KCN). Water used for test solutions was purified by an ion exchanger and its resistivity was greater than 50 k$\Omega$·m.

Before tests the specimens were abraded with an emery paper (JIS No. 400), followed by cleaning with petroleum benzine. The testing unit for SCC allowed tests on wires stressed in tension and immersed in hot solutions. The wire passed through the unit, being fixed to a frame at the upper end and loaded by means of a weight-carrying lever at the lower end. The unit consisted of a small vertical electric furnace and a glass tube container (15 mm diameter and 90 mm long) with a rubber plug at the bottom. Test solution was contained in the tube, which was held in the furnace and covered with chemical film at the top. The upper part of the tube was left in the air as a condenser.

The tests were conducted under a constant load of 216 N (initial stress of 275 MPa) at a temperature of 353 K and, except otherwise noted, at open circuit conditions. The stress value was equivalent to 46.1% and 44.1% of the ultimate tensile strength of DR81 and of 5H, respectively. Attack morphology after the test was examined and when fracture occurred within test duration, time to fracture ($t_f$) was recorded.

To examine the dependence of corrosion rates on the pseudohalide additions, potentiostatic polarization curves of unstressed specimens were measured in solutions at the same temperature as that for SCC tests. The potential was swept at a rate of 10 mV/(15 s) in the noble and less noble directions from corrosion potential ($E_{corr}$). All the potentials were determined and reported to the saturated calomel electrode (SCE).

### III. Results and Discussion

#### 1. Effects of KCN

Results of SCC tests in solutions with KCN are shown in Fig. 1. The specimens used were DR81. In the case of 1 kmol/m$^3$ H$_2$SO$_4$–KCN solutions, cracks were observed at 10 and 40 mol/m$^3$ KCN but no fracture occurred within the test times (120.3 ks and 113.7 ks, respectively). In 2 kmol/m$^3$ H$_2$SO$_4$ solutions containing KCN within 20 mol/m$^3$, the wires frac-

![Fig. 1 SCC test results of Type 304 (DR81) in H$_2$SO$_4$ solutions with KCN at an applied stress of 275 MPa at 353 K. Closed circle, general corrosion; Open circle, cracking; Circle with an oblique line, localized attack (trenches). Numerals in the Figure represent time to fracture (ks).](image-url)
tured because of thinning by general corrosion in a short time (within 15.7 ks). Cracks, however, occurred in the case of 30 mol/m³ and more KCN, where \( t_f \)'s were 35.3 ks for 30 mol/m³ KCN and longer than 90 ks for 50 kmol/m³ KCN. At high concentrations both of H₂SO₄ (3 and 4 kmol/m³) and of KCN (50 mol/m³), trenches occurred and \( t_f \)'s were relatively short (7.2 and 14.2 ks). Amounts of KCN addition necessary for cracking or trenching increased with increasing H₂SO₄ concentration.

Figure 2 shows the form of attack in 1 kmol/m³ H₂SO₄-40 mol/m³ KCN solution, which is like attack in H₂SO₄-NaI solutions. Paths of the attack are inter- and transgranular but the latter seems to be prevailing. The trenches in 3 kmol/m³ H₂SO₄-50 mol/m³ KCN solution are given in Fig. 3. These were not observed in the unstressed specimen immersed in the same solutions and applied stress was requisite for this attack.

The effects of KCN addition on polarization curves in 2 kmol/m³ H₂SO₄ solution are shown in Fig. 4. The addition (30 mol/m³) decreased the rate of anodic and cathodic reactions markedly at potentials below \(-0.21\) V and the corrosion current density \( (i_{corr}) \) decreased from 240 to 6 A/m², which was 1/40 of its original value. In general, CN⁻ ions are strongly adsorbed on the metal surface as mentioned before; however, most of KCN should change into HCN gas in strong acid test solutions of 1, 2 and 4 kmol/m³ H₂SO₄ (pH values are 0.08,
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In fact, HCN gas evolution was observed when KCN was added. Remaining HCN concentration in 2 kmol/m³ H₂SO₄-30 mol/m³ KCN solution was measured by AgNO₃ titration after the HCN was fixed by addition of alkali. The measured values were 10 mol/m³ immediately after addition of KCN at room temperature, equivalent to 1/3 of the added amount, and 4.6 mol/m³ after 1.8 ks of heating at SCC test temperature (353 K).

To estimate CN⁻ ion concentration, equilibrium concentration ratio of CN⁻ ion to remaining HCN, [CN⁻]/[HCN], is calculated from the following equation:

\[ \log \left( \frac{[CN^-]}{[HCN]} \right) = pH - pK_a \]

where, pK_a is the exponent of the acid dissociation constant of HCN, 9.36 at 293 K(14). In 2 kmol/m³ H₂SO₄ solution, for example, the calculated ratio was 2.19×10⁻¹⁰, which is nearly nil. Still, CN⁻ ligand of HCN is a soft base and must be chemisorbed to the metal surface (a soft acid) dissociating H⁺ ion (a hard acid). It follows that KCN addition acts as an anodic and cathodic inhibitor in test solutions.

Constant potential SCC tests with steel 5H were conducted in 2 kmol/m³ H₂SO₄-30 mol/m³ solution. The results are given in Fig. 5. Attack like cracks occurred at and near \( E_{corr} \).

(Th effect of the potential on \( t_f \) was not clear.) At less noble potentials (-0.44 and -0.48 V), specimens fractured owing to general corrosion, where \( t_f \)'s were relatively short, although the reason could not be understood. Attack morphology at -0.40 V is shown in Fig. 6. There are (a) a crack having crystallographically oriented paths, and (b) wide attack perhaps resulting from joining of the cracks like (a).

2. Effects of NH₄SCN

Steel DR81 was used for SCC tests in solutions with NH₄SCN. Cracking occurred in the following solutions: 2 kmol/m³ H₂SO₄-2 mol/m³ NH₄SCN, 3.2 to 3.5 kmol/m³ H₂SO₄-2 to 4 mol/m³ NH₄SCN, and 4 kmol/m³ H₂SO₄-4 to 10 mol/m³ NH₄SCN solutions, as shown in Fig. 7. At NH₄SCN concentrations less than the above values, specimens fractured...
due to thinning by general corrosion in relatively short times; above those concentrations, specimens corroded a little and no cracking occurred within the prolonged times shown in the figure.

The mode of attack and \( t_f \), as stated above, changed with \( \text{NH}_4\text{SCN} \) additions and patterns of the changes are like those in the case of Type 304 (DR81) in \( \text{H}_2\text{SO}_4\)-KCN solutions found in the present study and of Type 304 steel in \( \text{H}_2\text{SO}_4\)-NaCl solutions\(^{(15)}\). The concentration of \( \text{NH}_4\text{SCN} \) needed for cracking are smaller than those of KCN. Crack morphology in 4 kmol/m\(^3\) \( \text{H}_2\text{SO}_4 \) solutions with 10, 50, or 100 mol/m\(^3\) \( \text{NH}_4\text{SCN} \) is given in Fig. 8(a)–(b): dissolution within the metal was accelerated at 10 mol/m\(^3\) (a); cracks were not sharp and had preferential paths along the grain boundaries at 50 mol/m\(^3\), (b); attack was blunt at 100 mol/m\(^3\) \( \text{NH}_4\text{SCN} \), (c).

The effect of \( \text{NH}_4\text{SCN} \) addition on cathodic and anodic polarization curves in 4 kmol/m\(^3\) \( \text{H}_2\text{SO}_4 \) solutions is illustrated in Fig. 9. The addition (10 mol/m\(^3\)) decreased the cathodic current density, and did not change the apparent

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**Fig. 7** SCC test results of Type 304 (DR81) in \( \text{H}_2\text{SO}_4 \) solutions with \( \text{NH}_4\text{SCN} \) at an applied stress of 275 MPa at 353 K.

**Fig. 8** Microscopic morphology of Type 304 (DR81) in 4 kmol/m\(^3\) \( \text{H}_2\text{SO}_4 \) solutions with \( \text{NH}_4\text{SCN} \). (a) 10 mol/m\(^3\) \( \text{NH}_4\text{SCN} \), (b) 50 mol/m\(^3\) \( \text{NH}_4\text{SCN} \), and (c) 100 mol/m\(^3\) \( \text{NH}_4\text{SCN} \).
anodic current density at potentials below $-0.33\, \text{V}$. However, the true anodic current density must have decreased at those potentials in view of the decrease in the cathodic current density. Accordingly, $i_{\text{corr}}$ decreased from 600 to 5 A/m$^2$ and the corresponding $t_f$ was short, 6.2 ks (Fig. 7).

Concentration ratios $[\text{SCN}^-]/[\text{HSCN}]$ calculated from the $pK_a$ value of HSCN, 0.96$^{14}$, were 0.02 and 0.11 in 2 and 4 kmol/m$^3$ H$_2$SO$_4$ solutions, respectively. This indicates that appreciable amounts of SCN$^-$ ions existed in these solutions and the ions acted as inhibitor. However, part of HSCN in the solution would dissociate to H$_2$S etc., as stated before. To confirm the formation of H$_2$S, 2 kmol/m$^3$ H$_2$SO$_4$-30 mol/m$^3$ NH$_4$SCN solution at 353 K was examined with filter papers wetted with Pb(NO$_3$)$_2$ solution or with (NH$_4$)$_2$MoO$_4$-NaSCN-HCl solution. Each paper became black, the color of PbS, or red, that of thiocyanatomolybdenum complex, demonstrating the H$_2$S evolution from the solution.

SCC tests at constant potentials were made with steel 5H in 4 kmol/m$^3$ H$_2$SO$_4$-50 mol/m$^3$ NH$_4$SCN solution (Fig. 10). Cracking occurred at $-0.34\, \text{V}$, which was within the range of the change in $E_{\text{corr}}$. At slightly more anodic potentials ($-0.32$ and $-0.30\, \text{V}$, where anodic current densities were high), specimens fractured through uneven general corrosion in shorter times. At and near the active-passive transition potentials ($-0.11$, $-0.10$ and $-0.07\, \text{V}$), fracture due to general corrosion occurred.

In solutions containing NaSCN instead of NH$_4$SCN, cracking also occurred. This shows that the presence of NH$_4^+$ ion is not essential to cracking.

### 3. Effects of NaN$_3$

The results of steel 5H in solutions containing NaN$_3$ are shown in Fig. 11. Neither cracking nor localized attack was observed. The specimen exhibited either general corrosion or passive state according as an amount of NaN$_3$ addition was small or large.

Polarization curves in 2 kmol/m$^3$ H$_2$SO$_4$-0, 10, or 50 mol/m$^3$ NaN$_3$ solutions are shown in Fig. 12. Anodic and cathodic current densities increased through an addition of 10 mol/m$^3$ NaN$_3$. With 50 mol/m$^3$ NaN$_3$, cathodic current density so much increased that a loop of a cathodic curve appeared at potentials between $-0.18$ and $0.02\, \text{V}$. Intermittent gas evolution was observed on the metal surface in this solution; the steel exhibited active or passive states alternately for every several minutes at the early stage of immersion, which were followed by passive state. This phenomenon was also observed in the following solutions: 2 kmol/m$^3$ H$_2$SO$_4$-20 or 30 mol/m$^3$ NaN$_3$, 3 kmol/m$^3$ H$_2$SO$_4$-50 mol/m$^3$ NaN$_3$, and 4 kmol/m$^3$ H$_2$SO$_4$-50 or 100 mol/m$^3$ NaN$_3$. The ac-
The accelerating effect of NaN₃ on cathodic reaction is not fully understood, but NaN₃ may catalyze the following reactions: $2\text{HN}_3^- - 2e^- \rightarrow 2\text{HN}^-$, $2\text{HN}^- \rightarrow \text{H}_2 + 2\text{N}^-$, $\text{N}^- + \text{H}^+ \rightarrow \text{HN}_3$ as in the case of H₂S on steels in acid solution(16).

HN₃ is a considerably weak acid ($pK_a = 4.70(14)$) and its boiling temperature is 310K(17). Therefore, most of HN₃ would escape from the test solutions, although no gas evolution was visible. N⁻ ion in the capacity of the base is harder than CN⁻ or SCN⁻ ion(9) and azido complex ion does not adsorbed on the Hg surface in its solutions(7). In view of these facts, N⁻ ion or ligand of remaining HN₃ would be difficult to adsorb on the metal surface.

The results in the present work indicate that cracking and localized attack (due to stress) occur when $i_{corr}$ decreases considerably (for example, by a factor of 40 or 120) as a result of decreases both in the anodic current density near $E_{corr}$ and in the cathodic current density owing to KCN or NH₄SCN additions. This inhibitive action of the additives can be explained in terms of the softness of these pseudohalide anions as the bases, their adsorption on the metal surface, and the formation of corrosion product complexes that act as protective layers. As expected at the beginning of this study, the occurrence of SCC at decreased corrosion rates is similar to that of SCC of Type 304 steel in H₂SO₄-halide solutions(10)(13)(15).

According to the experiments with Fe in H₂SO₄-KI solutions by Tomashov and Ver- skinina(18), cathodic and anodic current densities increased when the metal surface was renewed by abrading; with vigorous abrading $i_{corr}$ increased by a factor of 63, where the anodic current density was the same as that in solution without KI. Inhibitive action of I⁻ ion for anodic dissolution disappears on the renewed surface. This suggests that, for the present SCC, anodic dissolution at the tips of the crack or of the localized attack may be accelerated by the loss of the inhibitive function of CN⁻ or SCN⁻ ions.

IV. Conclusions

Stress corrosion cracking tests with Type 304 steel in 1 to 4 kmol/m³ H₂SO₄ solutions with additions of KCN, NH₄ SCN, or NaN₃ were conducted at a stress of 275 MPa at 353 K and mainly at corrosion potentials. The following conclusions could be drawn from the present work:

1. Localized attack due to stress or SCC occurred in solutions with additions of KCN or NH₄SCN. They were the inter- and transgranular cracks or the attack like trenches in the case of KCN, and the inter- and transgranular cracks in the case of NH₄SCN. In solutions with NaN₃, general corrosion or the passive state occurred depending on whether the NaN₃ addition was small or large.

2. With increased amounts of KCN or of...
NH₄SCN, the attack changed from general corrosion to cracking or to the localized attack and the time to fracture increased.

(3) Corrosion current densities decreased by KCN or NH₄SCN additions (for instance, by a factor of 40 or 120 respectively). This inhibitive action of CN⁻ and SCN⁻ ions could be interpreted in terms of their softness as bases. A large quantity of NaN₃ was a strong activator of the cathodic reaction and led the metal to passive state.

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