Technical Report

Corrosion Resistance of Sn-added Stainless Steels

Nobuhiko HIRAIDE* Shunji SAKAMOTO Hiroyuki MATSUYAMA Haruhiko KAJIMURA

Abstract

The effect of Sn alloying on the corrosion resistance of ferritic stainless steels in sulfuric acid solutions and under a chloride environment was investigated. The addition of Sn was effective in decreasing the corrosion rate in sulfuric acid solutions. Electrochemical measurements have revealed that Sn has an anodic dissolution inhibiting effect and that this effect is due to the action of Sn^{2+} ions. Similar to the sulfuric acid environment, Sn was an effective alloying element for suppressing the anodic dissolution in the acidic chloride environment assuming the inside of the pit and the crevice. The maximum corrosion depths decreased after the cyclic corrosion tests, and it was confirmed that Sn is an effective alloying element.

1. Introduction

Stainless steels are alloy steels containing Cr or Cr and Ni in Fe. The former are classified as ferritic and the latter as austenitic. The excellent corrosion resistance of stainless steel is basically assured by the presence of a passive film where Cr is concentrated. If necessary, elements such as Ni and Mo are added to improve the corrosion resistance. Because stainless steels have necessary properties such as strength, formability, and weldability, they are widely used in home appliances, kitchen utensils, transport equipment, and various plant equipment. Thus they are indispensable materials for our life today. Among the stainless steels, ferritic stainless steels have price advantage and a small coefficient of thermal expansion. They are hence extensively used in electric home appliances, kitchen products, automobile exhaust system members, building exterior members, water storage tanks, and many other applications. The corrosion resistance of ferritic stainless steels is generally improved by increasing the Cr content and adding Mo. These two elements are rare metals. We thought that if Cr and Mo were replaced by other elements from the standpoint of resource conservation, the superiority of ferritic stainless steels would improve. Therefore, we focused on the Sn and clarified the mechanism for the Sn to improve the corrosion resistance of ferritic stainless steels. The results achieved are described here.¹⁻³⁾

For the corrosion resistance of Sn-added stainless steels, many studies are published on the corrosion resistance of austenitic stainless steels used in non-oxidizing acid environments such as sulfuric acid. These studies show that the Sn is effective in inhibiting general corrosion.⁴⁻¹²⁾ Here, both the cathodic and anodic effects of the Sn are shown, such as suppression of cathodic reactions^{5,6)} and reduction of the critical passivation current density $I_{\rm crit}$ ^{7,8)} The effects similar to those for austenitic stainless steel have been confirmed for the Sn in duplex stainless steels,¹³⁾ martensitic stainless steels,¹⁴⁾ and pure iron.¹⁵⁾ Detailed studies are not available on the effect of the Sn in ferritic stainless steels. The corrosion mechanism of coating defects on steels in atmospheric corrosion environments in the presence of chloride has been investigated in detail, and the Sn-added steel CORSPACETM has been developed.¹⁶⁻¹⁹⁾

In neutral chloride environments typified by atmospheric corrosion environments, stainless steels may develop local corrosion such as pitting and crevice corrosion. The anode part where corrosion has occurred, such as inside the pit, becomes an acidic environment where the pH is reduced. We thought that if we were able to clarify the effect of the Sn in providing the corrosion resistance of ferritic stainless steels in an acidic environment such as sulfuric acid and the mechanism involved, we could apply the mechanism to pitting and crevice corrosion.

2. Effect of Sn Addition on Corrosion Resistance 2.1 Electrochemical properties of Sn

Sn is well known as an alloy such as solder or bronze. It does not rust easily in a neutral environment and is one of the relatively familiar metals singly used for tableware, for example.

Figure 1 shows the potential-pH diagram for the $Sn-H_2O$ system.²⁰⁾ In general, Sn has valences of +2 and +4. The Sn^{2+} and Sn^{4+}

^{*} Group Manager, Dr. Eng., Solution Development Dept., Research & Development Center, Nippon Steel Stainless Steel Corporation 3434 Ooaza-shimata, Hikari City, Yamaguchi Pref. 743-8550

ions are stable in an acidic environment. SnO₂ is stable in a neutral environment. The region where the Sn⁴⁺ ions are stable is wider than the region where the Sn²⁺ ions are stable. When the potential-pH diagram of the Sn-H₂O system is compared with that of the Fe-H₂O system, it is evident that the equilibrium potential of the Sn/Sn²⁺ is higher than that of the Fe/Fe²⁺ and indicates a region where the Fe²⁺ ions are stable. This suggests the possibility that when the steel is actively dissolved, the Sn may be involved in either the metal Sn state or the Sn²⁺ ion state in the active dissolution of the steel.

2.2 Effect of Sn addition on corrosion resistance in sulfuric acid Figure 2 shows the effect of the Sn content on the corrosion rate of the 14Cr ferritic stainless steel in an aqueous solution of H₂SO₄ at a pH of 0.^{1,3)} All the test specimens were totally corroded, but it was confirmed that a Sn addition of 0.1 mass% more clearly reduced the corrosion rate in the sulfuric acid. Next, the effect of the Sn²⁺ ion concentration on the corrosion rate in a 5 mass% H₂SO₄ aqueous solution was investigated by using a Sn-free 14Cr steel.^{2,3)} The results are shown in Fig. 3.³⁾ The addition of Sn²⁺ ions reduced the corrosion rate. At a Sn²⁺ ion concentration of 10⁻² mol·1⁻¹, the surfaces of the specimens after the test retained a metallic luster. When the surfaces of the specimens after the test were analyzed by Auger electron spectroscopy (AES), the Sn was detected in a cation fraction of about 30 at%. This suggests that the Sn²⁺ ions adsorb on the surface and improve the corrosion resistance.

The polarization curves of Sn-added 14Cr steels measured in a 5



Fig. 1 Potential-pH diagram for Sn-H₂O (soluble metallic ion: 10⁻⁶ mol·I⁻¹)



Fig. 2 Effect of Sn content on corrosion rate in H₂SO₄ solution³⁾

mass% H₂SO₄ aqueous solution are shown in Fig. 4.^{1,3)} In the 0.1Sn steel, the active state is divided into two. The anodic current density on the less noble side greatly decreased as compared with the Snfree steel. The maximum anodic current density on the more noble side, that is, the critical passivation current density $I_{\rm crit}$, also declined. In the 0.5Sn steel, the anodic current density in the active state on the less noble side was further reduced, and a cathode loop was observed. The maximum anodic current density on the more noble side increased from that of the 0.1Sn steel, and the critical passivation potential also shifted to the more noble side. As described above, the addition of the Sn was found to inhibit the anodic dissolution near the corrosion potential $E_{\rm corr}$. The effect of the $\rm Sn^{2+}$ ion concentration on the polarization curve in a 5 mass% H₂SO₄ aqueous solution was investigated by using the Sn-free 14Cr steel as in the immersion test.^{2,3}) Figure 5 shows the cathodic current density at -0.3 V (versus the standard hydrogen electrode (SHE) here and hereinafter) for the cathodic polarization curve and the maximum anodic current density for the anodic polarization curve, both with respect to the Sn²⁺ ion concentration. The addition of the Sn²⁺ ions decreased both the cathodic current density and the maximum anodic current density. It was found that the Sn²⁺ ions were effective in suppressing both the cathodic and the anodic reactions.

The Sn was investigated for its effect on the polarization curves of the 14Cr steels in Na_2SO_4 aqueous solutions with a slightly high pH range of 0.5 to 2 in similar acidic environments, following the H_2SO_4 aqueous solutions.³⁾ Because the active state was divided into two in the same way as shown in Fig. 4, the effects of the Sn on the



Fig. 3 Effect of Sn²⁺ concentration in H₂SO₄ solutions on corrosion rate³⁾



Fig. 4 Effect of Sn on polarization curves in H₂SO₄ solutions³⁾





Fig. 6 Effect of Sn content on polarization curves in acidic Na2SO4 solutions

maximum anodic current density on the less noble side (first) and the more noble side (second) were organized. The results are shown in Fig. 6. The second maximum anodic current density at a pH of 0.5 increased in the 0.5Sn steel but decreased with the increase in Sn content at the other pH values. This revealed that the Sn has the effect of inhibiting the anodic dissolution in an acidic sulfuric acid environment with a wider pH range. Next, we investigated the potential range in which the anodic dissolution inhibiting effect appeared in Na₂SO₄ aqueous solutions with a pH range of 0.5 to 2. The difference in the anodic current value between the 0.1Sn steel and the Snfree steel was calculated in a pH range of 0.5 to 2. Then, the lower limit potential E_1 and the upper limit potential E_h at which this difference became 1 mA·cm⁻² or more were obtained. The results are shown in Fig. 7.³⁾ The thermodynamically stable ranges of Sn²⁺ ions are shown for the two cases where the Sn²⁺ ion concentration is 10⁻⁵ mol·l⁻¹ and 10⁻⁴ mol·l⁻¹, respectively.²⁰⁾ As shown in Fig. 7, the range in which the current value difference becomes 1 mA·cm⁻² or more, that is, the range in which the anodic dissolution inhibiting effect is high, corresponds well with the range in which the Sn²⁺ ions are stable. Here, the mechanism called "under-potential deposition (UPD)" where the Sn precipitates at a potential more noble than the equilibrium potential precipitates can be cited as the dissolution inhibiting mechanism by the Sn.²¹⁻²³⁾ The UPD mechanism may also apply to stainless steels. The upper limit potential $E_{\rm h}$ at which a large anodic dissolution inhibiting effect was recognized has a clear pH dependence. The pH dependence is also noted for the lower limit potential E_{i} . This is a characteristic not found in the UPD and suggests that the anodic dissolution inhibiting mechanism involving the



Fig. 7 Effective area of Sn to suppress anodic dissolution in acidic Na₃SO₄ solutions³⁾

Sn²⁺ ions operates in ferritic stainless steels. The anode dissolution is suppressed when the Sn²⁺ ions are added to the H₂SO₄ aqueous solution (Fig. 5) and also when the Sn²⁺ ions are added to the Na₂-SO₄ acidic aqueous solution.^{2,3)} This supports the anodic dissolution inhibiting mechanism involving the Sn²⁺ ions.

To further investigate the anodic dissolution inhibiting mechanism involving the Sn²⁺ ions, we measured the electrochemical impedance. **Figure 8** shows the potentiostatic polarization curve and complex impedance plots of the 0.1Sn steel in a 5 mass% H_2SO_4 aqueous solution.³ **Figure 9** shows the potentiostatic polarization curve and complex impedance plots of the Sn-free 14Cr steel in a 5





Fig. 8 Potentiostatic polarization curve and complex impedance plots of 14Cr-0.1Sn ferritic stainless steel in H₂SO₄ solution³⁾



Fig. 9 Potentiostatic polarization curve and complex impedance plots of 14Cr ferritic stainless steel in 10⁻² mol·l⁻¹ SnSO₄ added H₂SO₄ solution³⁾

mass% H_2SO_4 aqueous solution with 10^{-2} mol·l⁻¹ of Sn²⁺ ions added. The numbers shown in the complex impedance plots are the measurement frequencies. In the case of the 0.1Sn steel, in addition to two capacitive semicircles at -0.178 V (point B), -0.173 V (point C), and -0.163 V (point D), all more noble than the corrosion potential, a clear inductive semicircle is observed at the lower end of the frequency range. When 10^{-2} mol·l⁻¹ of Sn²⁺ ions are added, a capacitive semicircle is recognized at the corrosion potential (point A) and at -0.115 V (point B) and -0.103 V (point C), both more noble than



Fig. 10 Schematic diagram of anodic dissolution inhibiting effect of Sn in sulfuric acid environment

the corrosion potential. A clear inductive semicircle is also observed at the lower end of the frequency range. Here, the inductive semicircle that appeared when 10^{-2} mol·l⁻¹ of Sn²⁺ ions were added is the characteristic to be noted. This suggests the existence of an adsorption process.^{24–28)} **Figure 10** shows a schematic diagram of the anodic dissolution inhibiting effect of the Sn in a sulfuric acid environment as acquired from the above results. It is considered that the Sn added to the stainless steel is dissolved as Sn²⁺ ions by the dissolution of the substrate and that the Sn chemical species derived from the Sn²⁺ ions are adsorbed on the surface to suppress the anodic dissolution.

As shown in Fig. 5, the Sn^{2+} ions are effective in inhibiting the cathodic reaction in the H_2SO_4 aqueous solution. It is therefore considered that as the Sn inhibited both anodic and cathodic reactions, the corrosion rate decreased in the H_2SO_4 aqueous solution.

2.3 Effect of Sn addition in chloride environment

Corroded pits and crevices in a neutral chloride environment as exemplified by an atmospheric corrosion environment present an acidic chloride environment where the pH is lowered. We therefore investigated the effect of the Sn by electrochemical measurement in an acidic chloride environment as in a sulfuric acid environment.

Using the 14Cr ferritic stainless steels in the same way as described in the previous section, we measured anodic polarization curves in 0.36%, 3.6%, and 18% NaCl aqueous solutions with the pH adjusted to 1 by H_2SO_4 . Because the active state was divided into two as in the sulfuric acid environment, the effects of Sn on the less noble (first) and more noble (second) maximum anodic current densities were organized. The results are shown in **Fig. 11**. We found that the maximum anodic current density decreases as the Sn content increases in the acidic chloride environment as in the sulfuric acid environment. This finding indicates that the Sn is effective in inhibiting the dissolution in pits and crevices and is expected to reduce the corrosion depth as well.

We then investigated the effect of the Sn on the 13Cr ferritic stainless steels by cyclic corrosion testing. The specimens were initially heat treated at 673 K for 8 h and then cyclic corrosion tested for 100 cycles in accordance with the Japanese Automotive Standards Organization Standard JASOM 611-92. As evident from Fig. 12, the maximum corrosion depth decreased as the Sn content increased, thereby confirming the effectiveness of the Sn in improving the corrosion resistance in neutral chloride environments.

3. Conclusions

We investigated the effect of the Sn on the corrosion resistance of the 14Cr ferritic stainless steels in sulfuric acid environments and chloride environments.

The addition of the Sn to the steel reduces the corrosion rate of the steel in a sulfuric acid environment. Electrochemical measurements revealed that the Sn is effective in inhibiting the anodic disso-



Fig. 11 Effect of Sn content on polarization curves in acidic NaCl solutions



Fig. 12 Effect of Sn content on maximum corrosion depths after cyclic corrosion tests

lution and that the potential range where the Sn proves effective is the thermodynamically stable range of Sn^{2+} ions. We considered that Sn in the steel is dissolved as Sn^{2+} ions by the dissolution of the substrate and that the Sn chemical species derived from the Sn^{2+} ions are adsorbed on the surface to suppress the active dissolution.

The Sn exhibited the anodic dissolution inhibiting effect in an acidic chloride environment simulating the inside of pits or crevices in the same way as in a sulfuric acid environment. Also, the Sn reduced the maximum corrosion depth in cycle corrosion testing in a neutral chloride environment. We thus confirmed the Sn as an alloying element effective in improving the perforation resistance.

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Nobuhiko HIRAIDE Group Manager, Dr. Eng. Solution Development Dept. Research & Development Center Nippon Steel Stainless Steel Corporation 3434 Ooaza-shimata, Hikari City, Yamaguchi Pref. 743-8550

Hi Se Co Pr Ni

Hiroyuki MATSUYAMA Senior Manager Coil & Sheet Products Development Gr. Products Development Div. Nippon Steel Stainless Steel Corporation



Shunji SAKAMOTO Specialized Senior Manager, Dr. Eng. Yawata Unit Nippon Steel Technology Co., Ltd.



Haruhiko KAJIMURA Senior Fellow, Dr. Eng. Research & Development Center Nippon Steel Stainless Steel Corporation