

Synergy effects of Cu and Sn on pitting corrosion resistance of ultra-purified medium chromium ferritic stainless steel

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Abstract. The influence of combination of Cu and Sn on pitting resistance of ultra-purified medium chromium ferritic stainless steel in 3.5 wt.% NaCl at 25°C was investigated by using electrochemical method. The results show that there is synergy effect between Cu and Sn, and the strong interaction between Cu and Sn in ferritic stainless steels clearly affects their pitting corrosion behaviour in 3.5% NaCl. A mechanism of the synergy of Cu and Sn was discussed.

1. Introduction

As is known to all, Cu and Sn are detrimental to surface quality, hot workability, and low temperature toughness for steels [1-4]. It is very difficult to completely get rid of these tramp elements in steel making [5-7]. Thus, the researchers turn to study their effects on the performance of the steels, attempting to make the full use of their positive effects and to evade their negative ones. There is no doubt about the positive effect of Cu on the general corrosion behaviour of stainless steels in sulphuric acid solutions. The mechanism of beneficial effect of Cu is mainly based on the suppression of anodic dissolution by elemental Cu deposition and other Cu-containing particles on the steel surface [8-10]. Sn can effectively improve general corrosion resistance in H_2SO_4 , mainly due to both highly improved hydrogen evolution overpotential, and inhibitive effect of dissolved Sn^{2+} on elementary anodic reactions [11-12]. The beneficial influence of Sn on the behaviour of stainless steels against pitting corrosion is mainly attributed to the improved firmness or stability of passive film for the presence of SnO_2 , and decreased Fermi energy of steel by Sn addition [13-14].

Regarding the synergy effect of Cu and Sn on the corrosion behaviour of steel, a few researchers have paid some attention to it. Osozawa [15] and Takizawa et al. [16] observed positive synergy of Cu and Sn in austenitic stainless steel in both diluted sulphuric and organic-chlorinated acid mediums. They concluded that the synergy is derived from the formation of a stable film of metallic copper and tin oxides on the steel surface due to preferential dissolution of Cu and Sn. Pardo et al. studied the influence of Cu and Sn on the corrosion behavior of AISI 304 and 316 stainless steels in 30% H_2SO_4 solution, revealed that the corrosion resistance of both steels was greatly improved by positive synergy of Cu and Sn, and that Sn addition reduced the corrosion rate in lower magnitude than Cu addition [17]. It was also found that Cu addition favours pit nucleation but inhibits its growth, whereas Sn exerts the opposite effect, favouring pit growth and inhibiting its nucleation in AISI 304 and 316 in 3.5% NaCl [18].

However, the unified conclusions about the synergy of Cu and Sn on corrosion resistance of ferritic stainless steels have not yet to be reached. This paper attempts to evaluate the effect of the



combination of Cu and Sn on pitting corrosion behaviour of ultra-purified medium chromium ferritic stainless steels in chloride-containing media.

2. Experimental Procedure

2.1. Materials

Table 1 shows the chemical compositions of experimental steels. All specimens in this paper were cut from 2 mm thick cold rolled and annealed sheets.

Table 1. Chemical compositions of the tested steels (wt.%).

| No. | Cu | Sn | Cr | Si | Mn | Nb | Ti | C | N | Fe |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|--------|------|
| A | -- | -- | 16.00 | 0.433 | 0.236 | 0.108 | 0.023 | 0.019 | 0.0032 | Bal. |
| B | 0.243 | 0.220 | 16.50 | 0.500 | 0.250 | 0.160 | 0.070 | 0.006 | 0.0043 | Bal. |
| C | 0.451 | 0.238 | 16.80 | 0.522 | 0.260 | 0.116 | 0.026 | 0.010 | 0.0021 | Bal. |
| D | 0.448 | 0.464 | 16.70 | 0.530 | 0.251 | 0.101 | 0.009 | 0.007 | 0.0030 | Bal. |

2.2. Electrochemical measurements

Specimens cut from cold rolled and annealed sheets were ground into $1 \times 1 \text{ cm}^2$ with a series of SiC grit papers. After pre-passivation in 30 wt.% HNO_3 at 35°C for 30 min, specimens were cold mounted by using epoxy resin, leaving the surface area in the size of $1 \times 1 \text{ cm}^2$. Before the experiments, all the mounted specimens were ground by using 400–1500 SiC grit papers and cleansed with acetone.

Electrochemical tests were carried out in 500 ml 3.5 wt.% NaCl solution using three electrodes electrochemical flat cell, and open to the air at 25°C . Specimens were used as the working electrode, and platinum foil was used as the counter electrode. The reference electrode was a saturated calomel electrode (SCE) connected via a Luggin's capillary, and all potentials in this paper refer to the SCE scale. Cathodic reduction of passive film on working electrodes was performed at -1.5 V for 10 min to remove the possible existing surface film before electrochemical tests. Polarization measurements were carried out at a scan rate of 0.33 mV/s from an initial potential of -150 mV versus open-circuit potential (OCP) to pitting potential (E_{pit}) at which the current density continuously exceeded $10 \mu\text{A}/\text{cm}^2$. In each electrochemical measurement test, five parallel specimens were used to guarantee the reliability and reproducibility of the results.

3. Results and Discussion

Figure 1 shows representative potentiodynamic polarization curves obtained in 3.5 wt.% NaCl solution. As can be seen, all specimens present similar cathodic curves due to the same predominant cathodic half-cell reaction, $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ ($E^\theta \approx 0.157 \text{ V}$), while all the anodic polarization curves exhibit direct passivation after slightly active dissolution, and finally reach different E_{pit} with no apparent active-passive transitions. The E_{pit} values of A, B, C and D specimens are 189 mV, 252 mV, 229 mV and 235 mV respectively.

Figure 2 shows the relation between the contents of Cu, Sn and the E_{pit} of test steels. As compared to the A specimen (without Cu and Sn), E_{pit} values of B, C, and D specimens alloyed with both Cu and Sn, are improved by about 33%, 21%, and 24% respectively, revealing positive effect of Cu + Sn addition on pitting resistance of stainless steels. B specimen presents the highest E_{pit} value indicating the best performance among tested steels. However, it can also be found that with increasing the Cu content nearly two times than that in B specimen, E_{pit} values of both C and D specimens are decreased by about 9.1% and 6.7% respectively. Furthermore, compared with C specimen, E_{pit} of D specimen is slightly improved by increasing Sn content to 0.464 wt%. These interrelated results just indicate that Cu addition reduces E_{pit} value of ferritic stainless steels, while Sn addition can increase E_{pit} value in chloride-containing medium. This paradoxical effects of Cu and Sn are in good agreement with A. Pardo group's research results [18]. Figure 2 also reveals that there is a strong positive synergy between Cu and Sn in corrosion behaviour of ferritic stainless steel in chloride-containing medium.

Nevertheless, additions of Cu and Sn in appropriate proportion can further improve the corrosion resistance of experimental steels, just as B specimen shows in figure 2.

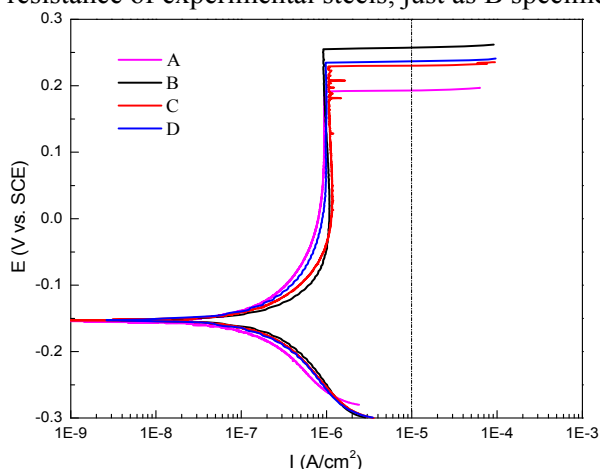


Figure 1. Potentiodynamic polarization curves of experimental ferritic stainless steels in 3.5 wt% NaCl solutions.

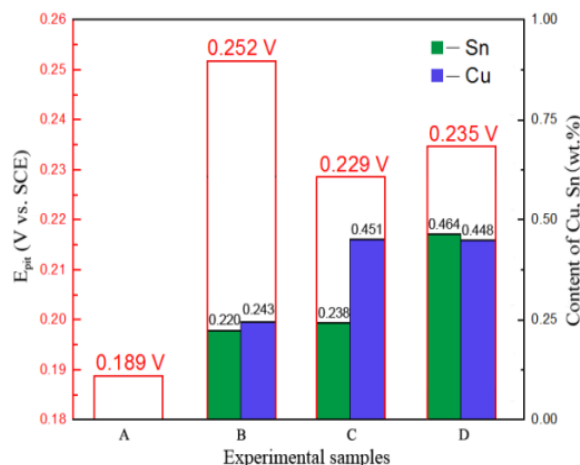


Figure 2. Variation of E_{pit} with Cu, Sn contents in test steels.

Our group has studied the effect of Sn alone on the pitting behaviour of ultra-purified 17% Cr ferritic stainless steel [19]. We found that Sn-bearing 17% Cr ferritic stainless steels can form faster growing and more compact passive films than that in Sn-free steel, probably due to the presence of SnO_2 and Sn in passive film. Nam et al. also concluded that the presence of SnO_2 on the surface of Sn-containing low alloy steel decreases the corrosion rate due to a decrease in anodic reaction kinetics [20]. Furthermore, we also observed that with increasing Sn in 17% Cr ferritic stainless steels, the charge carrier densities (both N_d and N_a) in passive film decrease effectively, with respect to those of Sn-free steel [19]. This beneficial effect of Sn on reducing the charge carrier density of passive film, probably owes to a very wide band gap of SnO_2 ($E_g = 3.6$ eV, at 300 K) detected in passive film, and decreased Fermi energy of steel by Sn addition [13-14]. This mechanism probably explains why E_{pit} values of B, C and D steels increase with increasing Sn, as shown in figure 2.

The beneficial effect of Cu on the corrosion behaviour of stainless steels was explained by the protective effect of Cu redeposition on anodic surface of steels during active dissolution, which improved the corrosion resistance by suppressing active dissolution even in acid chloride media [17]. However, Ujio et al. [10], and some other authors [21-23] concluded that Cu has a harmful effect on the localized corrosion resistance in noble potential range for both ferritic and austenitic stainless steels. According to their research, Cu induced decreasing of E_{pit} is mainly attributed to the fact that ϵ -Cu phases tend to precipitate in grain boundaries and grains of ferritic stainless steels. The solubility of Cu in ferrite was low, about 0.2 wt.%. Thus, with the increasing of Cu content, ϵ -Cu phases might occur at grain boundaries and grains in ferrite stainless steels [24]. The dispersed inclusions of precipitates, such as Cu precipitates and (Nb, Ti)(C, N) precipitates could negatively impair the stability of passive film of stainless steels, and therefore increase the susceptibility of ferrite to the pitting corrosion. This probably explains why E_{pit} values of both C and D steels decrease with further increasing Cu content up to about 0.45 wt.%, as shown in figure 2.

Besides, according to our previous study [19] effects of Sn on pitting corrosion resistance depends on the competitive relationship between beneficial effects and harmful effects of Sn. The excessive addition of Sn (about 0.33 wt%) in 17 wt% Cr ultra-purified ferritic stainless steel may deteriorate the corrosion resistance than good. Sn grain segregations [25-28] over increase of hydrogen evolution overpotential [29-30] and subsequent hydrolysis of Sn^{4+} ions ($\text{Sn}^{4+} + 4\text{H}_2\text{O} \rightarrow \text{Sn}(\text{OH})_4 + 4\text{H}^+$) [31] may accelerate the corrosion of steels. These intensively adverse effects can no longer be counteracted by beneficial roles of Sn. However, as shown in figure 2, the E_{pit} values of experimental steels B, C and D are improved due to Cu addition, indicating that there is indeed a positive synergy between Cu and

Sn. The mechanism of beneficial synergy could be probably attributed to the strong partitioning of large Sn atoms into Cu-rich precipitates. Sha et al. [32] reported that Sn segregates strongly to the precipitate/matrix interface of a large Cu precipitate, and particularly in the region where a dislocation appears to intersect the precipitate in a low-alloy pressure-vessel steel with 0.43 at.% Cu and 0.007 at.% Sn, as shown in figure 3. Liu et al. reported that Sn promotes more and smaller sulfides precipitation at low temperature, and these precipitates bearing Cu and Sn are shown to reduce the micro-segregation degree of Sn in ultra-low carbon steel [33]. Sarafianos found that with the presence of Cu the diffusion range of Sn decreases [34]. Thus, it is reasonable to conclude that Sn diffusion to the precipitate/matrix interface could also reduce the segregation degree of Sn in experimental steels herein. This probably explains why E_{pit} of specimen D (with the highest Sn content) is higher than that of C, and is not decreased for the excessive addition of Sn.

Furthermore, Liu et al. also concluded that the dissolved Sn in sulfide particles segregates to the sulfide/iron interface, and will restrict the growth of sulfide described by Ostwald ripening model [33, 35]. The Sn segregation at the interface can decrease the interfacial energy, and then stabilize small precipitates. This suppression effect of Sn on precipitate size is a much more common case in silicon

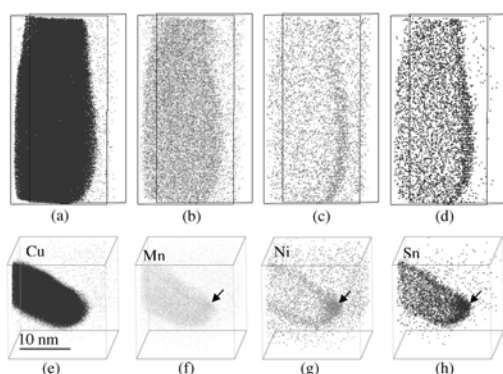


Figure 3. 3DAP maps of a large Cu-rich precipitate aged for 18,620 h at 405 °C. (a)–(d) Side view of the precipitate mapping Cu, Mn, Ni and Sn respectively; (e)–(h) plan view mapping Cu, Mn, Ni and Sn respectively.

The arrow points to a region of very high solute enrichment, probably associated with a dislocation [32]. Suzuki et al. found that the size of MnS precipitates may keep small in Sn-added Fe-3 wt.% Si alloys [36]. Nakashima et al. also found the fine and uniform dispersion of MnS and AlN precipitates in Sn added grain-oriented electrical steel [37]. Liu et al. reported that the sizes of AlN precipitates in high magnetic induction grain-oriented silicon steel are significantly decreased due to the Sn segregation at precipitate/matrix interface [38]. Iwayama et al. also reported that the precipitates in 0.23 mm thick high permeability grain-oriented silicon steel containing 0.1 wt.% Sn are much smaller in size than those without tin [39]. Thus, it can be concluded that the co-segregation of Cu and Sn may decrease the size and morphology of harmful precipitates in experimental steels. The much finer and high dispersion of the precipitates may have little negative impact on the pitting corrosion behaviour. This may explain why E_{pit} value of experimental steel D is further improved compared with that of steel C. Therefore, the pitting corrosion resistance of ultra-purified medium chromium ferritic stainless steel in 3.5% NaCl can be enhanced by the proper addition of Cu + Sn.

4. Conclusion

The result obtained from present work can be summarized in the following points.

- (1) Appropriate addition of Cu + Sn is in favor of improving the pitting corrosion resistance. The pitting corrosion resistance of the steel containing an equivalent amount of Cu and Sn (appr. 0.22 wt%) shows the best performance due to the beneficial synergistic effect of Cu + Sn.
- (2) The strong interaction between Cu and Sn in ferritic stainless steels clearly affects their pitting corrosion behaviour in 3.5% NaCl. A mechanism of Cu-Sn synergy was proposed: Cu can reduce the harmful micro-segregation of Sn in steel, and Sn restricts the growth of detrimental precipitates to the stability of passive film on the steel, such as ϵ -Cu, (Nb, Ti)(C, N) and other particles.

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