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Atomic scale understanding of the interaction between alloying copper and MnS inclusions in stainless steels in NaCl electrolyte

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ABSTRACT

The effect of alloying copper on the dissolution of manganese sulphide which triggers the pitting corrosion of stainless steels was studied by in-situ ex-environment transmission electron microscopy (TEM) with an atomic resolution. It was found that the benefits of Cu addition act in two ways: Cu ions replace the Mn ions in the surface layer of MnS and insoluble copper sulphide compound forms; on the other hand, Cu ions could stabilize harmful sulphur species released from dissolved MnS. The two processes are supposed to be helpful to reduce the detrimental effect of MnS on the corrosion resistance of stainless steels.

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1. Introduction

Alloying element copper is beneficial to improve the resistance to uniform corrosion of stainless steels in sulphuric acid [1–3], since the anode dissolution would be suppressed by the metallic Cu film depositing on the steel surfaces. However, its influence on the pitting corrosion of stainless steels is rather complex since it acts in different ways at different stages of pitting, i.e. pitting initiation, propagation and repassivation [4–12].

One benefit of copper addition was demonstrated to be that copper inhibits the pit initiation via reacting with harmful sulphur species generated from MnS dissolution [4,8,9]. Moreover, copper decreases the active dissolution rate by forming metallic copper film at the steel surfaces [2,4,5,8,9]. In a study of the corrosion of austenitic stainless steel in H₂S-Cl[−] environment, Tomio et al., indicated that the role of Cu addition was forming a copper sulphide thin film on the surface of the steel, which would enhance the formation of inner chromium oxide and consequently improve the pitting resistance of the alloy [13]. Following pitting nucleation, the corrosion pits either propagate or repassivate, mainly depending on the anolyte environment inside the pits, such as pH value, ion concentration, oxygen content etc. [14]. In general, the cathodic potential and low pH value at the pit bottom promote

Cu redeposition on the pit wall, which is considered to suppress the anodic dissolution of the steel [8]. Nevertheless, some authors claimed that the redeposited copper film may hinder pit repassivation, then enhance pit stabilization at lower pitting potentials, and as a result, hurt the pitting resistance of steels [2,9]. On the other hand, based on a metallurgical point of view, Jeon et al. [11] reported that the addition of Cu could advance precipitation of Cr-containing inclusions due to an increase in the activity of chromium. The interface areas between inclusions and matrix act as preferential sites for pitting nucleation thus decrease the pitting resistance of steels. Although Cu has a much higher solubility in the austenite (~4%) than in the ferrite (0.2%), large amount of alloying Cu and aging treatment would lead to the precipitate of ϵ -Cu phases in an austenitic steel and the increasing susceptibility of pitting corrosion in chloride media [12,15,16].

Even if there has been a large body of research focusing on the effect of copper on pitting corrosion of stainless steels, less attention has been paid to the influence of copper on MnS dissolution, the most important pitting source [17–23]. Except for some chemical analysis presenting the concentration of Cu on the surface of sulphide inclusions where pitting has occurred [9,20], we can hardly find more detailed descriptions through the literature available. This is possibly due to the fact that the commonly used analytical techniques in corrosion research, say, scanning electron microscope (SEM), or atomic force microscope (AFM) cannot simultaneously provide both structural and chemical information with high resolution, especially at the very beginning stage of pitting corrosion. To fully understand the above issue, special approaches

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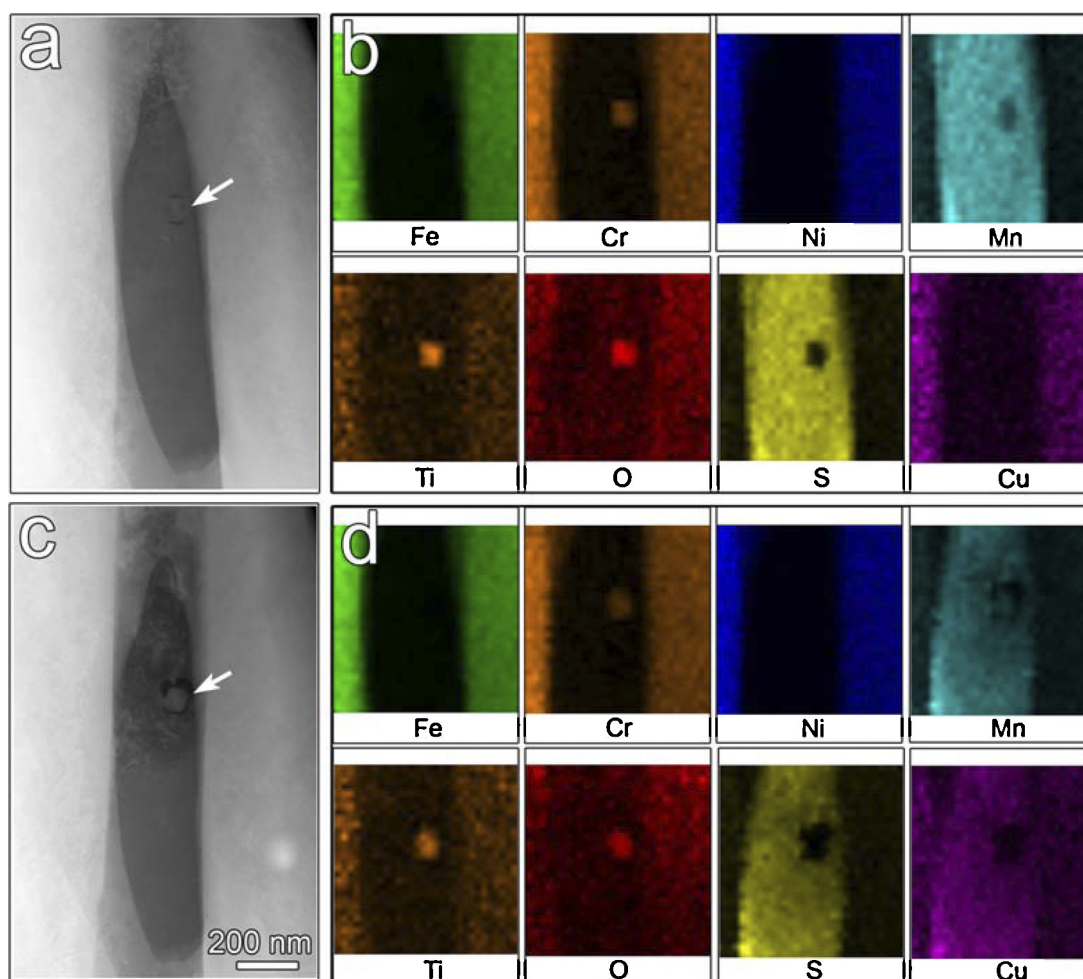


Fig. 1. Comparison of the MnS inclusion before and after corrosion test. (a) A HAADF-STEM image of the MnS, where a MnCr_2O_4 nano-particle is indicated with a white arrow. (b) EDS elemental maps taken at the area marked with red rectangle in (a). It should be noted that the Cu mainly distributes in the steel matrix. (c) The same MnS as that in (a), but suffered 35 min immersion in 1 mol/L NaCl solution. Dissolution of MnS began in the periphery of the nano-oxide. (d) EDS elemental maps of the same area as that in (b). The enrichment of Cu in MnS was clearly observed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are required. A recently developed technique in our research group called in-situ ex-environment TEM investigation has been successfully applied in the studies of pitting corrosion in stainless steels as well as in 2024-Al alloys [22,24–26]. The structural and chemical characteristics of the sites where pits preferably originate in the alloys are provided at an atomic scale. In the present work, such a quasi in-situ observation is carried out to reveal the reaction details between alloying copper and MnS inclusions in NaCl solution. We believe that the results will benefit the fundamental understanding of the effect of alloying Cu on the pitting initiation in stainless steels.

2. Material and methods

A commercial 316F stainless steel (Nippon Steel and Sumikin Stainless Steel Corporation) comprising 0.26 mass% Cu was chosen in this study. Sample pieces paralleling to the rolling direction of the steel rod were sliced with the thickness of 500 μm by linear precision saw. TEM samples were ground using silicon carbide papers, and then dimpled and further thinned by ion milling using a GATAN PIPS 691. After the first-round TEM observation, some of the specimens were plasma-cleaned and then immersed into a 1 mol/L NaCl solution at room temperature for various periods. After the corrosion test, the specimens were quickly cleaned (in

distilled water and methanol), dried, and transferred into the TEM for further investigation.

A Tecnai G² F30 TEM, equipped with a high-angle-angular-dark-field (HAADF) detector and X-ray dispersive spectrometer (EDS) systems, was operated at 300 kV for HRTEM imaging, HAADF-STEM imaging, and composition analysis. The atomic resolution HAADF-STEM images were acquired by a Titan G² Cube 60–300 aberration-corrected TEM with both probe and image correctors. The convergent semi-angle was 20.8 mrad, and the inner collection angle was set as 70 mrad.

3. Results

3.1. Enrichment of Cu in MnS inclusions

Fig. 1a shows a section of MnS, in which an embedded MnCr_2O_4 nanoparticle is marked with an arrow. The MnS inclusions develop into a needle-like shape in the steel suffered hot rolling. EDS elemental mapping technique under STEM mode was performed to characterize the chemical changes in the steel sample. Fig. 1b is the elemental maps of the area marked with red rectangle in Fig. 1a. The MnS inclusion is chemical homogenous except for the embedded nano-sized oxide. It should be noted that the Cu content in the sulphide is almost undetectable. After being immersed in 1 mol/L

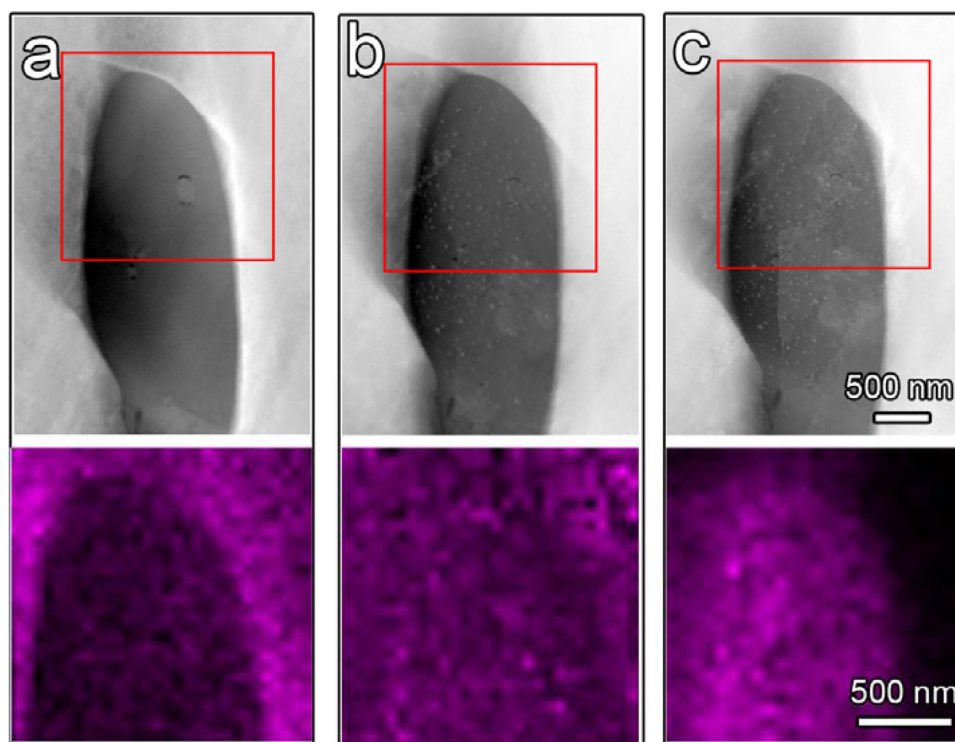


Fig. 2. HAADF images and Cu signal maps of the MnS inclusion showing that the content of Cu in MnS gradually increases with the extending corrosion periods. (a) A HAADF image of a section of MnS before corrosion. The inset in the bottom is Cu map of the area marked in the HAADF image. (b) It shows the increasing Cu content in the MnS suffered 15 min immersion in 1 mol/L NaCl solution. (c) The sample experienced 25 min immersion.

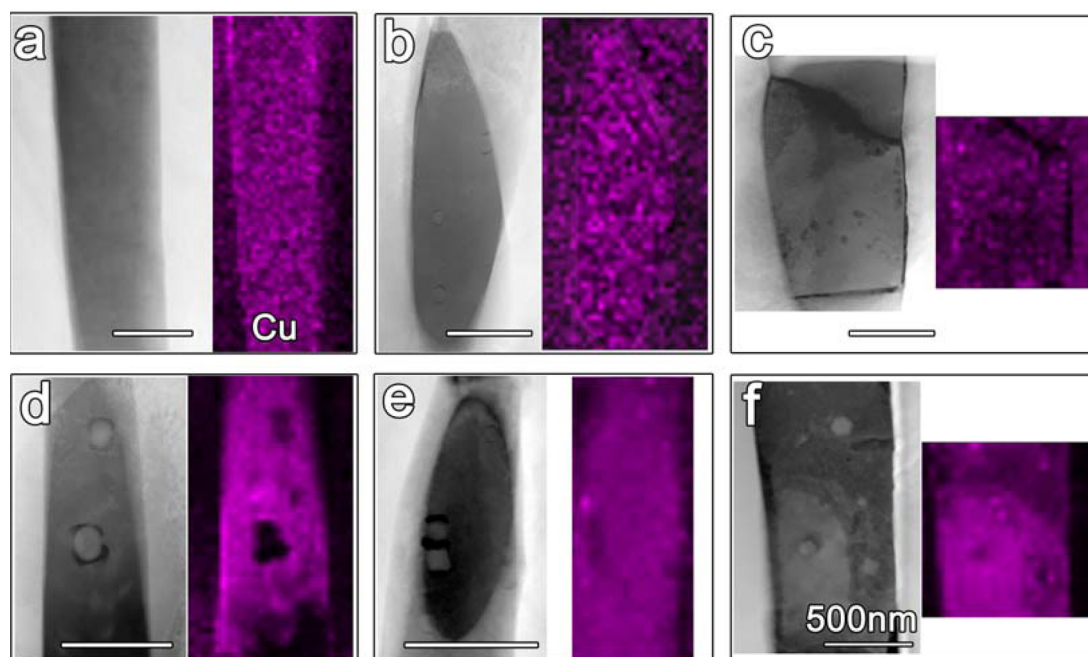


Fig. 3. HAADF images and corresponding Cu signal maps of MnS inclusions experienced corrosion in NaCl solution for various periods. Enrichment of Cu in MnS is evident (Scale bar: 500 nm).

NaCl solution for 35 min, the MnS dissolved locally in the periphery of the oxide (Fig. 1c). It is in agreement with the previous report that the dispersive MnCr_2O_4 particles generate the $\text{MnCr}_2\text{O}_4/\text{MnS}$ nanogalvanic cells and accelerate the local dissolution of MnS [24,27]. In order to reveal the composition change during dissolution, we performed EDS analysis on the same area as that in Fig. 1a. The results are shown in Fig. 1c and d. The weak signals of Mn and S around the

nano-particle indicate the dissolution pit forming there. However, the content of Cu in the MnS increases to a higher level than that in the steel matrix. Actually, enrichment of Cu in MnS begins when the steel sample experienced shorter immersion period. Fig. 2a shows another MnS inclusion in a steel sample. From the inset Cu-signal map, we can find the alloying Cu mainly distributes in the steel matrix as well. Fig. 2b and c gives the change of Cu content in the

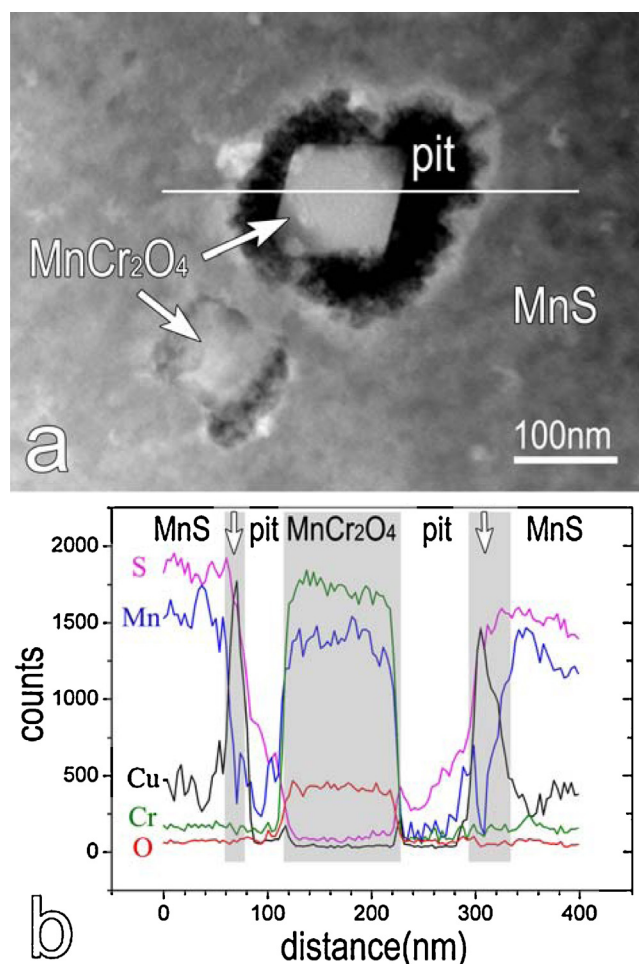


Fig. 4. (a) A zoom-in image of the dissolved area in MnS. Dissolution of MnS happened around the MnCr₂O₄ particles. The brighter contrast at the pit boundary indicates the concentration of elements with larger atomic numbers (b) EDS line scan result corresponding to the white line in (a) shows the higher content of Cu at the pit boundary.

same MnS inclusion as that in Fig. 2a but suffered corrosion test in 1 mol/L NaCl solution for 15 min and 25 min, respectively. It is seen that the Cu content in the MnS has already increased to the same level as that in the steel matrix after the sample experienced 15 min' immersion. After soaking for 25 min, the enrichment of Cu in the MnS became obvious, although the localized dissolution on the MnS has not nucleated yet.

Enrichment of Cu in MnS during corrosion process was frequently observed in our experiments. Fig. 3 shows a number of examples in which the sulphide inclusions present various degree of corrosion but all of them are clearly Cu-rich as evident in the Cu EDS signal maps.

Taking a zoom-in investigation on the dissolved area in MnS, we found higher Cu content around the dissolution pit. In Fig. 4a, a couple of MnCr₂O₄ particles are indicated by arrows, around which MnS dissolved locally. In the image, the bright contrast of the pit boundary is notable and demonstrates the local composition change, since the contrast in a HAADF image closely relates to the local chemical compositions [28]. A corresponding EDS line-scan analysis along the white line in Fig. 4a was performed (see Fig. 4b). In the pit boundary zone marked with shadow and downward arrows in Fig. 4b, the Cu signal is clearly strongest, in contrast to the decreasing Mn content, whilst the S signal shows no obvious change. It may imply that the replacement between Cu and Mn in MnS has happened.

Fig. 5a shows a typical HRTEM image of the dissolved area of MnS. It is seen that the Cu-enriched area contains high density

of {111} stacking faults, while the pit exhibits disordered structure. The structural features are also substantiated by a series of electron diffraction patterns which were respectively taken in the dissolution pit, at the pit boundary and in the area far from the pit (see Fig. 5b–d). As a rule of thumb, the stacking faults develop from the collection of vacancies during dissolution. The structure is beneficial for the Cu segregation, and will be discussed later.

3.2. Cu reacts with sulphur ions in solution

With extending corrosion duration to 1 h, the MnS inclusions dissolved severely. Some nano-particles appeared in the vicinity of the dissolved MnS inclusion. They are composed of copper and sulphur (see Fig. 6). Estimated from the EDS result, the chemical composition is close to Cu₂S. As reported by Wranglén [4,5] and Sourisseau et al. [9], the observed compounds should be the reaction product of dissolved Cu and sulphur species in solution. To obtain a full picture of the reaction, we extended the corrosion test duration as long as 20 days in dilute NaCl solution. In this sample, the MnS inclusions almost fully dissolved and a high density of copper sulphide nanowires grew on the steel surfaces (Fig. 7a). Fig. 7b is a magnified HAADF image of the nanowires with several hundred nanometers long. The nano-beam electron diffraction (NBED) pattern in Fig. 7c indicates these nanowires are cubic Cu₂S crystals (space group *Fm* $\bar{3}$ *m*, *a* = 0.558 nm [29]).

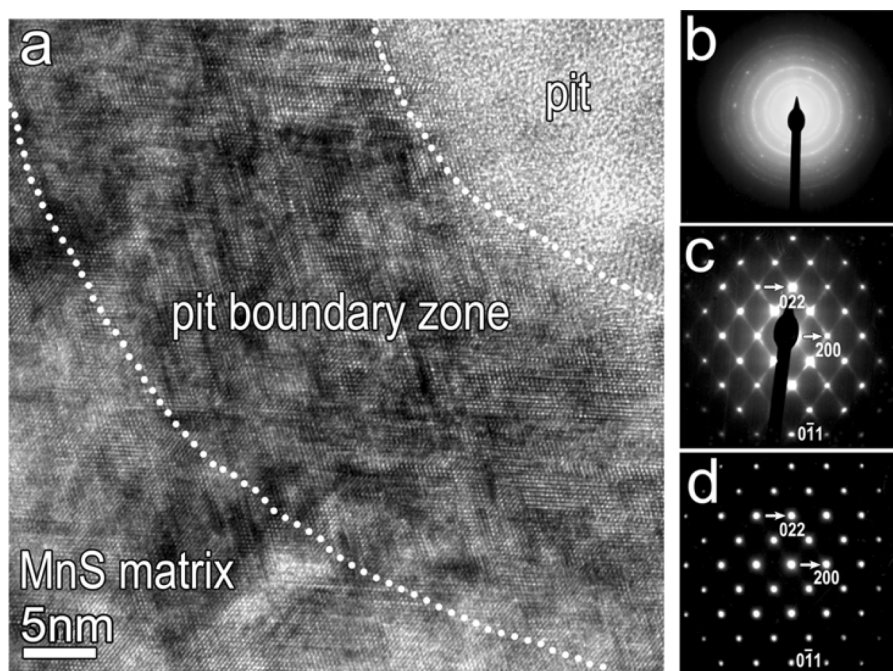


Fig. 5. (a) A high-resolution TEM image showing structure evolution from the pit to the MnS matrix. (b) An electron diffraction pattern (EDP) taken inside the dissolution pit. It indicates the disorder structure there. (c) An EDP taken at the pit boundary. High density of {111} stacking faults in this area results in the lines in the diffraction pattern. (d) An EDP taken from the area far from the pit.

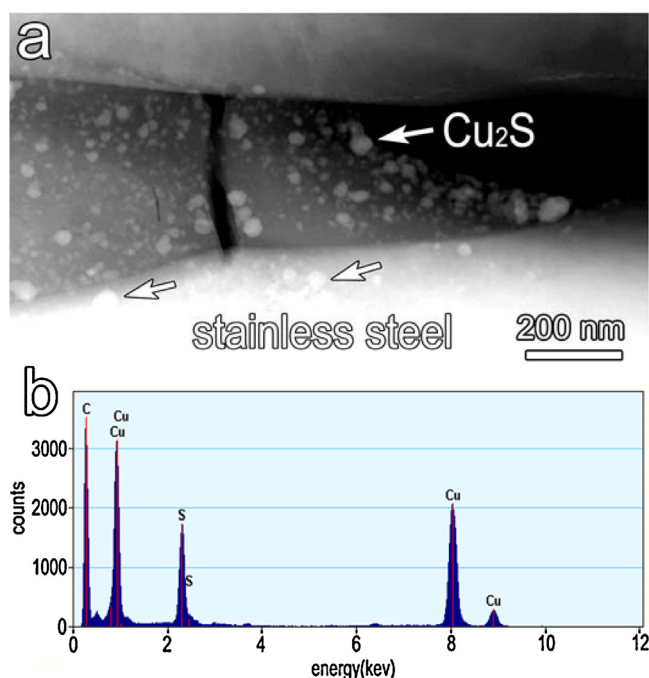


Fig. 6. Cu ions reacted with sulphur species and formed insoluble Cu₂S nanoparticles. (a) A HAADF-STEM image showing numerous Cu₂S particles deposited on the surfaces of the MnS and the neighboring steel matrix. (b) The corresponding EDS results of a particle whose composition is close to Cu₂S.

4. Discussion

The influence of alloying copper on the corrosion resistance of stainless steels has been widely investigated. Here, we focus on the interaction between alloying Cu and MnS inclusions which are generally accepted to be the major factor causing pitting. The mech-

anisms of Cu reacting with MnS in the Cl⁻-contained solution are discussed on the basis of our experimental data.

Firstly, we observed the Cu enrichment in MnS inclusions. We suggest the process includes two steps: (1) Cu ions releasing into electrolyte and (2) replacing the Mn²⁺ ions in MnS crystals. In the solution containing Cl⁻, alloying Cu in austenitic stainless steels is electrochemically unstable. According to Ujiro et al. [8], the released Cu would form CuCl₂⁻ species. The general reaction pathway follows:



After then, the dissolved Cu⁺ ions possibly replace the Mn²⁺ ions in the surface layer of MnS crystal, as suggested by the experimental results in Fig. 4. To verify the reaction mechanism, we add Cu²⁺ (CuCl₂) into the electrolyte (with a concentration of 0.01 mol/L) and repeat the corrosion test and TEM observations. As presented in Fig. 8a,b and d,e, the MnS inclusion in the steel sample after exposure to the solution for 5 min shows remarkable composition change. Particularly, the thin area of MnS in the TEM specimen totally transforms to Cu₂S crystal. Fig. 8f shows a high resolution STEM image of the product Cu₂S along its <100> direction. As a comparison, a high resolution STEM image of the pristine MnS is also given in Fig. 8c. The intensity of an atomic column in a HAADF image is proportional to Z^{1.7}, where Z is the atomic number [28]. The brightness of the spots in Fig. 8c are identical, because the columns along the <100> direction of MnS consist of alternating Mn and S. In Fig. 8f, however, the contrast of the spots show obvious distinction and the brighter ones represent Cu atomic columns. The structure of the crystal determined in Fig. 8f agrees well with a Cu₂S crystal which has an isotypic fluorite structure.

It unambiguously demonstrates a complete replacement of Mn²⁺ in MnS by Cu⁺ without breaking the S²⁻ lattice framework. Such reaction is known as cation exchange reaction (CER) and has been widely used to synthesize various nanomaterials [30–32]. The similar crystal lattices and a large difference in solubility

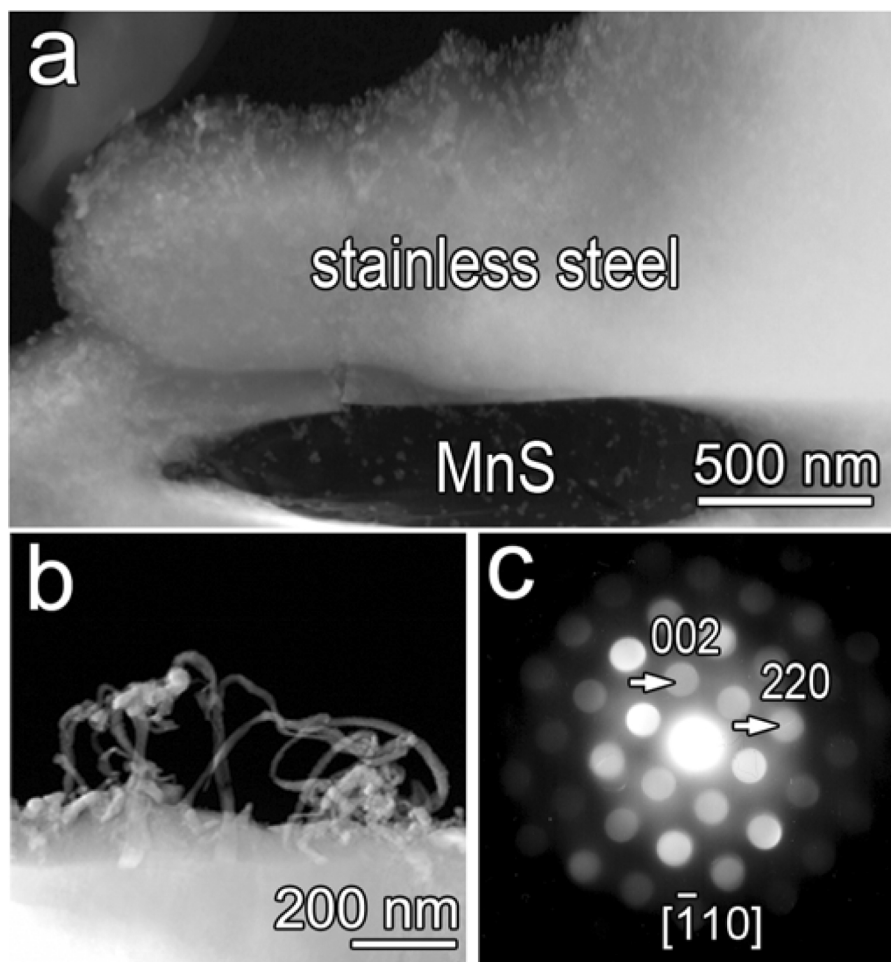


Fig. 7. Cu₂S nanowires grows on the surfaces of the steel which has been soaked in dilute NaCl solution for 20 days. (a) A HAADF image of the steel sample covered by Cu₂S nanowires. The MnS inclusion which shows black contrast has dissolved completely. (b) A zoom-in image of the nanowires whose length are about several hundred nanometers. (c) A nano-beam electron diffraction (NBED) pattern taken along the $[110]$ direction of Cu₂S.

between the precursor material and final product are required for CER happening [32]. In the present case, the two preconditions are fully met. The lattice parameters of the two crystals (α -MnS: $a = 0.522$ nm [33] vs. Cu₂S: $a = 0.558$ nm) and the driving force i.e. the difference in solubility between them (solubility product $K_{\text{MnS}} = 10^{-13}$, $K_{\text{Cu}_2\text{S}} = 10^{-48}$) make the spontaneous ions replacement in this reaction be more feasible. A similar experiment was reported by Xu et al. [34], who successfully synthesized hexagonal Cu₂S nanowires and Cu₂S/MnS junctions by replacing the Mn²⁺ ions in γ -MnS via cation exchange method. Moreover, now it is easy to explain the high concentration of Cu around the dissolution pit in the MnS. The numerous vacancies in the dissolving area as indicated by the dense stacking faults can provide fast path for Cu diffusion, thus the cation replacement takes place in a high rate.

Theoretically speaking, the enrichment of Cu in the surface layer of MnS may decrease the dissolution rate of MnS to some extent, since the copper sulphide is insoluble in salt water. However, the amount of the released Cu ions from the steel matrix is too little to effectively prevent the dissolution of MnS. Based on the knowledge above, we can imagine that if we bath the stainless steel in Cu ions-containing solutions to ensure the complete CER occurring, the compact layer of Cu₂S will form and prevent the MnS from dissolution. In fact, this way turns out to be quite convenient and pronounced. The chemical decoration yields a Cu₂S layer

with nearly 200 nm thick and consequently increases the pitting potentials of the steels by as much as 100 mV on average [35].

Another mechanism that Cu reacts with MnS is in an indirect way. The dissolution of MnS produces some sulphur species, such as elementary sulphur, thiosulphate, H₂S and so on, which were shown to promote the pitting propagation [17,36,37]. The released cuprous ions in solution are prone to unite with sulphur species and form insoluble Cu₂S depositions, and consequently inhibit the detrimental effect of the sulphur species [9]. In addition, the work of Tomio et al. [13] suggested that reducing the activity of sulphur species would enhance the formation of protective chromium oxide film on the steel surface.

As a summary of the discussion, Fig. 9 schematically illustrates the two reaction routes between Cu and MnS inclusions. In the left part, Reaction (I) involves the dissolved cuprous ions replacing Mn ions in MnS and transforming the skin layer of MnS into Cu-rich compound via cation exchange reaction. When localized dissolution of MnS nucleates, the concentrated vacancies in the boundary of dissolution pit provide fast diffusion path and result in the high Cu enrichment there. On the other hand, Reaction (II) proceeds after MnS dissolution has occurred and produces Cu₂S depositions. The released aqueous sulphur species can be stabilized. The two reactions can efficiently inhibit the harmfulness of MnS and, from this perspective, would show some benefits in retard pitting initiation in stainless steels.

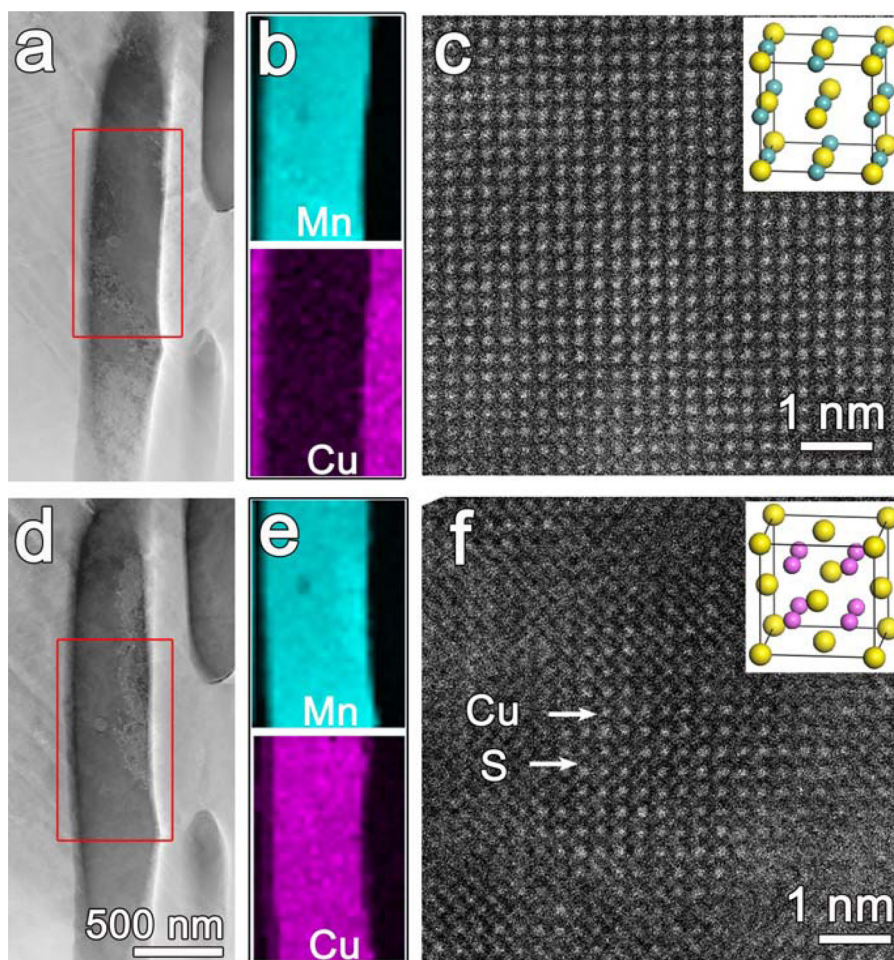


Fig. 8. The composition and structure transformation of a MnS inclusion suffered immersion in NaCl solution with adding Cu^{2+} ions. (a) A HAADF image of a section of MnS in the steel sample. (b) The EDS elemental maps of Mn and Cu taken in the area marked by the red rectangle in (a). (c) An atomic resolution HAADF image of the crystal MnS. According to the inset schematic illustration, the atomic columns along the $\langle 100 \rangle$ directions consist of alternation Mn and S ions, and hence should have the same contrast in HAADF image. (d) A HAADF image of the MnS inclusion in (a) but suffered 5 min immersion in Cu^{2+} containing NaCl solution. (e) The elemental maps demonstrate the entrance of Cu into MnS in such a short time. (f) A high resolution HAADF image taken at the thin area of MnS in the TEM specimen. It is seen the structure has completely transformed into Cu_2S . The Cu columns with brighter contrast and the S columns are both marked. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

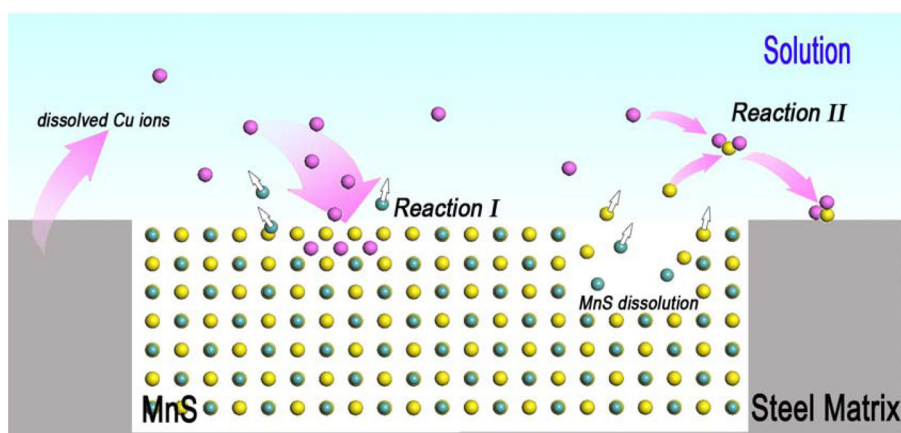


Fig. 9. A schematic illustration of the reaction between alloy Cu and MnS. In the left side, it shows the released Cu from steel matrix into solution. And then, the Cu ions enter the S framework and replace the Mn ions in the skin layer of MnS. When the dissolution occurs, aqueous sulphur species combine with Cu ions in solution and generate insoluble Cu_2S depositing on the surfaces of MnS and neighboring steel matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5. Conclusions

Advanced TEM techniques were applied to investigate the effect of alloying Cu on the dissolution of MnS inclusions and pitting initiation of stainless steels. The reaction details between alloying Cu and MnS in the NaCl solution is elucidated at an atomic scale. The observations suggest that the alloying Cu is useful to decrease the detrimental effect of MnS inclusions on the corrosion resistance of stainless steels.

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