

Investigation of Copper Corrosion Behavior in Various Sulfide Solutions

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Abstract. Copper, works as a protector of used fuel rods of nuclear power plant, can suffer most corrosion for its properties. While the copper, once reacting with sulfate/sulfide solutions from oil when buried deeply, may involve new corrosion problem. In this paper, mass loss experiments and potentiodynamic polarization are employed to investigate the corrosion behavior of copper in sulfide/sulfate solutions. The results of the mass loss indicated that when the temperature is 60 °C, the corrosion rates of copper decrease with the increase of concentration of Na₂S and Na₂SO₃. The potentiodynamic polarization of copper indicated that under the same temperature, the corrosion current densities of pure copper in Na₂S, NaCl and Na₂SO₄ aqueous solutions increased with the increase of solute concentrations. Keeping the concentration of each solution constant, the corrosion rate increases quickly with the rise of temperature. It should be highlighted that copper corrodes very fast in the Na₂S solution among these solutions.

1. Introduction

The copper is a metal which plays wide applications for its good anticorrosion properties. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion [1]. One of the uses of copper is as a protector of used fuel rods of nuclear power plant and buried in deep soil. Since the copper cladding is the only barrier shielding the radioactive nuclide, the corrosion of copper has been widely studied [1-10]. The copper plays high thermodynamic stability at room temperature, whereas at high temperatures, copper in corrosive mediums encounters serious corrosion. It has been reported that the copper reacts with sulfide extractives, such as pyrite, from the soil [11]. The sulfide corrosion of copper damaged the mechanical structure of the cladding for nuclear wastes. In addition, water and salts (such as NaCl, Na₂SO₄) in the soil will also accelerate the corrosion process of copper. The rich content of Cl⁻ and SO₄²⁻ in the soil will increase the rate of copper corrosion [12]. Therefore, the research of the corrosion behavior of copper in sulfide aqueous solutions, besides sulfate and chloride solutions, is urgent considering the protection of copper cladding buried in the soil.

The mechanism of copper corrosion in various sulfide solutions was studied. Under the condition of deoxidizing, the copper corrosion with sulfide aqueous solutions usually plays as electrochemical corrosion. With the pH of sulfide aqueous solutions increasing, the corrosion speed of system can be reduced. At the very beginning of copper immersing in the sulfide aqueous solution, a single layer of dense Cu₂S sulfide film formed on copper surface [7, 13-14]. The growth of sulfide film follows the dynamic mechanism of Parabola. With the extension of soaking time, sulfide film fractures, then falls off and grows again [15].

In this paper, the corrosion behavior of pure copper in sulfur-containing solution was investigated by chemical and electrochemical experiments. The copper corrosion behavior in sulfide aqueous solution was explained with a new mechanism with corrosion product analysis. Our results would be useful in the design and development of new copper corrosion inhibitors.

2. Experimental methods

2.1 Mass loss method to investigate the corrosion rates of Cu.

The ‘pure copper’ (oxygen free, > 99.5% mass) sheets of 40.0mm ×10.0 mm were prepared by mechanical grinding and polishing, followed by ultrasonic baths in acetone and alcohol for 10 minutes, respectively. After rinsing in deionized water, the copper specimens were blow-dried and weighted. These copper specimens were corroded at different concentrations of Na₂S and Na₂SO₃ solutions, pure water and sublimed sulfur powder at 60 °C as a simulated underground temperature for 7 days (168 hours) as ‘mass loss method’ to investigate the corrosion rates. After being taken out, the specimens were washed with distilled water, blow-dried and weighted again. Comparing the weight losses of these copper specimens before and after corrosion, the corrosion rates of copper in various solutions and solid matrixes were calculated.

2.2 Potentiodynamic polarization.

The specimens employed for potentiodynamic polarization measurements are pure copper (> 99.5%) rods of 10.0 mm diameter with a wire lead sealed one side by epoxy resin. The measurements were conducted in NaCl, Na₂SO₃, Na₂SO₄ and Na₂S solutions in various concentrations (0.1, 0.01 and 0.001 M) and at various temperatures (20, 40, 60 and 80 °C). The above sealed copper rods were used as working electrodes while a saturated calomel electrode (SCE) was used as the reference electrode and Pt sheet was the auxiliary electrode. Potentiodynamic polarizations were tested using CHI650D electrochemical work station, with a potential range from about 0.2V lower than the open circle potential (OCP) to the full anodic passivation state with a scanning rate of 1.0 mV/s. Before the test, the prepared specimens were immersed into various solutions for 10 mins to get steady OCPs.

3. Results and Discussion

3.1 Mass loss method.

Fig.1 showed the mass loss of copper in various sulfate/sulfide-containing solutions, besides pure water and sublimed sulfur powder at constant temperature of 60°C for 7 days. First, the corrosion of copper in S produced a hard and brittle surface. There is a surprising weight loss rather than increase of copper in S powders. Then in pure water, copper corroded at a certain rate as shown in Fig.1 at 60°C with slight weight gaining. In NaCl solution, when the concentration is very high at 0.1M, the copper suffered heave mass loss corrosion. While in very low concentration at 0.01 and 0.001M, the mass loss results of copper are very low. The copper samples played the same corrosion behavior in Na₂SO₄ solution. In 0.001 M Na₂S solution, Cu₂S produced. With the increasing of Na₂S concentration to 0.1M, the product changed into CuS. As CuS is more resistant to corrosion than Cu₂S, the increasing concentration of Na₂S causes the corrosion rate shrinking. Therefore, the copper corroded most slowly in 0.1 M Na₂S solution. In contrast, Na₂SO₃ plays as a reductive agent and the higher concentrations of Na₂SO₃ inhibit the corrosion of copper induced by oxygen. So the corrosion rate of copper in 0.1M Na₂SO₃ is also smaller than that of 0.001M.

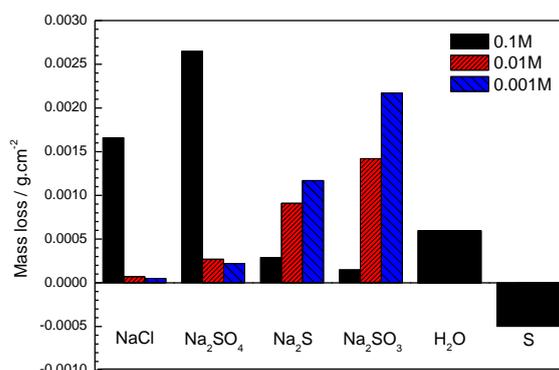


Fig.1 Mass loss of the copper sheets in different matrixes with varied concentrations at 60°C for 7 days (the concentrations for water and S have no meaning).

3.2 Potentiodynamic polarization

Fig.2 shows the polarization plots of copper in Na₂SO₄, NaCl, Na₂SO₃ and Na₂S solutions at 60 °C. As shown in Fig.2 (a), Na₂SO₄ is a kind of ineffective corrosion solution for copper and only play the role of supporting electrolyte. So, the differences of corrosion potential (E_{corr}) in Na₂SO₄ aqueous solution are not obvious except for that of in 0.1M. High concentration of sulfate decreased E_{corr} for the copper corroded in such a high ineffective salt solution.

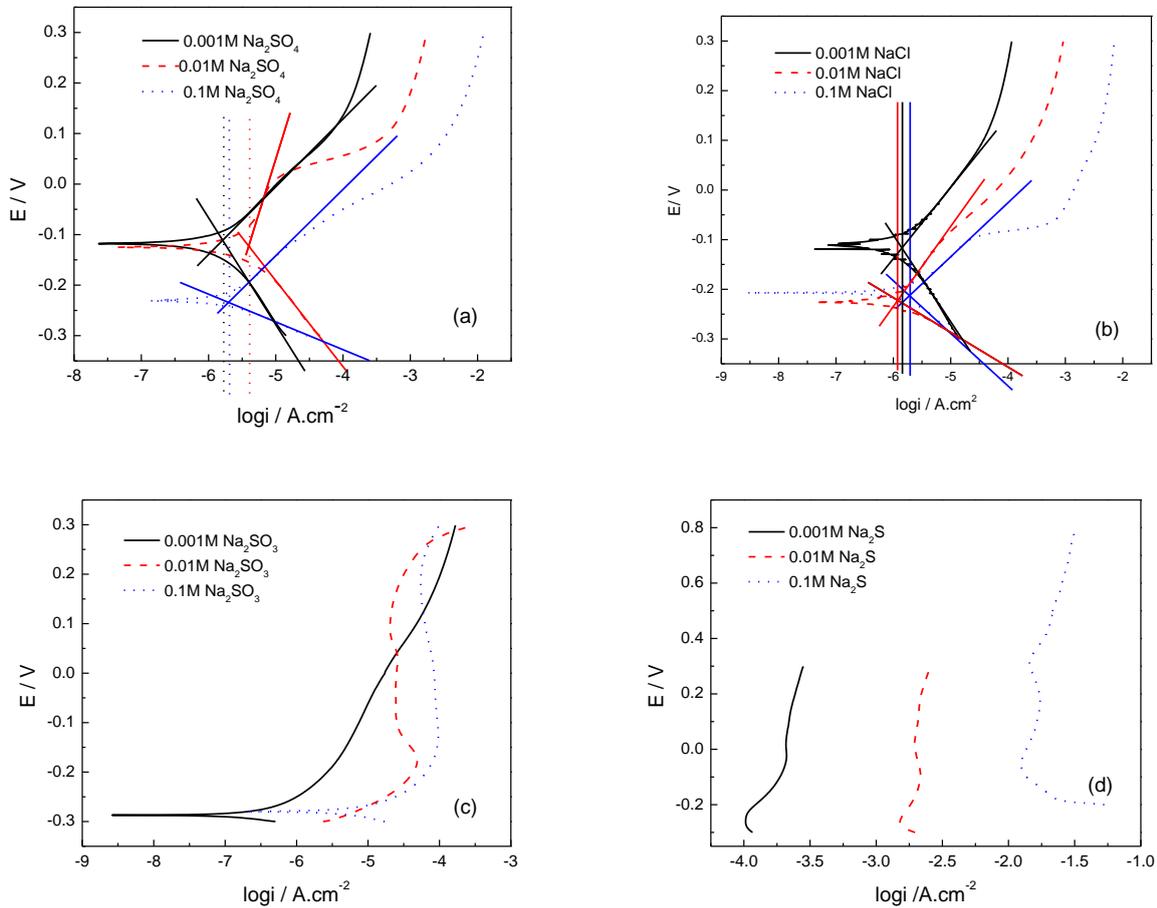


Fig.2 Potentiodynamic polarization plots of copper in Na₂SO₄, NaCl, Na₂SO₃ and Na₂S solutions for different concentration of 0.1, 0.01 and 0.001M at 60 °C with scan rate of 1mV.s-1.

The corrosion parameters such as E_{corr}, corrosion current density (I_{corr}) and corrosion resistance (R_p), in addition to the Tafel (cathodic, β_c, and anodic, β_a) slopes from Fig.2 are listed in Table.1. The values of E_{corr} and I_{corr} were evaluated from the cathodic and anodic curve by CHI Instrument Software. The values of β_c and β_a were determined after at least 50mV away from E_{corr} and at least one decade of I_{corr}. The R_p values from the different copper corrosion were calculated from the Stern-Geary equation [16] using parameters listed in Table.1 as below:

$$R_p = \frac{1}{I_{corr}} \left(\frac{\beta_c \beta_a}{2.3(\beta_c + \beta_a)} \right) \quad (1)$$

With the increasing of anodic potential, I_{corr} at high potential regularly increases with the increasing of the concentration. As shown in Fig.2(b), with the increase of concentration of NaCl solution from 0.001 to 0.01M, E_{corr} of copper significantly decreased. Unlike iron group materials, copper in NaCl solution does not show any obvious pitting corrosion phenomenon. This may be due to the surface treatment of copper failed to form effective passivation layer and Cl⁻ is not effectively corrosive toward copper. So when the concentration of NaCl solution increased from 0.01 to 0.1M, the change of E_{corr} is not significant (even lower). As shown in Fig.2(a), with the increasing of concentration of Na₂SO₄ solution, E_{corr} shows an obvious drop, and I_{corr} density changes little at the higher part of anode polarization voltage

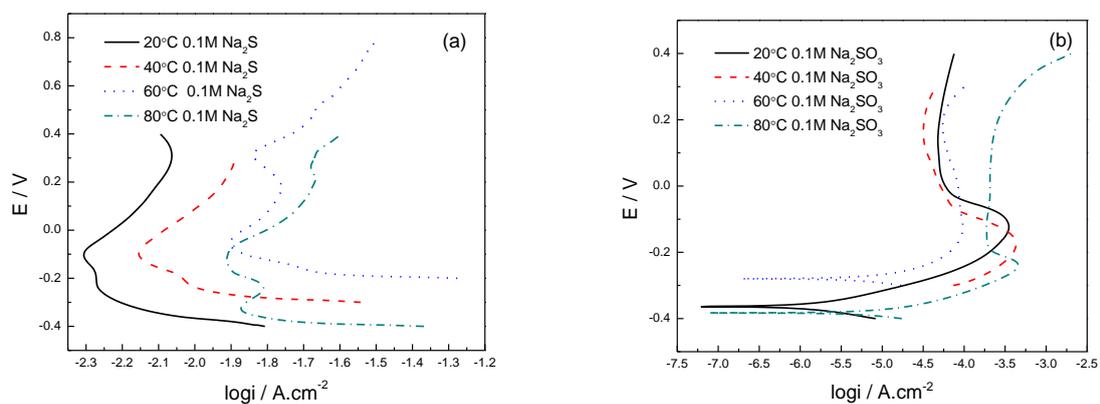
. The possible reason is that the Na_2SO_4 plays only a positive site at the surface of copper electrode. And high concentration of Na_2SO_4 lowers the corrosion resistance at the interface between electrode and solution. When the copper electrode deeps into Na_2SO_3 solution as Fig.2(c), the E_{corr} did not change much during the concentration increasing. The possible reason is that Na_2SO_3 plays as a reducing agent, so high levels of Na_2SO_3 inhibit the corrosion of copper from oxygen. As shown in Fig.2(d), for the lower concentration of Na_2S solution, the polarization plot of copper in sodium sulfide can be obtained. In high concentration of Na_2S solution, the polarization plot is not typical, and the current density is very large. This may be caused by S^{2-} reacting with copper which produces CuS . It should be pointed out that when the copper immersed into Na_2S solution, the reaction/corrosion started. So no steady OCP or a typical polarization plot can be obtained.

At 20, 40 and 80 °C, the polarization plots of copper in Na_2SO_4 , NaCl , Na_2SO_3 , Na_2S aqueous solutions indicated nearly similar corrosion laws as that at 60 °C.

The polarization plot shows that Na_2SO_3 solution as reducing agent may protect the copper from oxidation, which has a certain effect on the corrosion resistance of copper. The polarization plot of Na_2S solution is distinct from the other solutions because of the violent corrosive reaction of copper with S^{2-} . Fig.3 shows the potentiodynamic polarization plots of copper in Na_2S , Na_2SO_3 , Na_2SO_4 and NaCl solutions of 0.1M at different temperatures. In Fig.3(a), there is no clear cathodic to anodic polarization change shown from this figure because of the strong corrosion when copper was immersed in S^{2-} aqueous solution. Fig.3(a) shows that the corrosion current of copper in Na_2S solution significantly increased with the rise of temperature. The fitting results listed in Table.2 also indicated the corrosion behavior of copper in various solutions. Such as in NaCl solution, the corrosion resistance R_p reduced as temperature increasing from 20 to 80°C. As shown in Figs.3(b), (c) and (d), the corrosion current of copper in Na_2SO_3 , Na_2SO_4 and NaCl solutions increased with the increase of temperature slightly. So, with the increasing of solution temperature, corrosion rates of copper in Na_2S , Na_2SO_3 , Na_2SO_4 and NaCl solutions of 0.1M become larger.

It is investigated that there are two type of corrosion production for copper in the oxygen environments: Cu_2O (cuprous oxide) and CuO (cupric oxide)[20]. The amount of both oxides plays an essential effect on the growth of copper corrosion. The scales of Cu_2O and CuO formed on Cu in the oxygen environments and at elevated temperature depend on the thermodynamic stability of the oxides.

Comparison of the opposite trends of copper corrosion in Na_2S solution by immersing and potentiodynamic polarization, the former one suggested a protected layer when the copper specimen was immersed and this layer indicated a property to protect copper for further corrosion. So for the mass loss experiment, the copper corroded less in a higher concentration solution of Na_2S . When the copper specimen was immersed in Na_2S solution with electrochemical cell connection, the corrosion product could not protect the copper. So in the potentiodynamic polarization experiment, the copper corrosion was enhanced when the concentration of Na_2S increased.



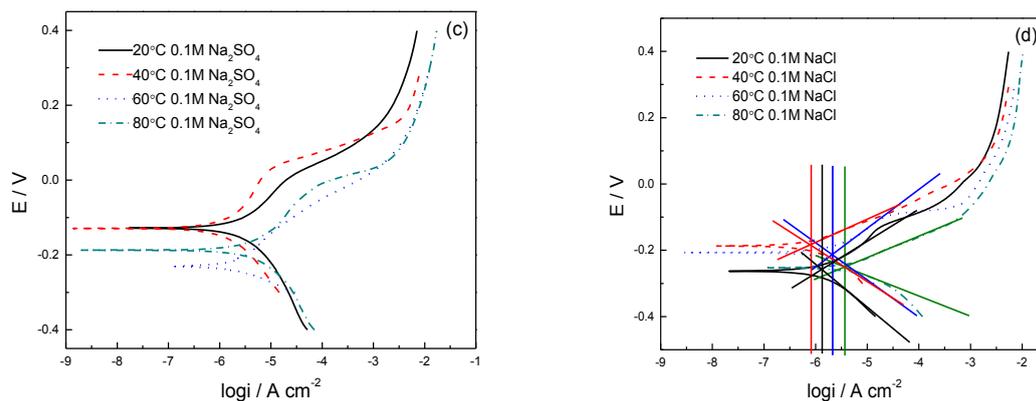


Fig.3 Potentiodynamic polarization plots of copper in Na₂S, Na₂SO₃, Na₂SO₄ and NaCl solutions of 0.1M at different temperatures of 20, 40, 60 and 80°C with scan rate of 1mV.s⁻¹.

4. Conclusion

The mass loss results show that when the temperature was 60°C, with the increasing of concentration of Na₂S and Na₂SO₃, the corrosion rate of copper decreased.

The potentiodynamic polarization plots indicated that at the same temperature, corrosion current of copper in Na₂S, NaCl and Na₂SO₄ solutions increased with the increasing of concentration. Under the same concentration in sulfide solutions, with the rise of temperature, corrosion current increased quickly.

Acknowledgments

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References

- [1]. Antonijević M M, Petrovic M B. Copper Corrosion Inhibitors. A review. *Int. J. Electrochem. Sci.* Vol. 3 (2008) p. 1-28.
- [2]. Rosborg B, Pan J, Leygraf C. Tafel slopes used in monitoring of Cu corrosion in a bentonite/groundwater environment. *Corros. Sci.* Vol. 47 (2005) p. 3267-3279.
- [3]. Rosborg B, Pan J. An electrochemical impedance spectroscopy study of Cu in a bentonite/saline groundwater environment. *Electrochim. Acta.* Vol. 53 (2008) p. 7556-7564.
- [4]. Bojinov M, Betova I, Lilja C. A mechanism of interaction of Cu with a deoxygenated neutral aqueous solution. *Corros. Sci.* Vol. 52 (2010) p. 2917-2927.
- [5]. Betova I, Beverskog B, Bojinov M, et. Al. Corrosion of Cu in nuclear waste repository conditions. *Electrochem. Solid-State Lett.* Vol. 6 (2003) p. B19-B22.
- [6]. Srivastava A, Balasubramaniam R. Electrochemical impedance spectroscopy study of surface films formed on Cu in aqueous environments. *Mater. Corrosion.* Vol. 56 (2005) p. 611-618.
- [7]. Chen J, Qin Z, Shoesmith D W. Long-term corrosion of Cu in a dilute anaerobic sulfide solution. *Electrochim. Acta.* Vol. 56 (2011) p. 7854-7861.
- [8]. Smith J M, Wren J C, Odziemkowski M, et al. The electrochemical response of preoxidized Cu in aqueous sulphide solution. *J. Electrochem. Soc.* Vol. 154 (2007) p. C431-C438.
- [9]. Chen J, Qin Z, Shoesmith D W. Kinetics of corrosion film growth on Cu in neutral chloride solutions containing small concentrations of sulfide. *J. Electrochem. Soc.* Vol. 157 (2010) p. C338-C345.
- [10]. Rosborg B, Kosec T, Kranjc A, et al. Electrochemical impedance spectroscopy of pure copper exposed in bentonite under oxic conditions. *Electrochim. Acta.* Vol. 56 (2011) p. 7862-7870.

- [11]. Saleem M, Essa M H, Chakrabarti M H, et al. An Economical Means for Remediating a Multiple-Metal Contaminated Soil Using Electro-Kinetic Technology Under Natural Conditions. *Int. J. Electrochem. Sci.* Vol. 7 (2012) p. 7809-7822.
- [12]. Wang Y, Lu Z, Li Y, Corrosion behavior of Cu and Al in western inland salty soil. *Journal of Chinese Society for Corrosion and Protection*, Vol. 25 (2005) p. 303-306.
- [13]. Chen J, Qin Z, Shoesmith D W. Rate controlling reactions for copper corrosion in anaerobic aqueous sulphide solutions. *Corros. Eng. Sci. Tech.* Vol. 46 (2011) p. 138-141.
- [14]. Smith J M, Qin Z, King F, et al. Sulfide film formation on copper under electrochemical and natural corrosion conditions. *Corrosion*. Vol. 63 (2007) p. 135-144.
- [15]. Johan M R, Suan M S M, Hawari N L, et al. Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition. *Int. J. Electrochem. Sci.* Vol. 6 (2011) p. 6094-6104.
- [16]. Wan Y, Wang X, Sun H, et al. Corrosion Behavior of Copper at Elevated Temperature. *Int. J. Electrochem. Sci.* Vol. 7 (2012) p. 7902-7914.