Copper Alloy Design for Suppressing Sulfur Diffusion and Mitigating Embrittlement

Minkyu Ahn [a], Jinwoo Park [a], Gyeongsik Yu [a], Sangeun Kim [a], Chansun Shin [a*]
[a]*Materials Science & Engineering., Myongji Univ., 116 Myongji-ro, Cheoin-gu, Yongin 17058, Republic of Korea*
[*]*Corresponding author: c.shin@mju.ac.kr*

1. Introduction

Spent nuclear fuels are managed via deep geological disposal in multi-barrier systems. Copper outer shells are used to provide corrosion protection due to their thermodynamical stability in anoxic environments [1]. However, sulfide-induced pitting corrosion and stress corrosion cracking can cause copper canister failure if sulfide is present [2]. Sulfur can diffuse into the copper shell along fast diffusion paths such as grain boundaries, forming Cu2S particles that act as crack initiation sites and cause embrittlement [3,4]. To protect copper canisters from corrosion, copper alloys are designed to prevent Cu2S precipitation along grain boundaries. Alloy elements are chosen as chemical anchors to suppress sulfur diffusion. Model alloys are manufactured and tested to reduce Cu2S precipitation.

2. Methods and Results

Ingots of copper alloys with compositions of Cu−0.2at%S and Cu−0.5at%Si−0.2at%S were produced through arc-melting of high-purity elements using a vacuum arc melting system manufactured by Samhan Vacuum Development CO.LTD. An example of a melted and solidified Cu ingot weighing 26 g in the vacuum arc melting system is shown in Fig. 1(a), while Fig. 1(b) displays the etched surface of a Cu ingot with a diameter of approximately 2.5 cm, revealing its grain morphology. The microstructures of the Cu alloys containing sulfur were examined using a Thermo Fisher Scios 2 focused ion beam scanning electron microscope (FIB-SEM) equipped with energy dispersive spectroscopy (EDS).

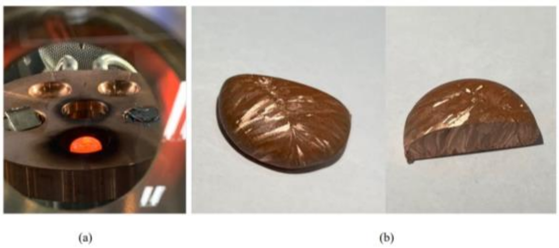

Fig. 1. (a) Melted and solidified Cu ingot in vacuum arc melting system, (b) Vacuum arc-melted Cu ingot

Fig. 2 displays SEM micrographs of Cu−0.2at%S taken at different locations, accompanied by the EDS mapping image for sulfur. In the SEM micrographs, particles with spherical and elliptical morphologies are visible along grain boundaries. The EDS maps indicate that these particles have a higher concentration of sulfur, identifying them as copper sulfide particles. Copper sulfides are known to form along grain boundaries in pure Cu, as shown in Fig. 2.

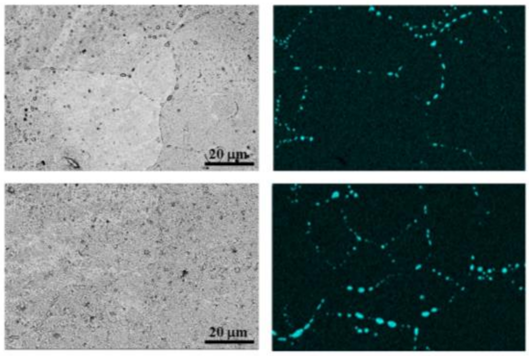

Fig. 2. SEM micrographs and EDS map for S of Cu−0.2at%S

The microstructures of Cu−0.5at%Si−0.2at%S are shown in the SEM micrographs of Fig. 3. In contrast to Cu−0.2at%S, sulfide particles are randomly distributed inside the grains, with no longer any alignment along grain boundaries. According to the Cu-Si phase diagram, there is appreciable Si solubility (~8at%) in Cu. The EDS map for Si indicates that there is no Si-rich phase and no spatial correlation with sulfur.

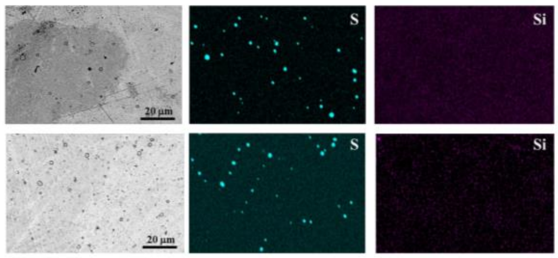

Fig. 3. SEM micrographs and EDS map for S and Si of Cu−0.5at%Si−0.2at%S

A tensile test was conducted to analyze mechanical properties. Looking at Fig. 4(a), there is a result of 20% elongation. grain boundary brittleness was expected at a 20% elongation specimen, and all other specimens showed elongation exceeding 40%. The EDS analysis was conducted near the fracture of the 20% elongation specimen, and the results are shown in Figure 5. A grain boundary crack can be seen in Figure 5, and the sulfide located in the crack indicates that the sulfide is the cause of the crack.

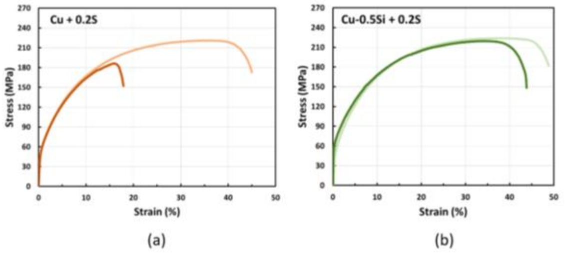

Fig. 4. (a) Tensile test graph of Cu−0.2at%S, (b) Tensile test graph of Cu−0.5at%Si−0.2at%S

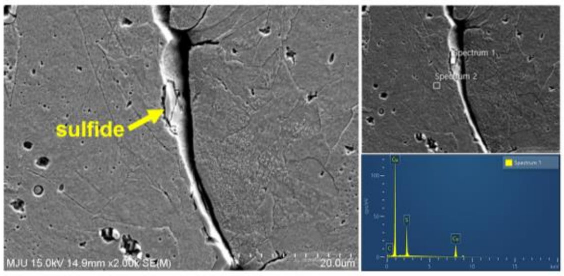

Fig. 5. SEM micrographs and EDS of Cu−0.2at%S

A verification experiment was conducted for an experiment in which sulfur was injected into copper from the outside. The pure copper wire was heated and exposed to a sulfur atmosphere. The temperature of the pure copper wire was measured by a thermal couple. The pure copper wire was exposed at 70°C for 10 minutes and 20 minutes, respectively, and Fig. 6(a) shows a graph of the temperature changes over time in a copper wire, which was measured using a thermocouple, and Fig. 6(b) is a schematic graph. Two types of wires exposed to the sulfur atmosphere and pure copper wires were tensile tested. The tensile test results are illustrated in Fig. 7, and it can be found that the elongation of the specimen exposed to sulfur has decreased. The difference between 10 minutes and 20 minutes of exposure time was insignificant, and in addition, a copper-silicon alloy will be tested by injecting sulfur from the outside.

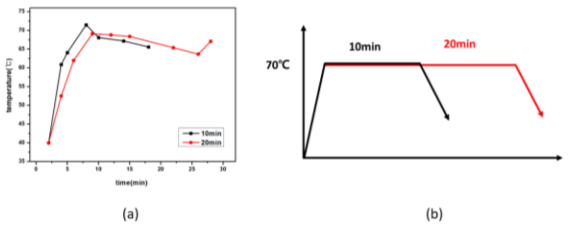

Fig. 6. (a) Temperature-time graph of the copper wire, (b) Temperature-time schematic graph

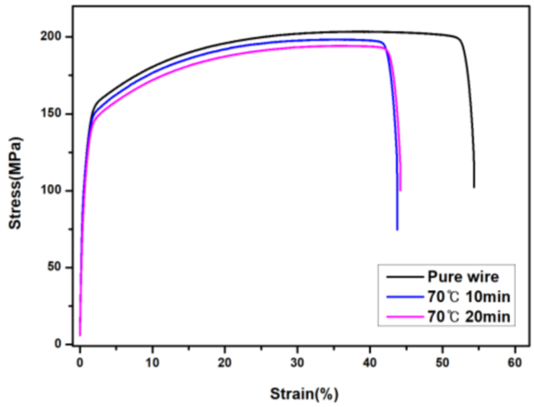

Fig. 7. Tensile test graph of pure copper wire

3. Conclusions

To address sulfur-induced embrittlement at grain boundaries in copper, alloying elements were employed, and the effectiveness of Si as an alloying element was demonstrated. While pure copper formed sulfides at the grain boundaries, Cu-Si alloy formed sulfides within the grains. Tensile tests showed that pure copper exhibited a decrease in elongation, and EDS analysis revealed cracks, including those containing sulfides. Sulfides were identified as the cause of the cracks and subsequent decrease in elongation. In contrast, the Cu-Si alloy did not exhibit a decrease in elongation. A future research plan is to inject sulfur from the outside and analyze it.

REFERENCES

[1] F. King, C. Lilja and M. Vähänen, “Progress in the understanding of the long-term corrosion behaviour of copper canisters”, J. Nucl. Mater., 438(1-3), 228-237 (2013).

[2] S. Kärnbränslehantering, Supplementary information on canister integrity issues, Swedish Nuclear Fuel and Waste management, Technical Report TR-19-15 (2019).

[3] E. Arilahti, T. Lehtikuusi, M. Olin, T. Saario and P. Varis, “Evidence for internal diffusion of sulphide from groundwater into grain boundaries ahead of crack tip in Cu OFP copper”, Corros. Eng. Sci., 46(2), 134-137 (2011).

[4] T. Meiners, Z. Peng, B. Gault, C.H. Liebscher and G. Dehm, “Sulfur–induced embrittlement in high-purity, polycrystalline copper”, Acta Mater., 156, 64-75 (2018).