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*] TEL: +82-31-330-6468, e-mail: c.shin@mju.ac.kr*
[a] Department of Materials Science and Engineering, Myongji University, Yongin 449-728 Korea

Abstract

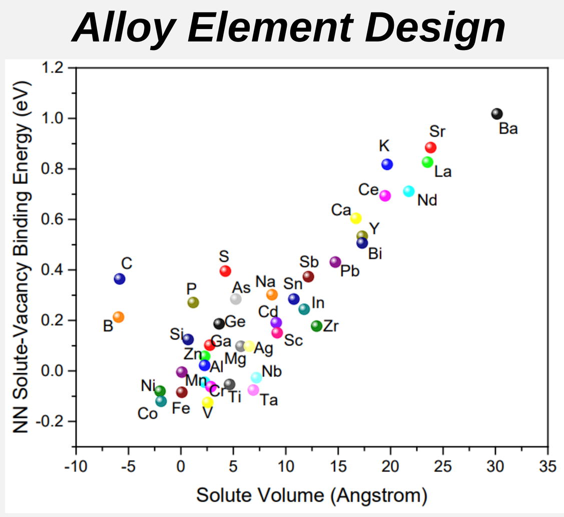
In this study, we investigate copper sulfide formation at grain boundaries and search for alloying elements to prevent it using computational methods. Comparing our computational findings with experimental data on copper embrittlement validates the proposed mechanisms and selected alloy elements. Binary copper alloys are prepared through vacuum arc melting with sulfur addition, followed by cold-rolling and homogenization heat treatment to produce plates. Microstructure and mechanical properties are analyzed after recrystallization. Scanning electron microscopy reveals randomly distributed Cu2S particles within the grains, rather than concentrated at grain boundaries, in all vacuum-arc melted copper alloys (Cu−Si, Cu−Ag, Cu−Zr). Tensile testing and fracture analysis show that Cu2S particles at grain boundaries reduce elongation and act as fracture initiation points. These newly developed copper alloys have the potential to enhance the long-term safety of deep geological disposal copper canisters by mitigating embrittlement due to sulfide formation.

introduction

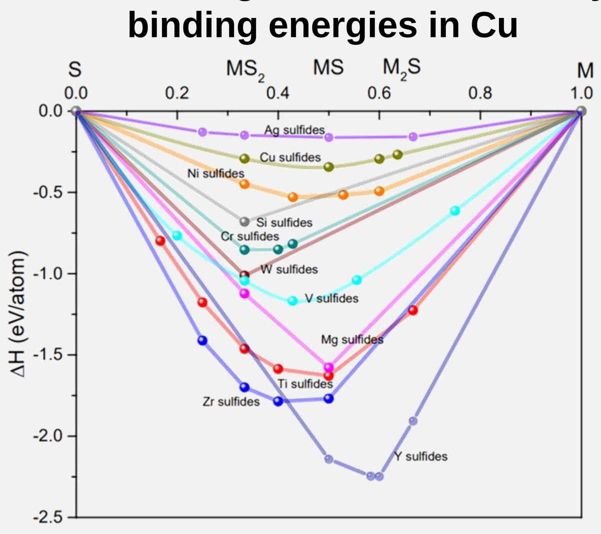
Spent nuclear fuels are managed via deep geological disposal in multi-barrier systems. Copper outer shells are used to provide corrosion protection due to their thermodynamical stability in anoxic environments [1]. However, sulfide-induced pitting corrosion and stress corrosion cracking can cause copper 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.

Experimental

Alloy Element Design

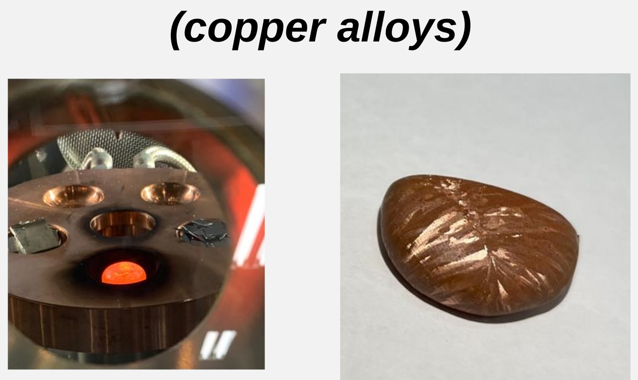


Nearest-neighbor solute-vacancy binding energies in Cu

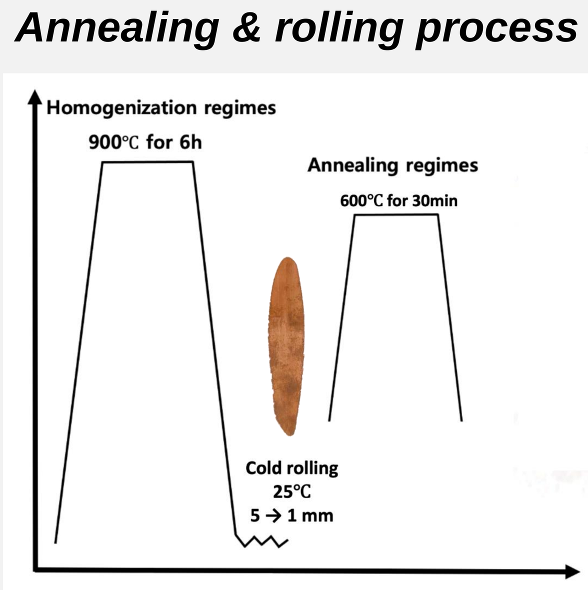


Formation enthalpy of metal sulfides

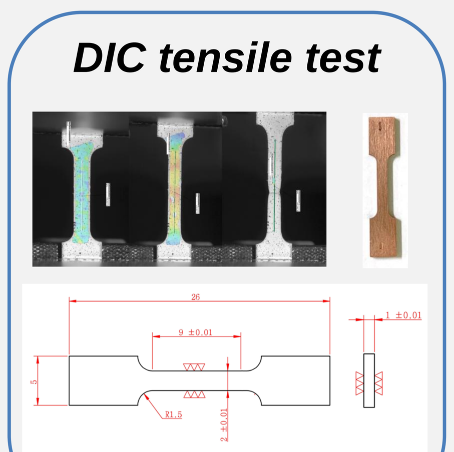
Vacuum Arc Melting (copper alloys)



Annealing & rolling process



DIC tensile test



Grinding (#320~#1200)

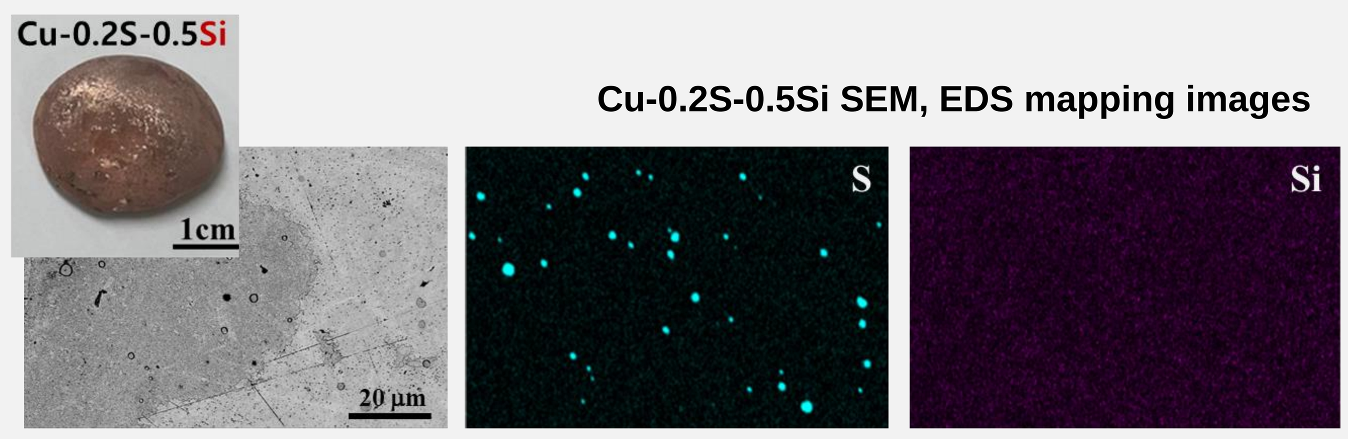
Mechanical polishing (9μm~1μm)

Etch (DI Watar 100ml + Nital 100ml)

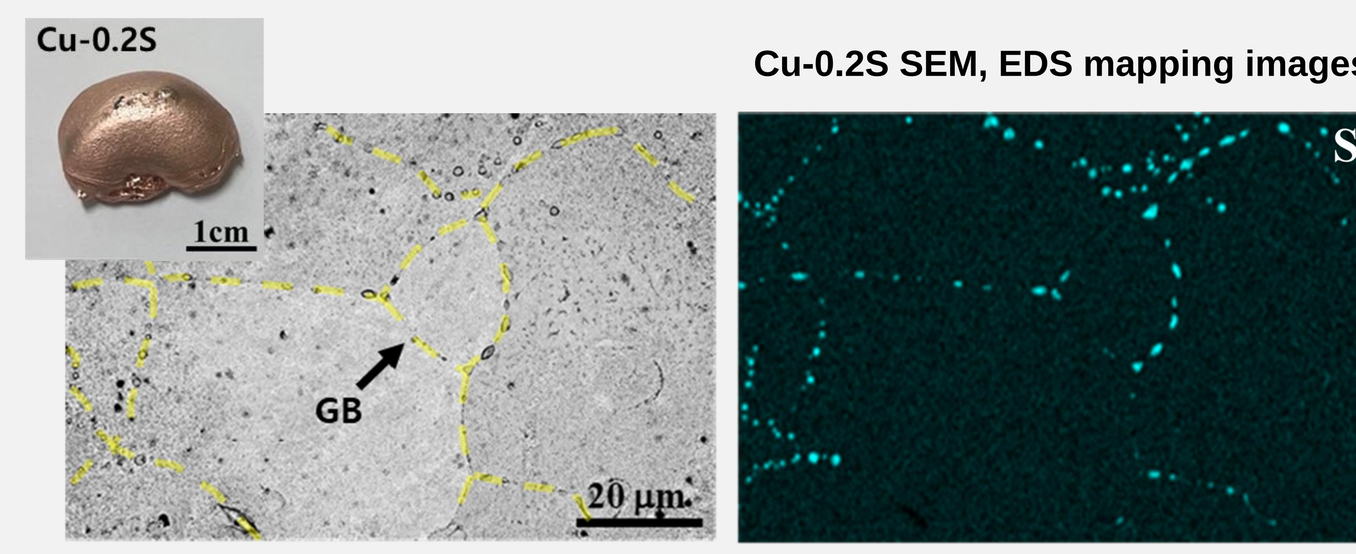
SEM and EDS map

Overall experimental process

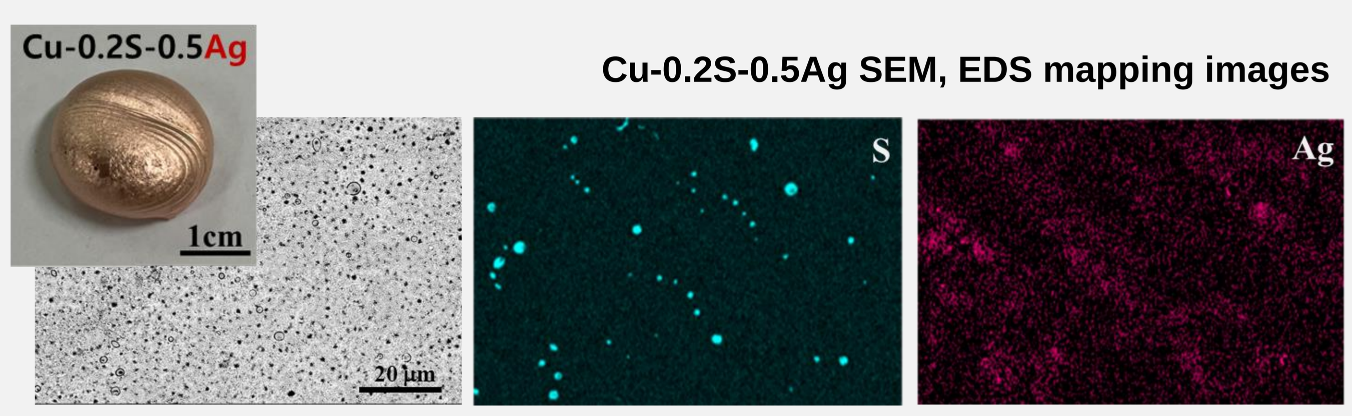
Result & Discussion



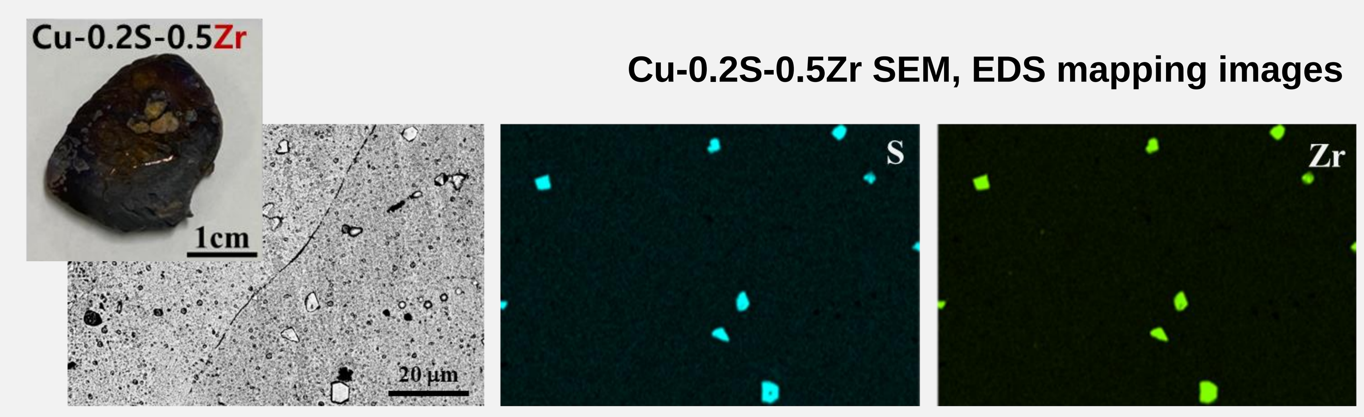
Cu-0.2S-0.5Si SEM, EDS mapping images



Cu-0.2S SEM, EDS mapping images

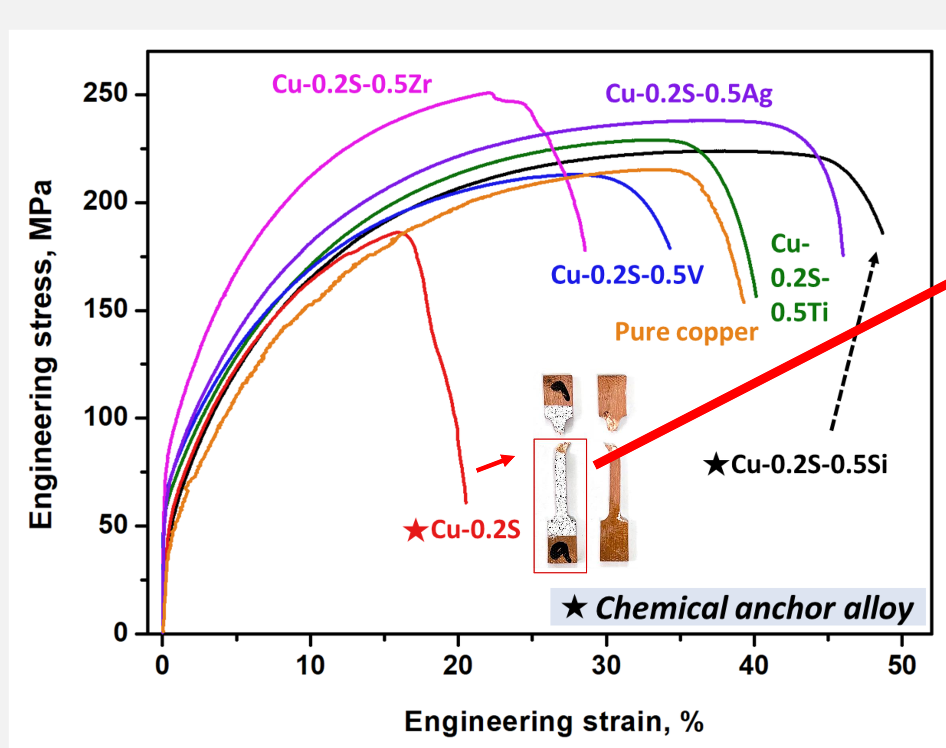


Cu-0.2S-0.5Ag SEM, EDS mapping images

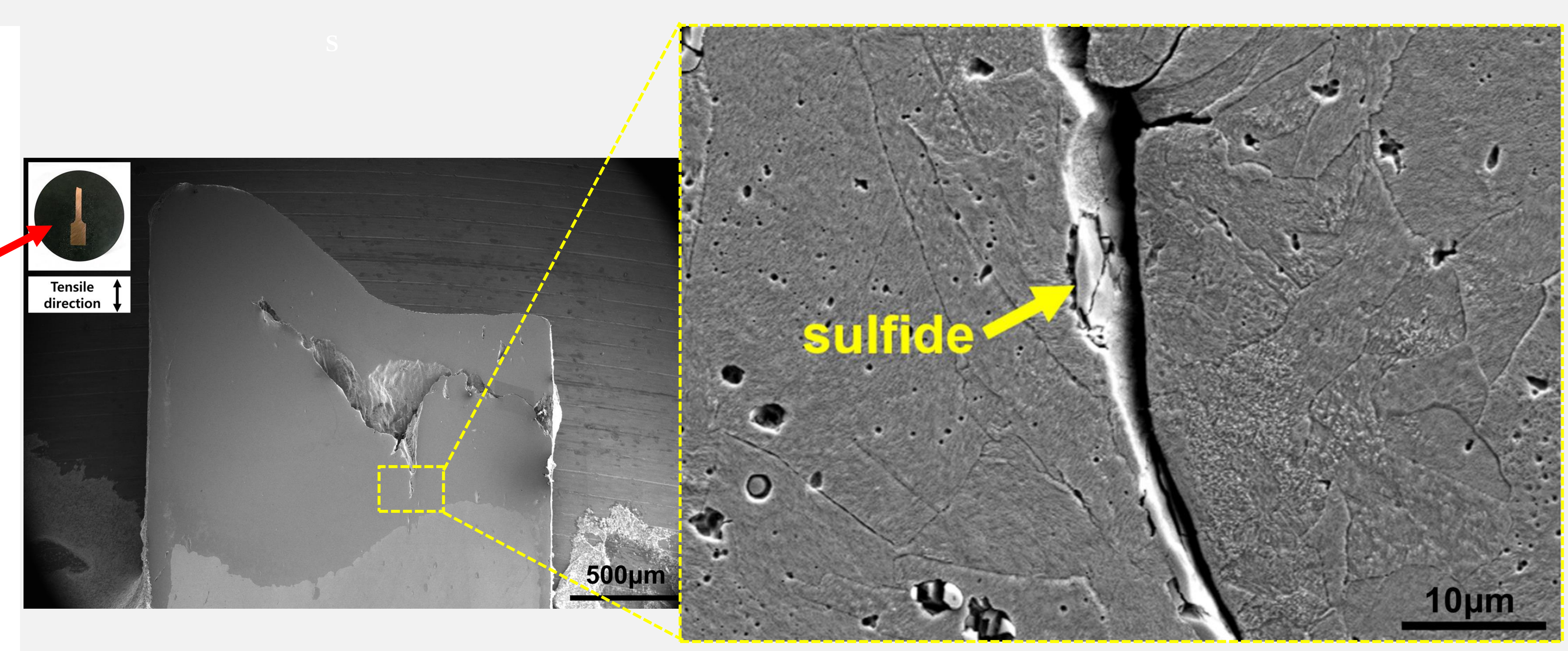


Cu-0.2S-0.5Zr SEM, EDS mapping images

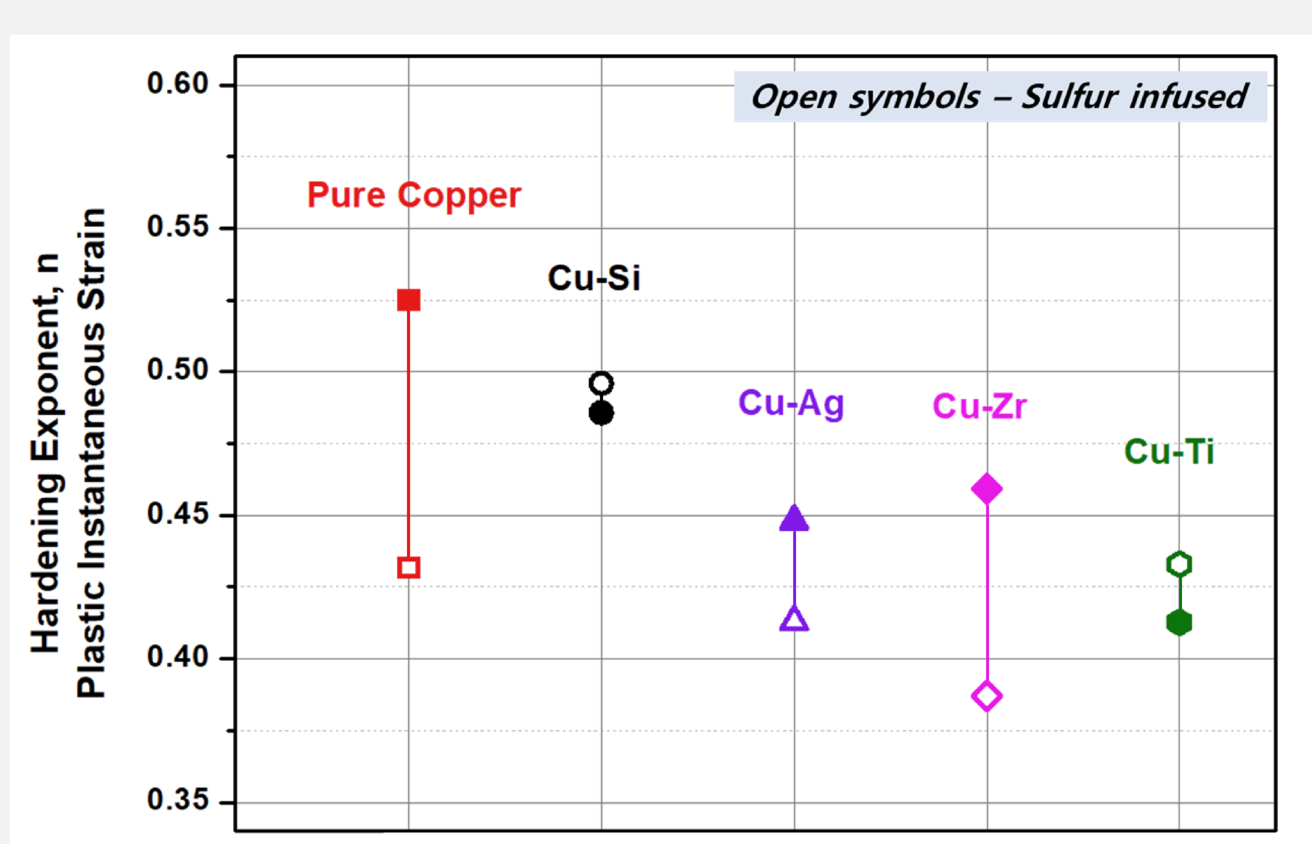
In the case of the casting alloy Cu-0.2S, sulfide was formed on the grain boundary as a result of EDS mapping analysis. For Cu-0.2S-0.5Si, Si is electrochemically dissolved while sulfide is randomly positioned. In the case of Cu-0.2S-0.5Ag, sulfide was formed around the Ag rich phase, and in the case of Cu-0.2S-0.5Zr, sulfide formation energy was lower than Cu, and thus Zr sulfide was formed.



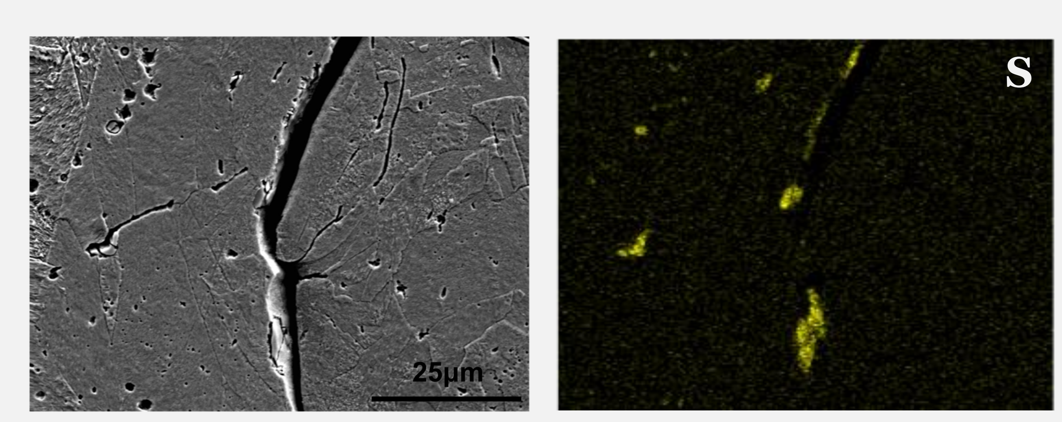
Engineering Strain-Stress Curve



Sulfide on crack tensile fracture of Cu-0.2S SEM image



Hardening exponent, n-value of designed copper alloys



Crack & Precipitate EDS mapping image of Cu-0.2S

As a result of fracture analysis of Cu-0.2S with extremely low elongation, the sulfide around the crack was identified, and it was confirmed that the sulfide became the starting point of the crack. The designed copper alloys demonstrate a reduced decrease in hardening exponent value when sulfur is infused, compared to pure copper. Both Cu-Si and Cu-Zr alloys exhibit minimal decrease in n-value, but Cu-Si alloy demonstrates higher n-value compared to Cu-Zr alloy.

Conclusion

Copper alloy elements Si, Zr, and Ag were used to prevent grain degradation by sulfur. Microstructure analysis of cast materials showed distinct observations: Copper-sulfur alloys: Sulfide formation occurred along the grain boundaries, leading to brittle fractures and crack initiation. Cu-Si alloys: Sulfides formed randomly throughout the material when silicon was added. Grain-boundary sulfide formation was inhibited. Cu-Zi alloys: Zirconium and sulfur combined directly, forming randomly located sulfides. Grain-boundary sulfide formation was inhibited. Cu-Ag alloys: Silver-rich phases with randomly distributed sulfides formed. Grain-boundary sulfide formation was inhibited. Tensile tests confirmed that the addition of alloy elements effectively prevented grain-boundary sulfide formation. Fractured specimens of copper-sulfur alloys showed sulfides around cracks, which acted as crack initiation sites. Overall, the Cu-Si alloy is highly effective in reducing the influence of sulfur, as evidenced by factors such as the location of sulfide formation, elongation rate, and the trend of hardness values. Future studies will investigate the behavior when sulfur is introduced from external sources rather than being directly alloyed into the material.

[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).