Design of Copper Alloys Preventing Grain Boundary Precipitation of Copper Sulfide Particles for a Copper Disposal Canister

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The major concern in the deep geological disposal of spent nuclear fuels include sulfide-induced corrosion and stress corrosion cracking of copper canisters. Sulfur diffusion into copper canisters may induce copper embrittlement by causing Cu_2S particle formation along grain boundaries; these sulfide particles can act as crack initiation sites and eventually cause embrittlement. To prevent the formation of Cu_2S along grain boundaries and sulfur-induced copper embrittlement, copper alloys are designed in this study. Alloying elements that can act as chemical anchors to suppress sulfur diffusion and the formation of Cu_2S along grain boundaries are investigated based on the understanding of the microscopic mechanism of sulfur diffusion and Cu_2S precipitation along grain boundaries. Copper alloy ingots are experimentally manufactured to validate the alloying elements. Microstructural analysis using scanning electron microscopy with energy dispersive spectroscopy demonstrates that Cu_2S particles are not formed at grain boundaries but randomly distributed within grains in all the vacuum arc-melted Cu alloys (Cu-Si, Cu-Ag, and Cu-Zr). Further studies will be conducted to evaluate the mechanical and corrosion properties of the developed Cu alloys.

Keywords: Copper alloy, Sulfur embrittlement, Disposal canister, Sulfide, Alloy design

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1. Introduction

Deep geological disposal of spent nuclear fuels is currently being developed to safely manage highly radioactive waste. The approach adopted by Sweden, Finland, Canada, and Korea is the utilization of a multi-barrier system design in which the spent fuels are sealed in canisters composed of a cast-iron inner vessel for structural integrity and a copper outer shell for corrosion protection. Copper is selected because of its thermodynamical stability in the anoxic environments anticipated in deep geologic repositories [1].

The copper outer shell design of the Scandinavian KBS-3 canister is a separate canister that is 25–50-mm thick. Oxygen free copper is chosen, and phosphorus is added to improve creep resistance [2, 3]; the composition is limited to 30−100 ppm of phosphorus, less than 12 ppm of sulfur, less than 0.6 ppm of hydrogen and less than 5 ppm of oxygen [4]. Canada is considering coating a fully welded iron canister with high-purity and low-oxygen copper to take advantage of the smaller dimension of the CANDU bundle [5, 6]. In Korea, the cold spray technique was employed to manufacture a copper-cast iron canister [7, 8].

The corrosion performance of copper in the environments of a deep geologic repository has been extensively studied. Copper corrosion by the initially trapped oxygen is predicted to be less than 1 mm in thickness, and copper is not anticipated to be susceptible to severe corrosion. However, canister failure due to corrosion of the copper could occur in situations where sulfide plays a key role as a corroding agent [9]. Sulfide ions such as HS^- can be produced by sulfate-reducing bacteria, the dissolution of pyrite, and groundwater [10]. Sulfide-induced pitting corrosion and stress corrosion cracking may cause canister integrity issues when sulfide concentrations and fluxes are substantial [9].

Once sulfur reaches the surface of a copper canister, it can diffuse into the copper outer shell along fast diffusion paths such as grain boundaries and form Cu_2S particles [11]. Immersion tests of pure copper in solution containing sulfide showed that copper is susceptible to intergranular attack by sulfide [12]. Cu_2S particles formed along the grain boundaries act as crack initiation sites and cause embrittlement [13]. This situation should be avoided because the inner iron canister may eventually be exposed to an outer corrosive environment and become vulnerable to corrosion.

In addition to the evaluation of the long-term behavior of copper canisters exposed to sulfide, a proactive approach for protecting copper canisters from corrosion and stress corrosion cracking induced by sulfur is required. To achieve this goal, copper alloys are designed in this study to prevent the grain boundary precipitation of Cu_2S. Based on the understanding on the microscopic mechanism of sulfur diffusion in copper and Cu_2S precipitation along grain boundaries, alloy elements are investigated to act as chemical anchors to suppress sulfur diffusion toward grain boundaries. Model alloys are experimentally manufactured to validate the alloy performance in reducing Cu_2S precipitation along grain boundaries.

2. Copper Alloy Design

Theoretical investigation shows that a sulfur impurity in copper strongly attracts a vacancy and forms stable and highly mobile sulfur-vacancy defects [14]. These sulfur-vacancy defects can rapidly diffuse due to their high mobility, and thus, the diffusion of sulfur in copper is high in the bulk and considerably higher at grain boundaries [15]. The sulfur-vacancy defects interact with each other and facilitate the formation of stable Cu_2S particles at grain boundaries.

The microscopic mechanism of Cu_2S formation reveals that the addition of solutes that compete to attract vacancies can decrease the number of vacancies available for the sulfur-vacancy defects formation and eventually inhibit the formation of Cu_2S.

Fig. 1(a) shows the calculated solute-vacancy binding energies of solute elements in Cu, obtained by using first-principle atomistic calculations based on density functional theory [16]. The calculated nearest-neighbor
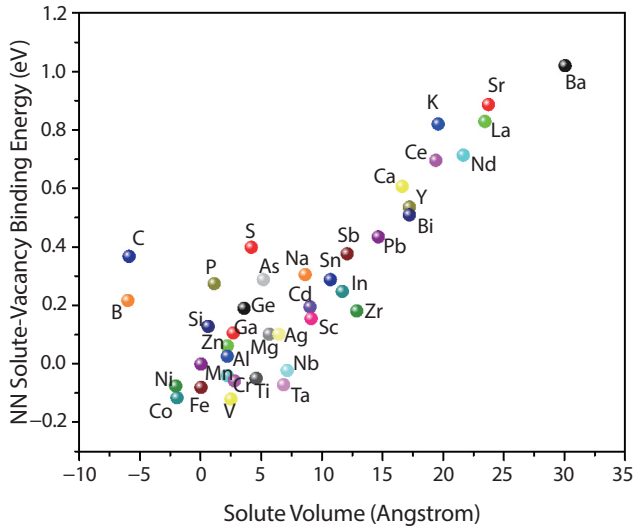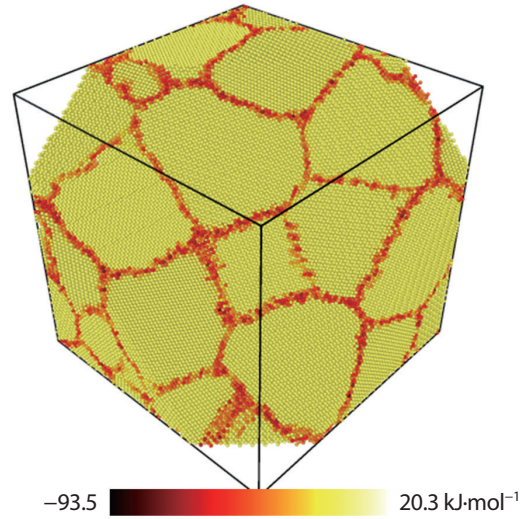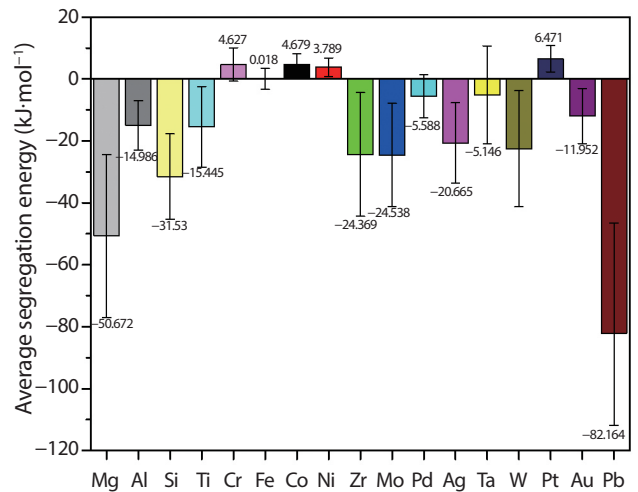
(a)
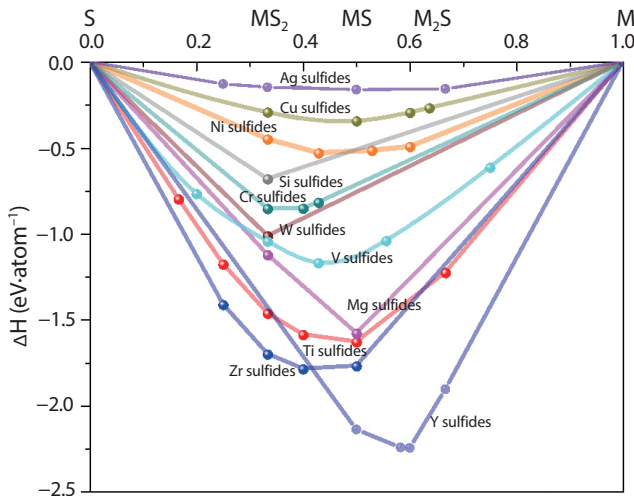
(b)

Fig. 1. (a) Nearest-neighbor solute-vacancy binding energies in Cu, (b) formation enthalpy of metal sulfides.

(a)

(b)

Fig. 2. (a) Si solute segregation energies at grain boundaries in a Cu polycrystal, (b) average grain boundary segregation energies of various solutes in Cu.

solute-vacancy binding energies show that the sulfur-vacancy has a positive (approximately 0.4 eV) binding energy. Solutes with high binding energies, such as Ba, Sr, and La, have a large solute volume, which leads to limited solubility in Cu. Hence, solutes with a binding energy greater than 0.5 eV may not be favorable for reducing the number of the sulfur-vacancy defects due to their limited solubility.

Solute elements that have a strong tendency to form sulfides may hinder the formation of Cu_2S by acting as scavenging solutes for sulfur. Fig. 1(b) shows the calculated change in enthalpy caused by the formation of metal sulfides [17]. A negative value represents the formation of stable metal sulfides. For example, the change in formation enthalpy of Cu_2S is -0.293 eV·atom^{-1}, and that of YS is -2.141 eV·atom^{-1}. As is shown in Fig. 1(b), solute elements such as Y, Zr, and Ti exhibit a strong tendency to form

(a)   (b)
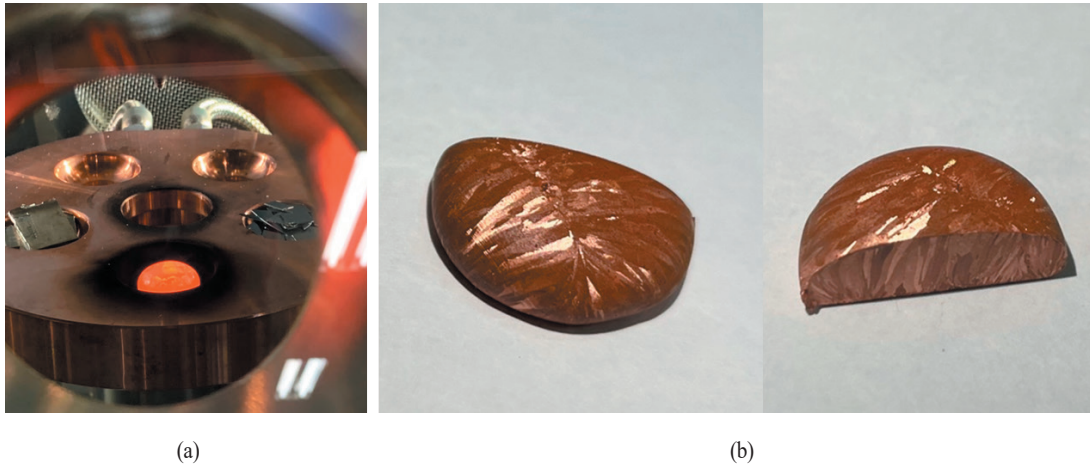
Fig. 3. (a) Melted-and-solidified Cu ingot in vacuum arc melting system, (b) vacuum-arc-melted Cu ingot.

sulfides.

Sulfur diffuses into the copper outer shell of spent fuel disposal canisters through grain boundaries. Solutes that tend to segregate around grain boundaries in Cu are good anchors for sulfurs to diffuse and form Cu_2S particles. Recently a machine-learning framework that can accurately predict the relaxed segregation energy of a solute atom in a grain boundary site was proposed [18]. Fig. 2(a) shows an example of the calculated segregation energy (the internal energy difference between the solute atoms occupying the grain boundary site and a bulk site) of Si atoms in Cu grain boundary sites for Si in Cu. A negative internal energy difference indicates that solute segregation occurs around grain boundaries. Average segregation energies for some solutes in Cu are shown in Fig. 2(b).

Si and Ag alloying elements show a strong tendency to bind with vacancies and enable grain boundary segregation based on the solute-vacancy binding energies (Fig. 1(a)), formation enthalpy of metal sulfides (Fig. 1(b)), and grain boundary segregation energy (Fig. 2(b)). Therefore, these elements are selected to test the effects of solutes in blocking the formation of Cu_2S at grain boundaries. A Zr alloying element is also chosen because of its strong tendency to form sulfides and allow grain boundary segregation.

3. Experimental

Ingots of Cu-0.2at%S, Cu-0.5at%Si-0.2at%S, Cu-0.5 at%Ag-0.2at%S, and Cu-0.5at%Zr-0.2at%S alloys were produced by arc-melting high-purity elements using vacuum arc melting system (Samhan Vacuum Development CO.LTD). Fig. 3(a) shows an example of a melted-and-solidified Cu ingot having a mass of 26 g in the vacuum arc-melting system. Fig. 3(b) depicts the slightly etched surface of a Cu ingot (approximately 2.5 cm diameter), which reveals grain morphology. The microstructures of the Cu alloys containing sulfur were investigated using focused ion beam scanning electron microscope (FIB-SEM; Thermo Fisher Scios 2) with energy dispersive spectroscopy (EDS).

Fig. 4 displays the SEM micrographs of Cu-0.2at%S at different magnifications along with the EDS mapping image for sulfur. The SEM micrographs show particles with spherical and elliptical morphologies along grain boundaries. The EDS maps indicate that these particles contain a higher concentration of sulfur and, thus, are copper sulfide particles. Copper sulfides form along grain boundaries in pure Cu, as shown in Fig. 4.

The microstructures of Cu-0.5at%Si-0.2at%S are shown in the SEM micrographs of Fig. 5. Sulfide particles are no longer aligned along grain boundaries but randomly
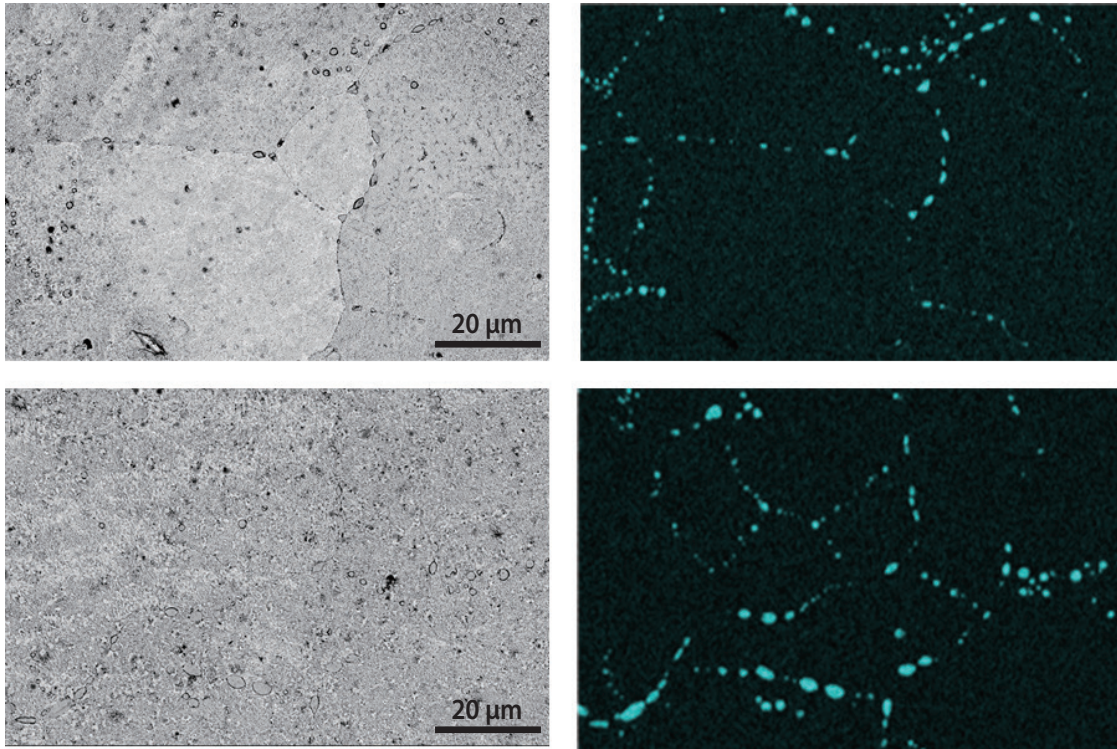
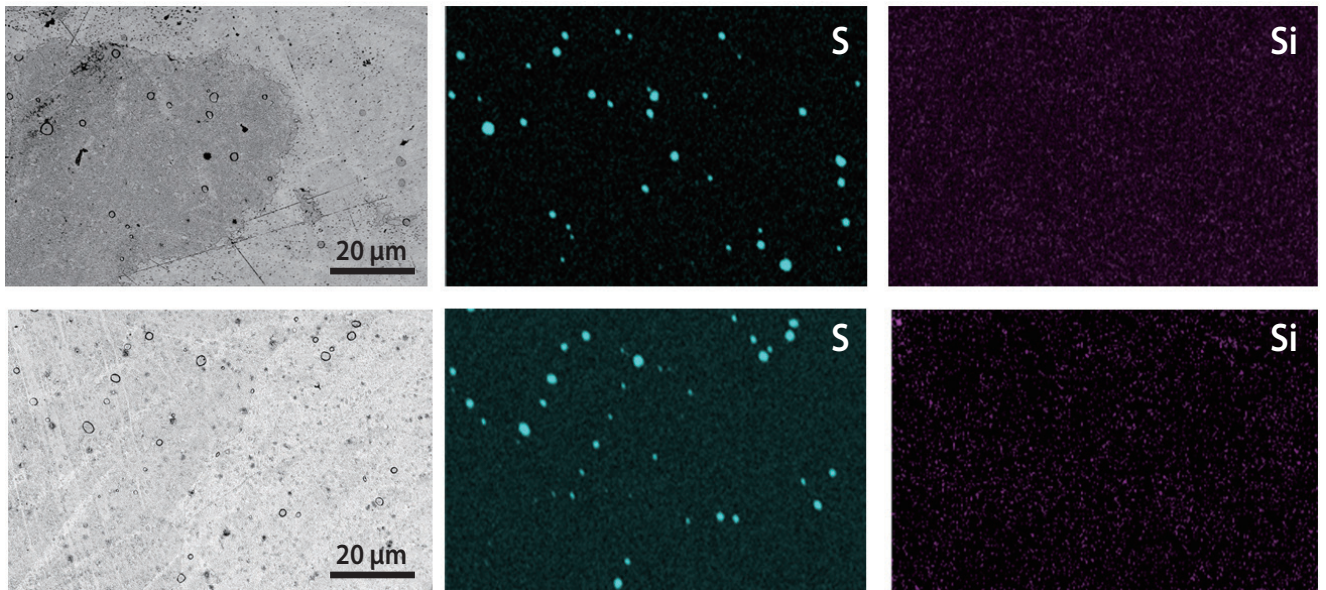Fig. 4. SEM micrographs and EDS maps for S in Cu-0.2at%S.

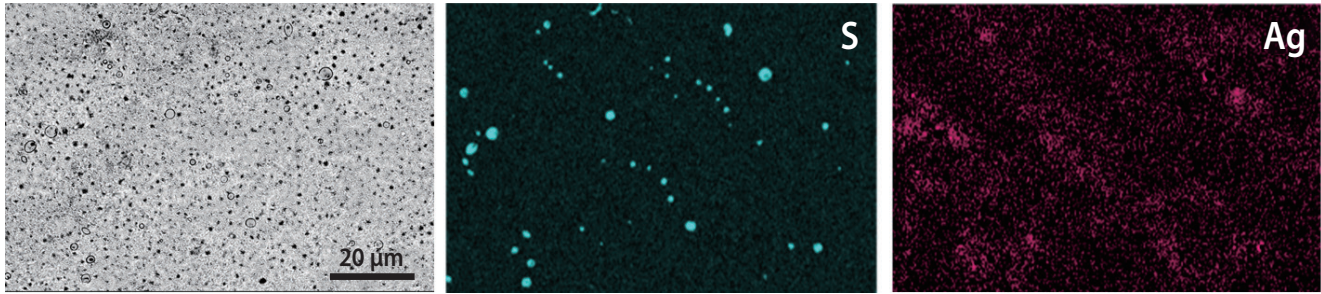Fig. 5. SEM micrographs and EDS map for S and Si in Cu-0.5at%Si-0.2at%S.

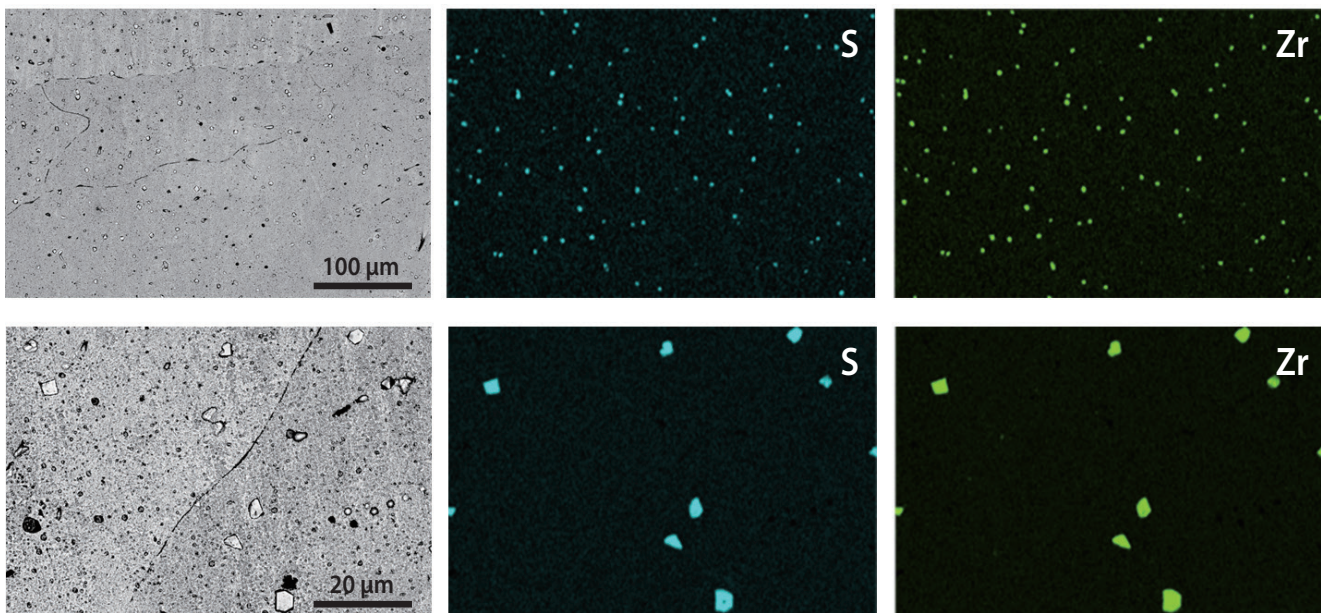Fig. 6. SEM micrograph and EDS map for S and Ag in Cu-0.5at%Ag-0.2at%S.

Fig. 7. SEM micrographs and EDS map for S and Zr in Cu-0.5at%Zr-0.2at%S.

distributed inside the grains. According to the Cu-Si phase diagram, Cu has significant Si solubility (~8at%). The EDS map for Si shows that no Si-rich phase and no spatial correlation with sulfur exist.

The SEM image and EDS map for S in Cu-0.5at% Ag-0.2at%S (Fig. 6) show that sulfide particles are formed inside the grains. The phase diagram of Cu-Ag illustrates that Cu-rich and Ag-rich phases are stable at room temperature. The EDS map for Ag (Fig. 6) shows that Ag-rich regions are present and that the sulfide particles seem to be more preferentially formed in Ag-rich regions.

Fig. 7 shows the SEM and EDS results for Cu-0.5

at%Zr-0.2at%S. Sulfide particles are randomly distributed inside grains and not aligned along grain boundaries, like the other Cu alloys. The EDS map for Zr clearly shows that the sulfide particles are zirconium sulfide rather than copper sulfide, as expected from the negative value of the formation enthalpy shown in Fig. 1(b).

4. Conclusions

Copper alloys are designed to prevent Cu_2S particle formation along grain boundaries, which leads to

sulfur-induced embrittlement of copper. Based on the understanding on the microscopic mechanism of copper sulfide formation at grain boundaries, alloying elements that exhibit positive binding energy with vacancies are selected to suppress the formation of sulfur-vacancy complexes. Alloying element with a stronger tendency to form sulfides than copper can also be suitable for the intended copper alloy design. Si, Ag, and Zr alloying elements are selected for this purpose and experimental validation. All the vacuum-arc melted Cu alloys (Cu-Si, Cu-Ag, and Cu-Zr) demonstrate that Cu_2S particles are not formed at grain boundaries but randomly distributed inside grains. In future studies, the mechanical and corrosion properties of the developed copper alloys will be evaluated and compared with those of pure copper.

Acknowledgements

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