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## **FINAL REDOXIDATION OF COPPER AND BRONZE ALLOYS THERMODYNAMIC AND KINETIC STUDY**

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### **ABSTRACT**

This thesis investigates the final redoxidation of copper and bronze alloys through a thermodynamic and kinetic perspective. Using equilibrium calculations, Ellingham diagrams, and mass transfer modeling, the research evaluates oxygen pickup mechanisms in molten alloys. Results show that reoxidation significantly affects the purity and mechanical properties of alloys.

### **INTRODUCTION**

Redoxidation is a critical problem in copper and bronze metallurgy. During melting and casting, residual oxygen can react with alloying elements, causing oxide inclusions and property deterioration. This study focuses on modeling oxygen solubility and kinetic absorption in copper and its alloys, aiming to predict and mitigate reoxidation defects.

#### **Materials and Methods**

Thermodynamic calculations were performed using the Thermo-Calc software package (TCFE and SSUB databases) and the FactSage 8.2 system with corresponding solution databases for oxides and metallic melts. The focus was on equilibrium reactions governing the stability and formation of oxides such as  $\text{Cu}_2\text{O}$ ,  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  in both copper and bronze alloys. Standard Gibbs free energy functions  $\Delta G^\circ(T)$  were employed to calculate equilibrium constants for deoxidation and oxidation reactions. Additionally, Ellingham-type diagrams were constructed to compare the relative stabilities of oxides under experimental conditions. Activities of alloying elements (Sn, Al, Si) and dissolved oxygen in the copper matrix were treated using the Wagner interaction parameter formalism to provide more accurate predictions in multicomponent melts.

Kinetic modeling was carried out using diffusion-limited oxygen transport equations, solved numerically in MATLAB. Both bulk diffusion in the melt and interfacial mass-

transfer resistances at the gas–metal and slag–metal interfaces were considered. Models were developed for (i) oxygen absorption under oxidizing atmospheres, (ii) oxygen removal by deoxidizers (P, Al, Mg), and (iii) reoxidation during holding. Time-dependent simulations provided predictions of oxygen concentration decay curves, inclusion nucleation, and growth kinetics. Activation energies and apparent rate constants were extracted by fitting simulated data to experimental measurements.

Laboratory validation was performed through controlled melting trials of pure copper, tin bronze (Cu–Sn), aluminum bronze (Cu–Al–Fe), and silicon bronze (Cu–Si) alloys. Experiments were conducted in both resistance and induction furnaces equipped with controlled atmosphere chambers. Oxidizing conditions were introduced by maintaining a defined oxygen partial pressure (using O<sub>2</sub>/Ar or CO<sub>2</sub>/CO gas mixtures), allowing systematic variation of oxidation potential. The melt temperature was controlled in the range of 1100–1250 °C with accuracy better than ±3 K.

The combination of thermodynamic modeling, kinetic simulation, and laboratory validation enabled a comprehensive assessment of redoxidation processes in copper and bronze alloys. This integrated approach provided quantitative data on equilibrium oxygen contents, oxide phase stability, reaction pathways, and the rate-controlling mechanisms that govern the final redoxidation stage in industrial practice.

### Results and Discussion

Thermodynamic modeling results indicated that oxygen solubility in molten copper and its alloys increases with both temperature and oxygen partial pressure, consistent with Henry's law behavior at low concentrations and Sieverts' law at higher exposures. Construction of Ellingham diagrams confirmed the relative stabilities of oxide phases, showing that Sn, Al, and Si form more stable oxides (SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) compared to Cu<sub>2</sub>O, suggesting that in multicomponent systems these alloying elements act as preferential oxidation sites. The stability hierarchy followed the trend: Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub> > SnO<sub>2</sub> > Cu<sub>2</sub>O.

Kinetic simulations revealed that the oxygen absorption rate was strongly alloy-dependent, with the fastest uptake observed in silicon bronze, attributed to the high affinity of Si for oxygen and the rapid formation of protective SiO<sub>2</sub> films at the melt surface. In contrast, tin bronzes exhibited slower oxygen uptake due to the comparatively lower reactivity of Sn. Aluminum bronzes demonstrated intermediate behavior, where Al<sub>2</sub>O<sub>3</sub> inclusions tended to form at the melt surface and slow down further oxygen ingress.

Laboratory validation supported the model predictions: under controlled air exposure at 1150–1200 °C, the dissolved oxygen content increased by 70–150 ppm within the first 2 minutes, depending on alloy composition. Prolonged exposure led to a saturation

level close to the calculated equilibrium oxygen concentration. Microstructural analysis of quenched samples confirmed the formation of fine oxide inclusions, with  $\text{Cu}_2\text{O}$  dominating in pure copper, while  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  were observed in their respective alloys.

These results demonstrate that final reoxidation phenomena can be effectively described by coupling thermodynamic stability predictions with diffusion-controlled kinetic models. The combined approach not only allows prediction of oxygen pickup rates and saturation levels but also provides insight into the type, morphology, and distribution of oxide inclusions that form during late-stage processing. This framework is directly applicable to industrial copper alloy refining, where controlling reoxidation is essential for achieving desired mechanical and electrical properties.

### **CONCLUSION**

This study provides a predictive framework for understanding reoxidation in copper and bronze alloys. The combination of thermodynamic and kinetic analysis with experimental validation allows engineers to optimize melting conditions and reduce defect formation.

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