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Development of novel Cu-Cr-Nb-Zr alloys with the aid of computational thermodynamics☆

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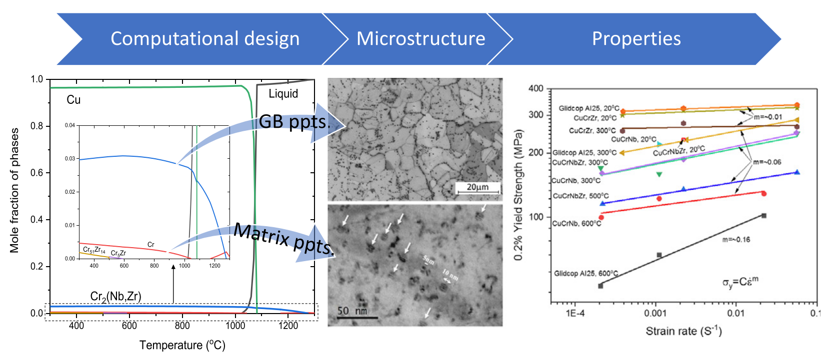
HIGHLIGHTS

- Novel Cu-based creep-resistant alloys were designed with the aid of computational thermodynamics.
- The new Cu alloys were fabricated using an economic ingot-making method.
- Multi-modal precipitate distribution with larger ones at grain boundaries or dislocations and smaller ones in the matrix have been produced in the microstructure of new Cu alloys.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-modal precipitate distribution in the microstructure, with coarse precipitates pinning the grain boundaries and finer precipitates strengthening the matrix, is beneficial to suppress grain boundary sliding and dislocation creep, respectively, of structural materials. However, achievement of a multi-modal precipitate distribution remains a challenge in developing creep-resistant advanced Cu alloys while retaining high strength and high conductivity at elevated temperature. This work overcame this challenge with the aid of computational thermodynamics. Thermodynamic models for Gibbs energy functions of phases in the Cu-Cr-Nb-Zr system have been developed in this study. These models were then used to calculate solidification paths and phase equilibria at different temperatures, guiding the design of chemical composition and heat treatment parameters of novel copper alloys with a target multi-modal distribution of precipitates. The new alloy, fabricated through traditional ingot metallurgy method, has achieved the desired microstructure as validated by optical and transmission electron microscopy. Electrical conductivity and mechanical properties were screened and compared with the existing commercial Cu alloys.

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1. Introduction

High strength, high conductivity copper alloys are a potentially attractive option for a variety of demanding high heat flux structural applications ranging from aerospace to fusion energy [1,2]. The performance requirements for fusion energy applications are particularly demanding, where high thermal heat flux capability and resistance to neutron irradiation-induced property degradation are simultaneously required [3,4]. High strength, high conductivity copper alloys are being utilized in the International Thermonuclear Energy Reactor (ITER), and are under consideration for next step fusion devices in Europe and elsewhere [2]. The optimized strength and conductivity near room temperature for copper alloys is typically achieved by introducing a small volume fraction (f~1–5%) of uniformly dispersed nanoscale (diameter ~3–10 nm) precipitates or dispersoids [5–10]. These precipitates can be either produced by solution anneal and aging, or powder metallurgy approaches [11]. Although impressive room temperature yield strengths of 300–1000 MPa and conductivities 200–360 W/m-K have been achieved in several Cu alloys, all current commercially available high strength, high conductivity Cu alloys suffer significant creep deformation at temperatures above 300–400 °C [5]. Since 400 °C in Cu is equal to 0.5 T_M (where T_M is the absolute melting temperature), such an operating temperature corresponds to the onset of pronounced thermal creep in simple metals due to high atomic mobility. In order to achieve improved strength near or above 400 °C, new Cu alloys specifically tailored for thermal creep resistance need to be designed. To date, there has been insufficient commercial incentive to develop high performance thermal creep-resistant Cu alloys since most of the current commercial applications for Cu alloys involve operating temperatures near room temperature (high field magnets, resistance spot welding electrodes, chill block molds, air- or water-cooled high heat flux apparatus, etc.).

Analysis of creep deformation mechanisms for existing Cu alloys near 400 °C suggests it is associated with dislocation (power law) creep and grain boundary sliding (Coble creep) mechanisms [5]. The design basis for improved high-temperature, high-performance radiation-resistant copper alloys relies on three key considerations (in addition to high conductivity) [5]: 1) thermally stable microstructure up to high temperatures; 2) specifically tailored radiation-stable microstructural features to inhibit the relevant thermal creep deformation mechanisms (dislocation creep, grain boundary sliding, etc.); and 3) sufficient matrix dispersoid density to enable suitable radiation resistance. Several authors have summarized the physical metallurgy principles for designing high performance creep-resistant Cu alloys [12–15]. Key design aspects include use of coarse particles along grain boundaries to suppress grain boundary sliding along with high-density fine-scale matrix precipitates to suppress dislocation motion. The fine-scale matrix particles also impart helpful radiation resistance by enhancing interstitial-vacancy radiation point defect recombination [16].

Despite the well understood design criteria, achievement of the desired multi-modal precipitate distribution in Cu alloys remains a challenge. Large grain boundary precipitates were introduced into a Cu-8Cr-4Nb (at.%) alloy to achieve excellent high temperature coarsening and creep resistance; however, a relatively expensive rapid solidification or powder metallurgy method had to be used to control the size and distribution of this high-melting point Cr_2Nb_Lave precipitate [17]. A high density of fine matrix Cr precipitates can be easily achieved by traditional precipitation hardening heat treatment techniques in Cu-(0.6–1.0)Cr-(0.1–0.2)Zr alloys which show excellent room temperature strength [3–10]. However, these Cr precipitates quickly coarsen and lose their strengthening effect at temperatures near or above the ~470 °C aging temperature [18]. Based on results obtained on rapidly solidified Cu-Cr-Nb [19] and precipitation-strengthened Cu-Cr-Zr alloys [20,21], the Cu-Cr-Nb-Zr system was identified to offer the opportunity to simultaneously form Cr_2Nb-type Laves-phase intermetallic precipitates that pin grain boundary motion and provide high temperature strength, and finer-scale Cr matrix precipitates to provide obstacles to dislocation climb/glide (and to serve as radiation defect recombination centers). Another major goal in this investigation was to utilize computational thermodynamics to guide the design of a new alloy that could be fabricated using conventional ingot metallurgy techniques for precipitation strengthened alloys rather than more expensive powder metallurgy/rapid solidification processes. Although Nb is not a low activation element (desirable for fusion energy applications), our initial efforts are focused on Cu-Cr-Nb-Zr alloys to examine the proof of principle of a newly designed thermal creep resistant alloy that also has good thermal and electrical conductivity and suitable neutron irradiation resistance at 300–450 °C.

2. Methodology

2.1. Thermodynamic modeling of the Cu-Cr-Nb-Zr system

To design new Cu alloys with a multi-modal precipitate distribution, i.e., coarse precipitates at grain boundary and fine precipitates in the matrix, computer coupling of phase diagrams and thermo-chemistry, i.e., the CALPHAD approach [22] was used to aid the accelerated alloy design for specific compositions and heat treatments. In this approach, the Gibbs energy of individual phases is modeled based on crystal structure, defect type and phase chemistry. The model parameters are collected in a thermodynamic database. The thermodynamic database is then coupled with phase diagram calculation software to predict the phase behavior in experimentally uninvestigated regions of a multi-component system. Thermodynamic modeling begins with the evaluation of the thermodynamic descriptions of unary and binary systems. By combining the thermodynamic descriptions of constitutive binary systems and ternary experimental data, a thermodynamic description of ternary systems is developed, and so forth. These descriptions cover the whole composition and temperature ranges including the experimentally uninvestigated regions. The Gibbs energy functions of the four unary systems Cu, Cr, Nb and Zr were adopted from the SGTE (Scientific Group Thermodata Europe) database compiled by Dinsdale [23]. The Gibbs energy functions of phases in the six constituent binaries were adopted from previous work done by Hämäläinen et al. [24] for Cu-Cr and Cu-Nb, and Zeng et al. [25] for Cu-Zr, Neto et al. [26] for Cr-Nb, Yang et al. [27] for Cr-Zr and Fernandez et al. [28] for Nb-Zr. The Gibbs energy functions in the constituent ternary Cu-Cr-Zr and Cu-Cr-Nb were adopted from the work done by Zeng et al. [29] and Liu et al. [30], respectively. No prior thermodynamic modeling work has been done on the Cu-Nb-Zr and Cr-Nb-Zr systems. The Gibbs energy functions of phases in these two systems were obtained from extrapolation, i.e., the weighted average of the energy functions of the same phase from the three constituent binaries using the Redlich-Kister geometric model [31]. No prior phase equilibria and thermodynamic property data for the Cu-Cr-Nb-Zr quaternary system were found in literature. Therefore, the thermodynamic functions for the quaternary alloy were obtained through extrapolation from the four constituent ternaries. Thermodynamic models and parameters in the Gibbs energy functions of phases in the Cu-Cr-Nb-Zr system are listed in the Appendix A.

2.2. Experimental procedure

The dramatic difference in the melting temperature of Nb (2468 °C) and Cu (1083 °C) would cause excessive vaporization of Cu if the four elements were melted simultaneously. To minimize Cu vaporization, Cr (T_M = 1907 °C) and Nb were pre-alloyed with a composition of Cr-18 at.%Nb, close to the eutectic composition of Cr and Laves_Cr_2Nb that melts at 1620 °C. The pre-alloy was crushed in small pieces in a steel mortar and then melted with Cu and Zr to form an ingot with the designed composition. The ingot was made in an argon protected arc-melting furnace followed by drop-casting into the shape of 1.25 × 1.25 × 0.75 cm bar, with an approximate mass of 100 g. The