Postprint: Study on Solidification Process of Cu-Co-Fe Atomized Droplets

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Abstract

Gas atomization rapid solidification experiments were conducted on Cu-10%Co-10%Fe (mass fraction, hereinafter) metastable liquid-phase immiscible alloys, preparing composite powders with Fe-Co-rich spherical particles uniformly distributed in the Cu matrix. The governing equations for temperature field, concentration field, and liquid-liquid phase transformation kinetics during cooling of Cu-Co-Fe alloy atomized droplets were established, and a simulation method coupling alloy thermodynamics and phase transformation kinetics was developed to simulate and analyze the solidification microstructure formation process of Cu-10%Co-10%Fe alloy atomized droplets. Experimental and simulation results show that under gas atomization rapid solidification conditions, the effects of Marangoni migration and Ostwald ripening of Fe-Co-rich phase droplets during the liquid-liquid phase transformation are very weak, and the spatial distribution of Fe-Co-rich phase particles is uniform in most regions of the powder center. For Cu-10%Co-10%Fe alloy powders with diameters less than 220 m, the average radius and number density N of Fe-Co-rich phase particles follow an exponential relationship with the atomized powder diameter d.

Full Text

Preamble

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Study on Solidification of Gas-Atomized Droplets of Cu-Co-Fe Alloy*

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Abstract

Rapid solidification experiments via gas atomization were conducted on Cu-10%Co-10%Fe (mass fraction) metastable immiscible alloy, producing composite powders with spherical Fe-Co-rich particles uniformly distributed in a Cu matrix. Governing equations for temperature field, concentration field, and liquid-liquid phase transformation kinetics during cooling of atomized droplets were established, and a simulation method coupling alloy thermodynamics with phase transformation kinetics was developed to analyze the microstructure formation process in gas-atomized Cu-10%Co-10%Fe alloy droplets.

Both experimental and simulation results demonstrate that under rapid cooling conditions of gas atomization, the effects of Marangoni migration and Ostwald ripening of Fe-Co-rich droplets during liquid-liquid transformation are very weak, yielding uniform spatial distribution of Fe-Co-rich particles throughout most of the powder interior. For Cu-10%Co-10%Fe alloy powders with diameters less than 220 m, the average radius (Ra) and number density (N) of Fe-Co-rich particles follow exponential relationships with powder diameter (d).

Keywords: Cu-Co-Fe alloy, liquid phase decomposition, rapid solidification, modeling and simulation

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Cu-Co-Fe alloys exhibit excellent properties including high strength, high electrical conductivity, and giant magnetoresistance (GMR) effects, making them promising candidates for electrical contact materials, integrated circuit lead frames, wires and cables, and ferromagnetic applications [1,2]. However, these alloys possess a metastable miscibility gap in the liquid state, and liquid-liquid phase transformation during cooling readily produces severely segregated microstructures [3,4]. In recent years, the Cu-Co-Fe system has served as a model alloy for investigating solidification behavior in alloys with metastable liquid miscibility gaps [5–14].

Previous research has focused primarily on thermodynamic aspects. Kim and Abbaschian [5] measured liquidus temperatures and metastable liquid-phase separation temperatures, identifying a metastable miscibility gap for certain Co and Fe compositions. Cao and Görler [6] performed differential thermal analysis (DTA) to determine liquidus and metastable liquid-phase separation temperatures for alloys with Cu atomic fractions between 10% and 84% and Co:Fe ratios of 1:3, 1:1, and 3:1. Curiotto et al. [7] employed differential scanning calorimetry (DSC) for similar measurements. Munitz et al. [8] optimized thermodynamic parameters for the Cu-Co-Fe system and calculated the metastable liquid-phase separation temperatures. Turchanin et al. [9] investigated liquid-phase mixing enthalpies using calorimetry and evaluated thermodynamic parameters via

phase diagram calculations. Additional thermodynamic optimizations were reported by Bamberger et al. [10], Wang et al. [11], and Palumbo et al. [12].

On the kinetic front, Munitz et al. [8] conducted deep undercooling experiments to examine the effects of undercooling and cooling rate on solidification microstructure, revealing that at high undercooling, liquid-liquid transformation occurs with Fe-Co-rich phase morphology evolving from dendritic to dendritic-plus-spherical to fully spherical with increasing undercooling. Munitz and Abbaschian [13] studied liquid-liquid separation behavior under high cooling rates using electron beam surface melting. Dai et al. [14] investigated the liquid-liquid phase separation process using drop tube techniques. These studies demonstrate that rapid solidification can effectively suppress liquid-phase separation and segregation in Cu-Co-Fe alloys.

Microstructure evolution during liquid-liquid transformation results from the combined effects of nucleation, growth, coarsening, and spatial migration of dispersed-phase droplets—a complex process with multiple interacting factors that is difficult to explore experimentally. Computational simulation provides an effective tool for elucidating solidification mechanisms in immiscible alloys [15,16]. In this work, we combine gas atomization rapid solidification experiments with computer simulation to investigate microstructure formation in Cu-10%Co-10%Fe alloy under rapid cooling conditions.

1 Experimental Methods

Cu-10%Co-10%Fe alloy (mass fraction) was prepared from raw materials with purity 99.9%. The experimental procedure consisted of: (1) heating the charge to 1420°C in a KGPS100/2.5 vacuum induction furnace and holding for 15–20 minutes to ensure complete dissolution and form a homogeneous melt; (2) atomizing the melt into droplets using N gas at 3 MPa pressure to achieve rapid cooling and solidification; and (3) sieving, mounting, and polishing the atomized powders for microstructural observation using an Axiovert 200MAT optical microscope (OM) and S-3400N scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) analysis. Quantitative metallographic analysis of second-phase particle size and distribution was performed using SISC IAS V8.0 software.

2 Results and Discussion

2.1 Microstructure

[Figure 1: see original paper] shows the microstructure and number density distribution of Cu-10%Co-10%Fe alloy powders with different diameters. Based on the vertical section phase diagram of the Cu-Co-Fe system [5] and EDS analysis (Fig. 2 [Figure 2: see original paper]), the dark second phase is identified as Fe-Co-rich phase while the light matrix is Cu-rich phase. For atomized powders smaller than 220 m, the microstructure consists of spherical Fe-Co-rich parti-

cles dispersed in a Cu-rich matrix. The size of Fe-Co-rich spherical particles increases with powder size.

According to literature [5], when the undercooling of Cu-10%Co-10%Fe alloy melt exceeds 24 K, atomized droplets undergo liquid-liquid transformation with Fe-Co-rich droplets nucleating and growing in the Cu-rich liquid. Since the binodal line in the Cu-Co-Fe system lies below the liquidus, Fe-Co-rich droplets become undercooled immediately upon formation and tend to solidify. If the cooling rate is sufficiently high to prevent solidification of Fe-Co-rich droplets while passing through the miscibility gap, these droplets will solidify below the peritectic reaction temperature, forming spherical Fe-Co-rich particles and yielding the microstructure shown in [Figure 1: see original paper]. The Fe-Co-rich spherical particles are essentially uniformly distributed, with only a slight reduction in number density observed in a thin surface region of the atomized powders ([Figure 1: see original paper]b and d).

2.2 Modeling and Simulation

2.2.1 Model Establishment During solidification, heat at the droplet surface is transferred via convection to the surrounding gas environment, while internal heat is transported through conduction and dispersed-phase droplet motion. The temperature field in an atomized droplet satisfies:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_P}\nabla^2 T + \frac{Q_{S/L}}{\rho C_P} - \frac{h(T_s - T_g)}{\rho C_P} - \frac{\rho_\beta C_{P\beta}}{\rho C_P}\mathbf{u}_\beta \cdot \nabla T$$

where T is temperature; ρ, C_P, and k are alloy density, specific heat, and thermal conductivity, respectively; ρ_β and $C_{P\beta}$ are density and specific heat of the dispersed phase; $Q_{S/L}$ is the latent heat release rate at solid/liquid interfaces; h is the convective heat transfer coefficient between droplet surface and atomizing gas [17]; T_s is droplet surface temperature; T_g is atomizing gas temperature [18]; and $\mathbf{u}_\beta$ is the Marangoni migration velocity of dispersed-phase droplets.

The convective heat transfer coefficient is given by:

$$h = \frac{k_g}{d}(2 + 0.6\mathrm{Pr}^{1/3}\mathrm{Re}^{1/2})$$

where d is droplet diameter, k_g is gas thermal conductivity, Pr is Prandtl number, and Re is Reynolds number.

Solute transport during liquid-liquid transformation occurs through diffusion and spatial motion of dispersed-phase droplets. Based on solute conservation, the concentration field for component i satisfies:

$$\frac{\partial C_i}{\partial t} = D_i\nabla^2 C_i - \mathbf{u}_\beta \cdot \nabla C_i - 4\pi R^2 N v_R (C_i^\beta - C_i)$$

where $S_i = (C_i - C_i^{eq})/(C_i^{\beta} - C_i^{eq})$ is supersaturation of component i in the matrix; C_i^{eq} is equilibrium concentration; C_i is actual concentration; C_i^{β} is concentration in dispersed-phase droplets; ϕ is matrix volume fraction; D_i is diffusion coefficient; and N is droplet number density.

The droplet radius distribution function $F(R, r, t)$, representing the number of dispersed-phase droplets per unit volume with radii between R and $R + dR$ at position r and time t, satisfies the continuity equation:

$$\frac{\partial F}{\partial t} + \nabla \cdot (\mathbf{u}_{\beta} F) + \frac{\partial}{\partial R}(v_R F) = I(R^*)$$

where v_R is droplet growth velocity, I is nucleation rate [19,20], and R^* is critical nucleation radius. The left terms describe temporal evolution, droplet motion, and growth effects, respectively, while the right term represents nucleation. Droplet coalescence was neglected due to its weak effect during rapid cooling [21].

The temperature field, concentration field, and droplet radius distribution equations were discretized using the finite volume method and solved numerically, coupled with Cu-Co-Fe thermodynamic phase diagram calculations to simulate the metastable liquid-liquid transformation.

2.2.2 Physical Parameters Thermodynamic data from literature [9,22–25] were used for phase diagram calculations. The liquid-liquid interfacial energy was expressed as [26]:

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^{1.78}$$

where σ is interfacial energy, $T_c = (1620 \pm 10)$ K is the critical temperature for Cu-10%Co-10%Fe alloy, and $\sigma_0 = 1.78$ J/m^2.

The temperature dependence of liquid metal dynamic viscosity follows [27]:

$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right)$$

where η_0 is a constant, Q is activation energy for viscous flow, and R is gas constant. The viscosity of Cu-rich liquid was approximated by pure Cu viscosity, while Fe-Co-rich liquid viscosity was taken as the arithmetic mean of pure Fe and pure Co viscosities.

Solute diffusion coefficients were calculated using the Stokes-Einstein relation. The diffusion coefficient D_i of Fe and Co solutes in the Cu-rich liquid matrix is [28]:

$$D_i = \frac{k_B T}{6\pi\eta r_i}$$

where k_B is Boltzmann constant, r_i is ionic radius ($r_{\mathrm{Fe}} = 0.055$ nm, $r_{\mathrm{Co}} = 0.053$ nm). The initial gas velocity was 300 m/s [29].

2.2.3 Simulation and Discussion Based on experimental conditions, the rapid solidification process was simulated. [Figure 3: see original paper] shows the temperature and cooling rate at the center of a 138 m droplet over time, demonstrating that cooling rate variation follows the convective heat transfer coefficient variation.

[Figure 4: see original paper] presents the driving force, nucleation rate, and number density for Fe-Co-rich droplets at the center of a 138 m droplet. Nucleation begins when the driving force reaches a critical value, proceeding rapidly with number density increasing sharply while average radius grows slowly ([Figure 5: see original paper]). After nucleation, high supersaturation drives rapid droplet growth, which gradually slows as supersaturation decreases.

[Figure 6: see original paper] shows the radial distribution of average radius and number density of Fe-Co-rich particles in a 138 m powder. The significant temperature gradient near the surface induces strong Marangoni migration, causing continuous droplet depletion without replenishment and resulting in reduced particle number density at the powder surface ([Figure 1: see original paper]b). In other regions, the number density remains nearly constant after nucleation, indicating weak Ostwald ripening under rapid solidification. The spatial distribution of Fe-Co-rich particles is very uniform throughout most of the powder center. Excellent agreement between calculated and experimental results ([Figure 5: see original paper] and [Figure 6: see original paper]) validates the model.

[Figure 7: see original paper] illustrates the relationship between maximum nucleation rate ($I_{\max}$) and cooling rate during nucleation. Smaller droplets experience higher cooling rates, greater undercooling, higher $I_{\max}$, larger droplet number density, and smaller average radius. The relationship follows $I_{\max} = B\dot{T}^{2.18}$, where B is a constant.

Further analysis reveals that for powders smaller than 220 m, the average radius R_a and number density N of Fe-Co-rich particles follow exponential relationships with powder diameter d ([Figure 8: see original paper]):

$$R_a \propto d^{0.71}, \quad N \propto d^{-2.1}$$

where C_1 and C_2 are constants. These relationships yield a constant dispersed-phase volume fraction, further validating the model.

Conclusions

1. Gas atomization rapid solidification experiments were conducted on Cu-10%Co-10%Fe metastable immiscible alloy. Governing equations for temperature field, concentration field, and liquid-liquid transformation kinetics were established, enabling coupled thermodynamic-kinetic calculations. Excellent agreement between experimental and simulation results validates the model.

2. Under gas atomization rapid solidification, Cu-10%Co-10%Fe alloy can be undercooled into the metastable miscibility gap to undergo liquid-liquid transformation. For powders smaller than 220 m, Fe-Co-rich droplets solidify below the peritectic temperature, forming composite powders with spherical Fe-Co-rich particles uniformly distributed in the Cu matrix. Smaller powder diameters yield smaller Fe-Co-rich particle radii, with both average radius and number density following exponential relationships with powder diameter.

3. During rapid solidification of Cu-10%Co-10%Fe alloy droplets, the number density of dispersed-phase droplets remains essentially constant after nucleation throughout most of the droplet volume. Marangoni migration and Ostwald ripening of Fe-Co-rich droplets are minimal, resulting in highly uniform spatial distribution of Fe-Co-rich particles in the central regions of the powders.

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Note: Figure translations are in progress. See original paper for figures.