Study on the Solidification Process of Atomized Cu-Co-Fe Alloy Droplets (Postprint)

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Abstract

Gas atomization rapid solidification experiments were conducted on Cu-10%Co-10%Fe (mass fraction) metastable liquid-immiscible alloy, preparing composite powders with Fe-Co-rich spherical particles uniformly distributed in the Cu matrix, establishing the governing equations for temperature field, concentration field, and liquid-liquid phase transformation kinetics during cooling of Cu-Co-Fe alloy atomized droplets, developing a simulation method coupling alloy thermodynamics and phase transformation kinetics, and simulating and analyzing 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 mm, the average radius Ra and number density N of Fe-Co-rich phase particles follow an exponential relationship with the atomized powder diameter d.

Full Text

Study of Solidification in Gas-Atomized Droplets of Cu-Co-Fe Alloy

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Abstract

Cu-Co-Fe alloys exhibit excellent properties including high strength, high electrical conductivity, and giant magnetoresistance (GMR), making them promising candidates for applications in electrical contacts, integrated circuit lead frames, wires and cables, and ferromagnetic materials. However, manufacturing these alloys is extremely challenging due to the presence of a metastable miscibility gap in the liquid state. The liquid-liquid decomposition typically leads to severe phase segregation during conventional solidification. Recent studies have demonstrated that rapid solidification techniques can effectively suppress liquid phase separation.

In this work, rapid solidification experiments were conducted on Cu-10%Co-10%Fe (mass fraction) alloy using high-pressure gas atomization. Composite powders with Fe-Co-rich particles homogeneously dispersed in a Cu matrix were successfully obtained. A comprehensive model was developed to describe the microstructure evolution in atomized droplets during the liquid-liquid phase transformation, incorporating temperature field, concentration field, and liquid-liquid phase transformation kinetics. By coupling thermodynamic calculations with kinetic simulations, the solidification process of gas-atomized Cu-10%Co-10%Fe alloy droplets was analyzed.

Both experimental and simulation results reveal that under the rapid cooling conditions of gas atomization, the effects of Marangoni migration and Ostwald ripening of Fe-Co-rich droplets are very weak, resulting in 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 the powder diameter (d).

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

Cu-Co-Fe alloys possess high strength, high electrical conductivity, and giant magnetoresistance effects, offering significant potential for applications in electrical contact materials, integrated circuit lead frame materials, wire and cable materials, and ferromagnetic materials [1,2]. However, these alloys exhibit a metastable liquid miscibility gap, and liquid-liquid phase transformation occurs during melt cooling, readily forming severely segregated microstructures [3,4]. In recent years, the Cu-Co-Fe alloy system has frequently served as a model alloy for investigating solidification behavior in systems with metastable liquid miscibility gaps [5–14].

Previous research has primarily focused on thermodynamic aspects. Kim and Abbaschian [5] measured the liquidus temperature and metastable liquid phase separation temperature of Cu-Co-Fe alloys, identifying a metastable liquid miscibility gap when Co and Fe contents fall within certain ranges. Cao and Görler [6] performed differential thermal analysis (DTA) on Cu-Co-Fe alloys, determining liquidus and metastable liquid phase separation temperatures for compositions where Cu atomic fraction ranged from 10% to 84% with Co:Fe atomic ratios of 1:3, 1:1, and 3:1. Curiotto et al. [7] employed differential scanning calorimetry (DSC) to measure these critical temperatures. Munitz et al. [8] optimized thermodynamic parameters for the Cu-Co-Fe system and calculated the metastable liquid phase separation temperature. Turchanin et al. [9] investigated liquid-phase mixing enthalpy using calorimetry and evaluated thermodynamic parameters via phase diagram calculations. Additional thermodynamic optimizations and phase diagram calculations 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 solidification experiments on Cu-Co-Fe alloys, examining the influence of undercooling and cooling rate on microstructure. Their results showed that at high undercooling, liquid-liquid phase transformation occurred, with Fe-Co-rich phase morphology evolving from dendritic to dendritic-plus-spherical to fully spherical structures as undercooling increased. Munitz and Abbaschian [13] studied liquid-liquid phase 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 demonstrated that rapid solidification enables Cu-Co-Fe alloys to pass quickly through the miscibility gap, effectively suppressing phase separation and segregation.

Generally, microstructure evolution during liquid-liquid phase transformation results from the combined effects of nucleation, growth, coarsening, and spatial migration of dispersed phase droplets—a complex process with numerous interacting factors that is difficult to explore comprehensively through experiments alone. Computational simulation provides an effective means to reveal the solidification mechanisms of immiscible alloys [15,16]. This work investigates the microstructure formation of Cu-10%Co-10%Fe alloy under rapid solidification conditions using a combined approach of gas atomization experiments and computer simulation.

1. Experimental Methods

High-purity Cu, Co, and Fe ($ 99.9$mass_{2}$ gas at 3 MPa pressure, achieving rapid cooling and solidification. Third, the atomized powders were sieved, mounted, and polished for microstructural observation using an Axiovert 200MAT optical microscope (OM) and S-3400N scanning electron microscope (SEM), with energy-dispersive spectroscopy (EDS) analysis performed. Quantitative metallographic analysis of second-phase particle size and distribution was conducted 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 (FIGURE:2), 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 particles distributed in a Cu-rich matrix. As powder size increases, the size of Fe-Co-rich spherical particles gradually increases.

According to literature [5], when the undercooling of Cu-10%Co-10%Fe alloy melt exceeds 24 K, atomized droplets undergo liquid-liquid phase transformation, with Fe-Co-rich droplets nucleating and growing in the Cu-rich liquid. Since the binodal line in the Cu-Co-Fe alloy system lies below the liquidus line, Fe-Co-rich droplets formed during metastable liquid-liquid phase transformation are immediately in an undercooled state and tend to solidify rapidly. If the cooling rate is sufficiently high such that Fe-Co-rich droplets remain liquid while passing through the miscibility gap, they will solidify below the peritectic reaction temperature, forming spherical Fe-Co-rich particles and producing the microstructure shown in [Figure 1: see original paper]. Furthermore, Fe-Co-rich particles are essentially uniformly distributed throughout the powder, except for a slight reduction in number density near the powder surface (FIGURE:1b and d).

2.2 Modeling and Simulation

2.2.1 Model Formulation During solidification, heat at the droplet surface is transferred through convection with the surrounding gas environment, while internal heat is transported via diffusion and dispersed phase droplet movement. The temperature field in atomized droplets satisfies:

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

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; $\dot{Q}_{S/L}$ is the latent heat release rate at the solid/liquid interface; h is the convective heat transfer coefficient between droplet surface and atomization gas; T_s is droplet surface temperature; T_g is atomization gas temperature; and $\mathbf{u}_\beta$ is the Marangoni migration velocity of dispersed phase droplets.

The first term on the left describes heat conduction, the second term accounts for latent heat release at the solid/liquid interface, the third term represents surface convective heat transfer, and the fourth term describes heat transport due to dispersed phase droplet migration. The right side represents the temporal temperature change of the melt.

During liquid-liquid phase transformation, solute is transported through diffusion and spatial movement of dispersed phase droplets. Based on solute conservation, the concentration field for component i satisfies:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i) - \nabla \cdot (\mathbf{u}_\beta C_i) - 4\pi \int_0^\infty R^2 v_R F(R, \mathbf{r}, t)(C_i^\beta - C_i) dR$$

where $S_i = (C_i - C_i^{eq})/C_i^{eq}$ is the supersaturation of component i in the matrix melt; C_i^{eq} is the equilibrium mole fraction; C_i is the mole fraction of solute i in the matrix melt; C_i^β is the mole fraction of solute i in dispersed phase droplets; ϕ is the volume fraction of the matrix liquid phase; D_i is the diffusion coefficient of solute i; and C_i^{alloy} is the concentration of component i in the alloy (two-liquid mixture). The first term on the left describes solute diffusion in the matrix, the second term accounts for the effect of droplet movement on the concentration field, and the right side describes the temporal concentration change.

Under the combined effects of nucleation, diffusion growth, and spatial movement of dispersed phase droplets, the droplet radius distribution function satisfies the continuity equation:

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

where v_R is the diffusion growth velocity of dispersed phase droplets, I is the nucleation rate [19,20], and R^* is the critical nucleation radius. The first term describes temporal evolution of the distribution function, the second term accounts for the effect of droplet movement, and the third term describes the effect of droplet growth. The right side represents the source term describing nucleation. Since droplet coalescence is weak during rapid cooling of atomized droplets [21], collision-coalescence effects were neglected in the calculations.

The temperature field, concentration field, and continuity equation for the dispersed phase droplet radius distribution function were discretized and solved numerically using the finite volume method, coupled with thermodynamic phase diagram calculation routines for the Cu-Co-Fe system to simulate the metastable liquid-liquid phase transformation process.

2.2.2 Main Physical Parameters Used in Calculations Thermodynamic data for the Cu-Co-Fe alloy system from literature [9,22–25] were used for phase diagram calculations. The liquid-liquid interfacial energy was calculated using the general expression [26]:

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

where σ is the liquid-liquid interfacial energy; $T_c = (1620 \pm 10)$ K is the critical temperature for Cu-10%Co-10%Fe alloy; and fitting calculations yield $\sigma_0 = 1.78$ 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 the activation energy for viscous flow, and R is the gas constant. The dynamic viscosity of Cu-rich liquid was approximated using pure Cu viscosity, while that of Fe-Co-rich liquid was approximated as the arithmetic mean of pure Fe and pure Co viscosities.

Solute diffusion coefficients were related to melt viscosity via the Stokes-Einstein equation. The diffusion coefficient D_i of Fe and Co solute atoms in liquid Cu matrix was calculated as [28]:

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

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

2.2.3 Simulation and Discussion Based on experimental conditions, the rapid solidification process of atomized droplets was simulated. [Figure 3: see original paper] shows the temperature and cooling rate at the center of a 138 m droplet as functions of time. The cooling rate variation correlates with the change in convective heat transfer coefficient at the droplet surface.

[Figure 4: see original paper] presents the driving force, nucleation rate, and number density for liquid-liquid phase transformation at the droplet center. When the driving force reaches a critical value, Fe-Co-rich droplets begin to nucleate, initiating metastable liquid-liquid phase transformation. The nucleation period is very brief, during which the number density of Fe-Co-rich droplets increases rapidly while their average radius grows slowly ([Figure 5: see original paper]). Immediately after nucleation, the matrix melt remains highly supersaturated, causing rapid droplet growth. Subsequently, as supersaturation decreases, the growth rate gradually diminishes.

[Figure 6: see original paper] shows the radial variation of average radius and number density of Fe-Co-rich particles in a 138 m powder. Due to the large temperature gradient near the droplet surface, Marangoni migration of Fe-Co-rich droplets is strong and cannot be replenished, leading to a continuous reduction in droplet number density and consequently lower particle density near the powder surface ([Figure 1b: see original paper]). In other regions of the droplet, the number density remains nearly constant after nucleation, indicating weak Ostwald ripening under rapid solidification conditions. The spatial distribution of Fe-Co-rich particles is very uniform throughout most of the powder center. Excellent agreement between calculated and experimental results in [Figure 5: see original paper] and [Figure 6: see original paper] demonstrates the validity and rationality of the model.

[Figure 7: see original paper] illustrates the relationship between maximum nucleation rate I_{max} and cooling rate during the nucleation stage. Smaller droplet sizes yield higher cooling rates during nucleation, greater melt undercooling, higher maximum nucleation rates, larger droplet number densities, and smaller average radii. The relationship follows $I_{\text{max}} = B\dot{T}_{\text{Nuc}}^{2.18}$, 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: $R_a \propto d^{0.71}$ and $N \propto d^{-2.1}$ ([Figure 8: see original paper]), where C_1 and C_2 are constants.

From these relationships, the dispersed phase volume fraction ϕ can be derived, further validating the model.

Conclusions

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

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

3. Under rapid solidification, the number density of dispersed phase droplets remains essentially constant after nucleation throughout most of the droplet volume, with only a thin surface region showing reduced density. Marangoni migration and Ostwald ripening of Fe-Co-rich droplets are weak, resulting in highly uniform spatial distribution of Fe-Co-rich particles in the powder interior.

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