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## Design and formation mechanism of self-organized core/shell structure composite powder in immiscible liquid system

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Under the guidance of the calculation of phase diagrams method, the self-organized Cu alloy/stainless steel composite powders with a core/shell microstructure were developed based on the gas atomization process, and the formation evolution of self-organized core/shell structure composite powders was modeled by the phase field method. This paper gives a more detailed explanation for the formation of self-organized core/shell structure composite powders from the viewpoints of thermodynamics and kinetics. Such core/shell structure composite powders have good combination of high strength and corrosion resistance (Fe-rich phase) and high electric and thermal conductivities (Cu-rich phase) with many potential advanced applications in electronic devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2794415]

Core/shell structure composite powders, which are generally made by the composite process, have wide applications in many fields. For example, Cu alloy/stainless steel (Cu/SS) core/shell structure composite powders have potential advanced applications in many fields such as electronics and catalyst because of their optimal combination of high electric and thermal conductivities with low thermal expansion and high strength. However, it is difficult to fabricate such composite powders by conventional processes due to the repulsive interaction and poor wetting between Cu and Fe. Recently, a method was developed to produce composite powders and composite bulk ingots with core-type microstructures by means of gas atomization process<sup>1</sup> and conventional solidification method.<sup>2</sup> Results have indicated that it is possible to develop the Cu/SS core/shell structure composite powders for practical applications. The main objective of the present study is to develop the self-organized Cu/SS core/shell structure composite powders based on gas atomization process, and to explain the formation mechanism of self-organized core/shell structure composite powders from the viewpoints of the thermodynamics and kinetics.

Thermodynamic calculations were firstly carried out based on the calculation of phase diagrams (CALPHAD) method<sup>3</sup> with the thermodynamic database of the Cu-based alloys.<sup>4,5</sup> The purpose of the thermodynamic calculation is (1) to determine the composition range for stable miscibility gap in the liquid state and monotectic reactions in Cu-Fe base alloys with the addition of different alloying elements, (2) to calculate the changes in volume fractions of the two coexisting liquid phases with temperatures, and (3) to choose the optimal alloy compositions for the processing of the

Cu/SS composite powders based on the above calculations.

The Cu-Fe-Cr-C alloys were melted in a high frequency induction furnace under an argon atmosphere. The powders with 10–250  $\mu\text{m}$  in diameter were prepared using conventional nitrogen gas atomization under an argon atmosphere, where the melting temperature is about 1800–2120 K and the gas pressure for atomizing is about 5 MPa. The cooling rate is  $10^3$ – $10^4$  K/s, depending on the size of the powder. Observation of microstructure morphology of powder was performed by optical microscopy. The etched solutions were the fluorine acid for such powders. The compositional analysis of Cu-rich and Fe-rich phases in the powders was carried out by electron probe microanalysis (EPMA) (JXA-8100R).

It is known that the typical composition of martensite stainless steels is Fe-(10–18)Cr (wt %) with certain amount of carbon to easily form the martensite microstructure and to enhance its hardness. Therefore, the Cu-Fe-Cr-C quaternary system is chosen in the present work. The calculated vertical sections of the phase diagram at 11 wt % Cr and 7.2 wt % Cr, where the effect of carbon is neglected, indicate that a stable miscibility gap of liquid phases exists (Fig. 1). In order to study the effect of the volume fractions of the two immiscible liquid phases on the final core / shell microstructure in the composite powders, we have chosen two alloy compositions of Cu-44Fe-11Cr (wt %) and Cu-32.8Fe-7.2Cr (wt %). It is seen from Fig. 1 that the volume fraction of the Cu-rich liquid phase is smaller than that of Fe-rich liquid phase in the whole temperature region for Cu-44Fe-11Cr (wt %) alloy and the opposite is true for Cu-32.8Fe-7.2Cr (wt %) alloy.

According to our previous studies,<sup>1</sup> the phase with smaller volume fraction always locates in the center of a composite powder. Figure 2 shows the typical microstructures of the self-organized core/shell structure composite powders made of Cu-32.4Fe-7.2Cr-0.4C (wt %) and Cu-

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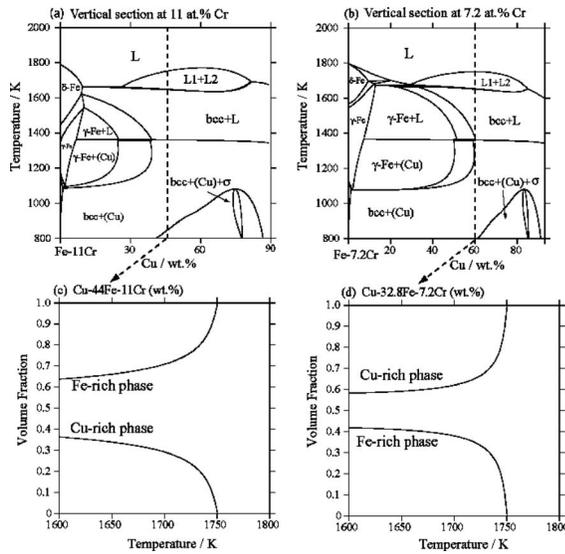


FIG. 1. Calculated vertical section diagrams at (a) 11 wt % Cr and (b) 7.2 wt % Cr in the Fe–Cu–Cr system, and calculated volume fractions of the two liquid phases in the (c) Cu–44Fe–11Cr (wt %) alloy and (d) Cu–32.8Fe–7.2Cr (wt %) alloy.

44Fe–11Cr–0.2C (wt %) alloys. It is readily seen that the Fe-rich phase appears at the center of a composite powder for Cu–32.4Fe–7.2Cr–0.4C (wt %) alloy, while the Cu-rich phase appears at the center for Cu–44Fe–11Cr–0.2C (wt %) alloy. This means that droplets of the minor phase in the matrix liquid phase move rapidly on cooling to the center of the powder against the temperature gradient. It is interesting to note that dendrites form in the Fe-rich phase in Cu–32.4Fe–7.2Cr–0.4C (wt %) alloy. This fact indicates that the droplets of the Fe-rich phase with smaller volume fraction have moved and congregated to the center of the powder before the solidification of the liquid phase, and then the Cu-rich phase located outside of the powder is firstly solidified, then the Fe-rich phase with higher melting point begins to nucleate on the interface between the Cu-rich and Fe-rich phases and grows to become a dendrite microstructure, as shown in Fig. 2(a). In Fig. 2(b), the powders of different sizes show a triple-layer core structure consisting of a Cu core, an Fe periphery, and a thin Cu surface layer. The reason for its formation has been discussed in our previous work.<sup>1</sup>

The compositions of the Cu-rich and Fe-rich phases of the powders in the Fe–Cu–Cr–C system were measured by EPMA. The results indicate that the compositions of the Fe-rich phase are respectively, Fe–17.16Cr–9.01Cu–0.25C (wt %) for the Cu–43.8Fe–11Cr–0.2C (wt %) alloy and Fe–19.48Cr–4.75Cu–0.61C (wt %) for the Cu–32.4Fe–7.2Cr–0.4C (wt %) alloy, which are close to that of typical 18Cr (0.3–0.6)C stainless steel.

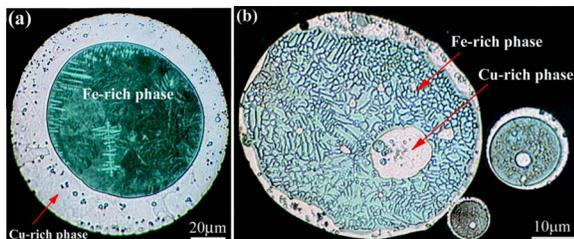


FIG. 2. (Color online) Typical microstructures of the self-organized composite powders made of (a) Cu–32.4Fe–7.2Cr–0.4C (wt %) and (b) Cu–44Fe–11Cr–0.2C (wt %) alloys.

In order to understand the mechanism for the formation of the self-organized core/shell structure composite microstructure, phase field simulations of microstructural evolution during phase separation in liquid phase were carried out, where liquid and vapor phases in a simple Cu–Fe binary system were considered. The Gibbs free energy in this system including the liquid and vapor phases is described by<sup>6,7</sup>

$$f(x_i, \rho, T) = h(\rho)G_m^{\text{liq}} + [1 - h(\rho)]G_m^{\text{vap}} + g(\rho), \quad (1)$$

where  $h(\rho) = \rho^3(6\rho^2 - 15\rho + 10)$  and  $g(\rho) = \omega\rho^2(1 - \rho)^2$ , and it is assumed that  $\rho$  equals 1 in the liquid phase and 0 in the vapor phase, respectively. The parameter  $\omega$  is the height of the imposed double-well hump, which can be determined from the interfacial energy and interface thickness.  $G_m^{\text{liq}}$  and  $G_m^{\text{vap}}$  are the molar Gibbs free energy of the liquid and vapor phases, respectively.

In the present work, the Gibbs free energy of the Cu–Fe liquid phase is described by the CALPHAD method,<sup>8</sup> as follows:

$$G_m^{\text{liq}} = \sum_{i=\text{Cu,Fe}} {}^0G_i x_i + RT \sum_{i=\text{Cu,Fe}} x_i \ln x_i + x_{\text{Cu}} x_{\text{Fe}} L_{\text{Cu,Fe}}, \quad (2)$$

where  $x_i$  is the molar fraction of component  $i$  in the liquid phase.  $R$  is gas constant, and  $T$  is absolute temperature.  $L_{\text{Cu,Fe}}$  is the interaction parameter with dependence on composition and temperature.

On the other hand, the Gibbs free energy of the vapor phase is described by

$$G_m^{\text{vap}} = \frac{a_2}{2} (x_i - x_v)^2, \quad (3)$$

where  $x_v$  is the equilibrium composition in vapor phase and  $a_2$  is a constant.

Thus, total free energy in a system can be described as

$$F = \int dx \left[ f(X, \rho, T) + \frac{\alpha}{2} |\nabla X|^2 + \frac{\beta}{2} |\nabla \rho|^2 \right], \quad (4)$$

where  $\alpha$  and  $\beta$  are the gradient-energy coefficients for the concentration and density inhomogeneities.<sup>9</sup>

Since the composition and density are the conserved field variables, the spatial-temporal evolution of these two fields are governed by the nonlinear Cahn–Hilliard diffusion equation<sup>10</sup>

$$\frac{\partial X}{\partial t} = M_X \nabla^2 \frac{\delta F}{\delta X}, \quad (5)$$

$$\frac{\partial \rho}{\partial t} = M_\rho \nabla^2 \frac{\delta F}{\delta \rho}, \quad (6)$$

where  $M_X$  and  $M_\rho$  are related to atomic motilities.

The microstructural evolution during the formation of the self-organized composite powders is obtained by simultaneously solving Eqs. (5) and (6) in a two-dimensional system. The simulation results of microstructural evolution in three alloys of 25 at. % Cu, 50 at. % Cu, and 75 at. % Cu, corresponding to the volume fractions of the Cu-rich liquid phase ( $V_{\text{Cu-rich phase}}$ ) of 26.1%, 51.6%, and 76.2% at 1680 K, respectively, are shown in Fig. 3. In these simulations, the surface tensions of Cu-rich and Fe-rich liquid phases are assumed to be the same and the temperature gradient and fluid flow in the droplet are ignored. From the simulation results,

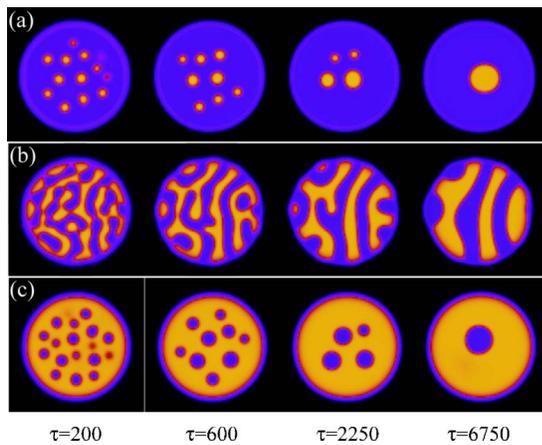


FIG. 3. (Color online) Phase field simulation of microstructural evolution in the Cu–Fe system with the composition of (a) 25 at %, (b) 50 at %, and (c) 75 at %. (Yellow color: the Cu-rich phase, blue color: the Fe-rich phase.)

it is clear that the liquid phase of small volume fraction ends up with an isolated island surrounded by the liquid phase of larger volume fraction during the spinodal decomposition process. If the volume fractions of the two liquid phases are almost equal, i.e., when  $x_{\text{Cu}}=50$  at. % ( $V_{\text{Cu-rich phase}}=51.6\%$ ), a typical irregular microstructure was obtained. These results agree well with the experimental observations.<sup>1,2</sup> They indicate that the volume fractions of the two liquid phases play an important role in determining the morphology of the two-phase microstructure in the composite powders. The details of the simulation study of the self-organized core/shell structure composite microstructures with consideration of difference in interfacial energy of the liquid phases, spinodal decomposition and subsequent coarsening, and Marangoni motion using the phase field method will be presented in a separate paper.<sup>11</sup>

The formation of self-organized core/shell powder is because the liquid phases with smaller volume fraction in the matrix liquid phase move to the center of a powder during the gas atomization process, and their movements are related to two velocities: one is the velocity ( $v_m$ ) of a droplet pointing to the center of a powder due to the Marangoni effect,<sup>1,12–14</sup> and another is the velocity ( $v_s$ ) of a droplet pointing to ground by gravity.<sup>15</sup> The calculation methods of these two velocities were reported in the previous paper.<sup>1,2</sup> In this report, the equations of calculation are omitted due to the limit of space.

Figure 4 shows the calculated results of the ratio of

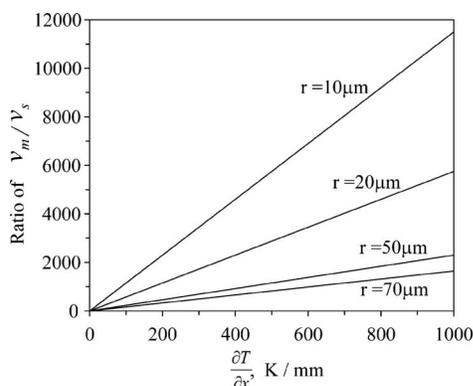


FIG. 4. Calculated ratio of  $v_m/v_s$  for different radii of droplets with the change of temperature gradient for Cu–32.8Fe–7.2Cr (wt %) alloy at 1680 K.

$v_m/v_s$  as a function of temperature gradients at the different droplet sizes for the Cu–32.8Fe–7.2Cr (wt %) alloy, where the ratio of  $v_m/v_s$  rapidly increases with increasing temperature gradient and decreasing droplet radius. It is seen that the effect of gravity becomes smaller when the temperature gradient becomes larger and the droplet size becomes smaller. In the case of a droplet with  $r=10$   $\mu\text{m}$ , for example, its migration rates ( $v_m$ ) at a temperature gradient of 1000 K/mm is about 266 mm/s, which is about  $1.15 \times 10^4$  times larger than  $v_s$  induced by the gravity. This result indicates that the minor phase droplets in the major liquid phase can rapidly migrate toward the center of the powder under gravity conditions by the Marangoni effect. The gravity has a dominant effect on the motion of a liquid phase droplet when the temperature gradient is very small, as reported in our previous work.<sup>2</sup>

We reported here a method to fabricate self-organized core/shell structure Cu/SS composite powders by conventional gas atomization. By controlling the volume fractions of the two coexisting phases in the liquid state and the cooling rate, various types of composite powders with sizes from about 10 to 250  $\mu\text{m}$  have been produced. Such composite powders have good combination of high strength and corrosion resistance (Fe-rich phase) and high electric and thermal conductivities (Cu-rich phase) with many potential advanced applications in electronic devices. In addition, this paper also gives an explanation of the formation of the self-organized core/shell structure composite powder from the viewpoints of thermodynamics and kinetics, which will provide important information for development of such self-organized core/shell structure composite powder.

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