Relation between Widths of the Grain Boundary Energy Cusps at Special Misorientations and the Microstructural Characteristics in the Sintering of a Fe–Cu–C Alloy

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A new Monte Carlo model, three-dimensional multi-particle model, was developed to simulate the three-dimensional microstructural characteristic in the sintering of a Fe–Cu–C alloy. The probability model incorporated the energy-misorientation relationship assigned to randomly generated neighboring grains. The effect on microstructural characteristics of adding doped materials was also quantified and related to the energy-misorientation relationship. The present Monte Carlo model accounts for the relationship between the grain boundary energy and the dihedral angle distribution and determines the effect of the width of the grain boundary energy cusp at the special misorientation on the contiguity and coordination number in the sintering of a Fe–Cu–C alloy. All specimens show a strong correlation between the contiguity \( \hat{C} \) and coordination number \( N \), irrespective of the width of the grain boundary energy cusp at the special misorientation. The correlation can be expressed as: \( N / \hat{N}_O = \hat{C}_N / \hat{C}_O \), where \( \hat{N}_O \) is the mean coordination number, \( \hat{C}_O \) is the mean contiguity, and \( \hat{C}_N \) is the mean contiguity having the coordination number \( N \).

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1. Introduction

Common liquid phase sintering systems of Fe–Cu and Fe–Cu–C alloys are used in the automotive industry, in which the inherently low costs are important.\(^1\) Adding copper to iron in mixed powder compacts causes swelling, called copper-growth. Introducing elements such as graphite to prevent dimensional instability has widely been reported.\(^2\)\(^–\)\(^8\) Two dominant methods have been proposed to restrain volumetric expansion: (a) carbon addition prevents the grain boundary penetration of a liquid Cu rich phase and increases the dihedral angle;\(^2\)\(^,\)\(^3\)\(^,\)\(^8\) and (b) carbon addition reduces the grain-boundary energy of iron and induces grain boundary pinning.\(^2\)\(^,\)\(^7\)\(^,\)\(^8\) No investigation has yet completely resolved the problem and accounted for all the experimental observations, such as the relationship between the grain boundary energy and the dihedral angle distribution during liquid phase sintering.

The location and magnitude of grain boundary energy cusps at specific misorientations were found to change when the pure metal was alloyed.\(^5\)\(^,\)\(^10\) Thus, lowering grain-boundary energy of iron due to carbon segregation on grain boundaries suggests that the width of the grain boundary energy cusp at the special misorientation increases with increasing the concentration of carbon. It is, however, difficult to calculate the energy stored in dislocation networks in boundaries deviating from special misorientations.\(^11\) Consequently, no study has attempted to analyze the effect of the width of the grain boundary energy cusp at the special misorientation on microstructural characteristics governing dimensional instability, such as contiguity (defined as the measure of the solid-solid contact in a liquid phase sintered material) and coordination number (defined as the number of contacts per solid grain). The present study aims to construct a three-dimensional multi-particle model which improves on the theoretical description of sintering processes of powder compacts. In addition, the arrangement of particles in a powder compact is so complicated that analytical methods can hardly solve the correlation between the width of the grain boundary energy cusp at the special misorientation and the microstructural character. Thus, a Monte Carlo method is proposed to solve such a complicated system. This method combines stereological approaches and thermodynamics to offer a possible description of progress during liquid phase sintering of a Fe–Cu–C alloy.

2. Model Geometry

The method presented herein attempts to simulate and investigate the effect of the width of the grain boundary energy cusp at the special misorientation on the dihedral angle distribution, contiguity, and coordination number. For the sake of clarity, some of the basic characteristics at the time of liquid formation in the sintering process are required to construct a three-dimensional model.

2.1 Basic assumptions of liquid phase sintering

Mixed powders, including base powders and additive powders, are heated to a temperature at which liquid forms in sintering. These powders are assumed to be spherical particles. The assumption greatly aids the calculation, although corresponds to ideal conditions. All particles in the powder compact are mixed and packed together. The effect of gravity is assumed negligible in the initial stage of liquid phase sintering. In this model, all particles are assumed to bond together during heating, prior to liquid formation. The additive particles are assumed to melt into the liquid phase at the sintering temperature.

2.2 The random packing of spheres of various sizes

A realistic model is generated by employing powders of the liquid (additive powders) and solid phases (base powders)
whose particle size distributions exhibit truncated normal distributions. In the truncated normal distribution, only the particle sizes situating in the interval between \( R - 3\sigma \) and \( R + 3\sigma \) are generated in the calculation, where \( R \) is the mean particle radius and \( \sigma \) is the standard deviation of the distribution. We assume that the size distribution of particles is a truncated normal distribution with a mean radius \( R = 8 \mu m \) and a standard deviation \( \sigma = 1 \mu m \) in the interval \((R - 3\sigma, R + 3\sigma)\). The relative volumetric ratios of solid phase to liquid phase, designated 25, 50, 75, and 90 vol% solid phase particles with the remainder of the liquid phase particles, was treated as an input variable that determined their relative probabilities in probabilistic generation of particles. Each particle was randomly generated according to the size distribution function and the relative volume fraction of each phase.

2.3 Irregular particle packing

To calculate the particle arrangement in three-dimensional space, the position of each particle with respect to the center of the original particle is denoted as:

\[
\vec{V}(r, \theta, \phi) = r \hat{e}(\theta, \phi),
\]

where \( \hat{e} \) is a unit vector, \( r \) denotes the distance between the centers of the original particle and the newly generated particle, \( \theta \) represents the angle between \( \vec{V} \) and the \( z \) axis, and \( \phi \) represents the angle between the \( x \) axis and the projection of \( \vec{V} \) on the \( x-y \) plane (Fig. 1). In this approach, two numbers (\( \theta \) and \( \phi \)) are generated randomly to determine the direction of a newly generated particle. The direction depends on two random angles, \( \theta \) randomly selected from zero (for a point on the positive unit-axis) to 360 degrees (\( 2\pi \) radians), and \( \phi \) randomly selected from zero to 180 degrees (\( \pi \) radians). In such a manner, a group of particles sequentially attached around the central particle. The particle packing in a three-dimensional space was thus formulated. Figure 2 illustrates such an arrangement of particles. In such an arrangement, the newly generated particle was in point contact with the central particle.

2.4 Anisotropy in grain boundary energy

In liquid phase sintered systems, solid grains can either exist as isolated grains or bond with the adjacent grains, which accordingly yields a distribution of dihedral angle. Anisotropy in grain boundary energy causes such a phenomenon. In fact, grain boundary energy between two adjacent grains is determined by the misorientation angle of these two grains. The relation between the grain boundary energy and the misorientation angle can be described by a dislocation model.\(^{12-14}\) However, this model becomes invalid when the misorientation angle exceeds 15 deg, due to the overlapping of dislocation cores.\(^{12, 14}\) Thus, for both low and high angle grain boundaries, a coincidence-site-lattice model is usually utilized.\(^{13, 15-18}\) In the coincidence-site-lattice model, each grain has a random orientation. The relative orientation between two neighboring grains can be expressed by a rotation matrix, which represents the rotation of one grain around a certain axis by a deviation angle \( \Delta \theta \). In addition, the maximum permissible deviation angle from coincidence can be expressed as the Brandon angle \( (\Delta \theta_c) \) by

\[
\Delta \theta_c = \pi / \left( 12 \times \sqrt{\Sigma} \right),
\]

where the notation \( \Sigma \) gives the reciprocal of the fraction of sites which are coincident between two grains.\(^{19}\) With the above definition, the anisotropy in grain boundary energy
observations was assumed to be energy angle relations as in the earlier cited experimental ob-
the special misorientation. Therefore, the general feature of increasing in the width of the grain boundary energy cusp at

ditive phase, is not a pure material. A small amount of solute
phase sintered material that includes a base phase and an ad-

γ
gamma-iron, Γ

narrow. For this reason, the grain boundary energy parameter

≥

Γ

energy cusp at the special misorientation is very narrow when

makes grain boundary energy cusps sharper and more local-
ized. According to the eq. (3), the width of the grain boundary energy cusp at the special misorientation is very narrow when

Γ ≥ 9. Theoretically, the width of the grain boundary energy cusp at the special misorientation of a pure material should be

small. For this reason, the grain boundary energy parameter of a pure material is assumed to be Γ = 9. In fact, a liquid phase sintered material that includes a base phase and an ad-

itive phase, is not a pure material. A small amount of solute segregation on grain boundaries of a pure material causes the increasing in the width of the grain boundary energy cusp at the special misorientation. Therefore, the general feature of energy angle relations as in the earlier cited experimental observa-
tions was assumed to be Γ = 3.20) In order to quantify the relation between the grain boundary energy configuration and the amount of adding solutes, we assume that the parameter, Γ, of the grain boundary energy configuration decreases when a small amount of solute was added to a pure metal. As shown in Fig. 3, Γ ranges from 9 to 3 in 3 decrements on adding solute in the present model.

2.5 Dihedral angle

Bonding of adjacent grains occurs prior to the formation of liquid phase. When liquid phase is formed, the liquid phase can penetrate and dissolve the grain boundary, if the following thermodynamic criterion is met:

\[ 2\gamma_{dl} \leq \gamma_{GB}. \]  \hspace{1cm} (4)

where \( \gamma_{dl} \) denotes the energy of a solid-liquid interface.22–26) If the above criterion is not fulfilled, the liquid phase does not penetrate and dissolve the grain boundary completely. Under such a condition, there will exist an equilibrium dihedral angle \( \Psi \) among the solid grains and the liquid phase, which can be expressed by:27)

\[ \gamma_{GB} = 2\gamma_{dl} \times \cos(\Psi/2). \]  \hspace{1cm} (5)

Herein, the energy of a solid(Fe)-liquid(Cu) interface, \( \gamma_{sl} \), is taken as 444 mJm\(^{-2}\).4)

2.6 Coordination number

As mentioned earlier, a group of particles is randomly generated according to the size distribution function and the relative volume fraction of each phase. These particles sequentially attached around the central particle. Consider the central particle which is in point contact with neighboring particles. According to the basic assumptions, additive particles are assumed to melt into liquid phase at the sintering temperature. Therefore, only base particles may bond together during liquid phase sintering. Alternatively, the number of contact particles depends on that the grain boundary between the central particle and each contact particle does not separate by a liquid film. The inter-particle contacts of the central particle, the three-dimensional coordination number \( N_{c} \), were counted in this model. For example, the condition of \( N = 2 \) was shown in Fig. 4.

2.7 Contiguity

The contiguity of solid phase in a liquid phase sintered system is the total area of solid-solid contacts as a fraction of the total area of solid-solid and solid-liquid contacts. For two spherical solid grains with radii of \( R_{1} \) and \( R_{2} \) being in contact (Fig. 4), a geometrical relationship exists as:28–30)

\[ R_{1} \sin \Psi_{1} = R_{2} \sin \Psi_{2} = R_{C} \sin \alpha, \]  \hspace{1cm} (6)

where

\[ 2\alpha = \Psi_{1} - \Psi_{2}, \]  \hspace{1cm} (7)

\[ \Psi = \Psi_{1} + \Psi_{2}, \]  \hspace{1cm} (8)

\[ R_{C} = 2 \cos(\Psi/2) R_{1} R_{2}/(R_{2} - R_{1}). \]  \hspace{1cm} (9)

With these relationships, the solid-solid interfacial area, \( S_{SS} \), yields as:29,31)

\[ 2\pi R_{C}^{2}(1 - \cos \alpha), \hspace{1cm} R_{1} \neq R_{2}; \]  \hspace{1cm} (10)

\[ \pi (R_{1} \sin(\Psi/2))^{2}, \hspace{1cm} R_{1} = R_{2} \]  \hspace{1cm} (11)

\[ \pi (R_{1} \sin \Psi_{1})^{2}, \hspace{1cm} R_{1} \approx R_{2}. \]  \hspace{1cm} (12)

When such a geometric calculation is calculated three-
dimensional multi-particle model with a Monte Carlo tech-
nique, the contiguity (\( \hat{C} \)) can be expressed as:

\[ \hat{C} = 2A_{SS}/(2A_{SS} + A_{SL}). \]  \hspace{1cm} (13)
where
\[ A_{SS} = \sum_{i=1}^{n} (S_{SS})_i, \]  \hspace{1cm} (14)
\[ A_{SL} = 4\pi R_O^2 - \left\{ \sum_{i=1}^{n} 2\pi R_O^2 (1 - \cos \Psi_i) \right\}. \]  \hspace{1cm} (15)

where \( A_{SS} \) is the solid-solid surface area, \( A_{SL} \) is the solid-liquid surface area, \( n \) is the coordination number \( \tilde{N} \), \( R_O \) is the radius of the central particle, and \( \Psi_i \) is the dihedral angle among the central particle, the \( i \)-th particle, and the liquid phase.

3. Numerical Simulation

The program of this model was run on a workstation of SunOS Release 4.1.3 of UNIX system using SIMSCRIPT as the computer programming language. It is best suited for representing complex simulation models. Statistical comparisons of 1000 simulated particles were made between the present results of the both effects of the matrix fraction and the grain boundary energy spectrum during liquid phase sintering of a Fe–Cu–C alloy. Subsequently, the results by numerical computation are briefly discussed.

4. Results and Discussion

This study has proposed a new approach for solving a well-known class of problems. The parameter, \( \Gamma \), of the grain boundary energy configuration was originally assumed to decrease when a small amount of solute was added to pure metal. Figure 5 presents the histogram for the dihedral angle distribution simulated for various \( \Gamma \) values. The Monte Carlo simulation results indicate that the dihedral angle distribution broadens with a decrease in the \( \Gamma \) value, as expected. Adding a small amount of carbon to iron-copper in mixed powder compacts reduces the grain-boundary energy of iron and increases the dihedral angle at the grain boundaries with the copper-rich liquid phase. \(^2,8\) Figure 6 shows that the coordination number increases with the volume fraction of solid, irrespective of \( \Gamma \) values or widths of grain boundary energy cusps at special misorientations. Figure 7 reveals that the contiguity increases with an increase in the mean dihedral angle or with a decrease in the value of \( \Gamma \), indicating that the dihedral angle increases as the value of \( \Gamma \) decreases. According to the results presented here, changing the width of the grain boundary energy cusp at the special misorientation, as represented by the value of \( \Gamma \), significantly influences the contiguity. In other words, carbon atoms in iron induce grain boundary pinning and prevent the copper penetration into the grain boundary. \(^3\) Consequently, the increased probability of mutually contacting gamma-iron grains causes an increase in contiguity.

Fig. 5 Effect of \( \Gamma \) values on a dihedral angle distribution: (a) 3, (b) 6, and (c) 9.
Figures 5 and 7 show that the presented data are accurate and consistent with those obtained by experiments for Fe–Cu–C alloys. Recent experimental observations have indicated that the structure of grain boundaries differs from that of the matrix. Therefore, two locations exist a difference in free energy. The difference in free energy is the driving force for grain boundary segregation of carbon during heating. Grain boundaries provide a high density of energetically favorable sites for carbide precipitation. Following carbon depletion, the free energy of segregation for carbon decrease at no coincident atoms, supporting the claim of the original assumption of the grain boundary energy configuration. The reducing grain-boundary energy of iron at no coincident atoms, together with the increase of the dihedral angle, induces grain boundary pinning and prevents the grain boundary penetration of a liquid Cu rich phase. Following an increase of volume fraction of solid, interconnected solid particles inhibiting the copper penetration have a tendency for liquid copper to remain at particle corners or at its original location. Therefore, the fraction of the solid particle surface shared by adjacent solid particles, or contiguity, increases with an increase of dihedral angle or a decrease of $\Gamma$. Above results prove the approach for solving that carbon addition prevents the gamma-iron grain boundary penetration of a liquid Cu rich phase and explain previous suggestions that solute segregation modifies the shape of the energy-misorientation curve of the pure metal.

In liquid phase sintered microstructures, a correlation between the contiguity and coordination number affects each other. Therefore, a bivariate frequency distribution between contiguity and coordination number is a good technology to be studied. Figure 8 illustrates bivariate contiguity-coordination number frequency functions predicted from the model for $\Gamma = 3$, when volume fractions of solid are 0.25, 0.5, 0.75 and 0.9, respectively. Dramatically, there is a significant difference in the bivariate frequency functions with the change in the volume fraction of solid. The distribution reveals that both contiguity and coordination number decreased with the decrease in the volume fraction of solid, owing to the higher probability for wetting. At present, there are no theories or computer simulations whose predictions can be compared with this result.

Moreover, it can also be observed that there exists a strong correlation between the contiguity $\hat{C}$ and the coordination number $\hat{N}$. To quantify this correlation between $\hat{C}$ and $\hat{N}$, we normalize both the variables: divide the average contiguity $C_N$ having coordination number $\hat{N}$ by total average contiguity $\hat{C}_O$, and divide $\hat{N}$ by mean coordination number $\hat{N}_O$. We find that $\hat{N}/\hat{N}_O$ is a direction proportion to $C_N/\hat{C}_O$, irrespective of the width of the grain boundary energy cusp at the special misorientation. For example, the correlation for $\Gamma = 3, 6,$ and $9$ in 0.5 volume fraction of solid was shown in Fig. 9.

5. Conclusions

This study has demonstrated the feasibility of applying the Monte Carlo method to analyze the effect of the width of the grain boundary energy cusp at the special misorientation on microstructural characteristics in the sintering of a Fe–Cu–C alloy. The three-dimensional Monte Carlo model combines multi-particle arrangement, non-uniform particle size, irregular packing and a continuous spectrum of grain boundary energy to solve that the relatively low grain boundary energy at no coincident atoms causes an increase in contiguity and dihedral angle. The contiguity can be expressed through a simple mathematical relationship related to their coordination number, irrespective of the width of the grain boundary energy cusp at the special misorientation.

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Fig. 8 Bivariate coordination number-contiguity distribution: (a) 0.25, (b) 0.5, (c) 0.75, and (d) 0.9 volume fraction of solid with the $\Gamma^*$ value of 3.

Fig. 9 Normalized mean contiguity ($\bar{C}_g/\bar{C}_0$) vs their normalized mean coordination number ($\bar{N}/\bar{N}_0$). Data points vary with $\Gamma^*$ values for 0.5 volume fraction of solid.

REFERENCES
