MICROGRAVITY LIQUID PHASE SINTERING AND PORE EVOLUTION


The effect of microgravity on liquid phase sintering (LPS) in the Fe-Cu system was investigated through experiments on four sounding rockets and on three Space Shuttle missions. Three compositions, namely, Fe-33 wt.%Cu, Fe-43 wt.%Cu and Fe-53 wt.%Cu were processed for times ranging from 2.5 minutes to 66 minutes. The samples did not exhibit slumping or shape distortion during processing. However, extensive pore formation and metamorphosis was observed in all these samples. Microstructural characteristics such as densification, dihedral angle, contacts per grain, grain growth and pore metamorphosis were evaluated. The evolution of LPS microstructure in microgravity is explained using energy considerations because the liquid, solid and gaseous phases in the Fe-Cu samples seek to attain the minimum energy configuration in the absence of gravitational forces. Therefore, the volume fractions of liquid, solid and gaseous phases and processing times significantly influence the LPS microstructure in microgravity. This paper documents the effect of composition and processing time on microstructural development in the Fe-Cu samples that have been liquid phase sintered under microgravity.

KEYWORDS: Liquid Phase Sintering, Microgravity, Fe-Cu Alloys, Pore Metamorphosis, Critical Solid Volume Fraction, Critical Coordination Number, Equilibrium LPS Composition

I. Introduction

Liquid phase sintering (LPS) is widely used in the fabrication of metallic materials. The coexistence of a liquid phase with a particulate solid phase at the sintering temperature enhances densification under unit gravity on earth. There are several system variables associated with LPS. For example, solubility of the solid in the liquid, wetting of the solid (interfacial energy differences) and grain boundary penetration (capillary force) have significant effects on the stability and microstructure of the resultant product (1). These variants coupled with other process variables such as particle size, solid volume fraction, sintering temperature, sintering time, atmosphere and green densities have profound effects on the resultant microstructures of LPS products (1-3).

Gravitational forces produce sedimentation and buoyancy effects that play a significant role in the stability of LPS systems. Sedimentation and buoyancy, driven by differential densities, affect the stability, densification and microstructure of liquid phase sintered products. For example, the gravitational force can produce a gradient in the volume fraction of solid along the height of a powder compact that is liquid phase sintered in unit gravity. Such gradients would result in differences in dihedral angles and coordination numbers across the height of the specimen. The net result is that, depending on density differences, there could be significant variation in microstructural development within a liquid phase sintered sample.

In contrast, sedimentation effects are absent in microgravity. Processing in a microgravity environment provides a unique opportunity to isolate transport from sedimentation mechanisms, thereby permitting the study of transport effects on macrostructure, pore morphology and microstructure. Pores, for example, are not buoyant in microgravity as it is in unit gravity and therefore remain in equilibrium with the solid and liquid phases during LPS. Surface tension and capillary forces become dominant in the absence of gravitational forces. Therefore, studies in microgravity enable the
understanding of thermodynamic equilibria between the solid, liquid and gaseous phases at LPS temperatures.

II. Experimental Approach

Several powder compact samples from the Fe-Cu system were processed in LPS experiments on four sounding rockets and on three Space Shuttle missions. The three compositions that were evaluated were Fe-33 wt.%Cu, Fe-43 wt.%Cu and Fe-53 wt.%Cu, where the processing times of the samples ranged from 2.5 minutes to 66 minutes. High purity powders of Fe (6-9 microns diameter) and Cu (8-11 microns diameter) were pressed into small cylindrical compacts. The compacts were ~10 mm high and 18.8 mm in diameter. These compacts were reduced under high purity hydrogen and placed in stainless steel ampoules. LPS experiments were conducted in an argon environment using an automated, isothermal furnace. The experimental details pertaining to flight hardware and processing have been published elsewhere (4-8).

The samples were metallographically polished prior to characterization. Densities were measured using the liquid displacement method. Dihedral angles, contacts per grain and grain sizes were measured using Jandel Scientific’s image analysis software, Sigmascan.

III. Results and Discussion

1. Densification

The effect of composition and processing time on densification is presented in Figure 1. The Fe-33 wt.%Cu sample displays a continuous improvement in densification with time in contrast to the behavior of the Fe-43 wt.%Cu and Fe-53 wt.%Cu samples. While there is a sharp increase in densification in the Fe-33 wt.%Cu sample, there is a sharp decrease in densification (swelling) in the Fe-43 wt.%Cu and Fe-53 wt.%Cu samples during the initial (rearrangement) stage of LPS. In Fe-33 wt.%Cu, densification continually increases at a much lower rate after this initial increase. In contrast, densification follows swelling in both the Fe-43 wt.%Cu and the Fe-53 wt.%Cu samples with increase in the LPS time.

These differences appear to be directly related to pore metamorphoses in these samples. In the Fe-33 wt.%Cu samples, larger pores break up into smaller pores, the mechanism for which has been discussed in previous publications (6-8). As a result, pores would be uniformly distributed in the microstructure. In the Fe-43 wt.%Cu and Fe-53 wt.%Cu samples, there appears to be pore coalescence in the initial stages of LPS. The distribution of large pores within the microstructure could induce the Fe-Cu mixture to swell until subsequent grain growth, pore break up and shrinkage induce densification. Pore metamorphosis will be discussed further in a later section in this paper.

Figure 1  Densification as A Function of Processing Time

2. Dihedral Angle

Measurement of dihedral angles for the Fe-Cu samples (standard error < 5°) show that the variation in the mean dihedral angle with time is dependent on the volume fraction of liquid during LPS (Figure 2). However, there is a general trend that is common to all the samples. In the Fe-33 wt.%Cu and Fe-43 wt.%Cu samples, the dihedral angle steadily decreases toward an apparent equilibrium value of about 60°. The

![Figure 2](image-url)
dihedral angle in the Fe-53 wt.%Cu decreases below and then increases toward an apparent equilibrium value of approximately 60°.

The decrease in the dihedral angle with processing time is indicative of a tendency toward agglomeration of the Fe particles. Additionally, its tendency toward an equilibrium value of 60° is indicative of the possible existence of an equilibrium LPS composition in microgravity. This would imply that deviation from such a composition could provide the driving force for segregation of the solid and liquid phases to attain the equilibrium composition on a localized scale. Further evaluation is in progress to make a more definitive statement.

3. Contacts per Grain / Coordination Number

Figure 3 shows the number of two-dimensional contacts per grain (C_g) associated with each of the samples, where the standard error is ± 0.2. In the Fe-33wt.%Cu and Fe-43 wt.%Cu samples, there is a steady decrease in C_g with increase in sintering time. However, in the Fe-53 wt.%Cu sample, there is an initial increase in C_g which is followed by a decrease in this number with increase in sintering time. C_g and dihedral angles were used to compute the three dimensional coordination number on the basis of the equation derived by German (9):

\[ N_e = C_g / 0.805 (\cos \phi/2) \]

where N_e is the three dimensional coordination number and \( \phi \) is the dihedral angle. Figure 4 presents the variation of N_e with sintering time.

It is important to determine the minimum volume fraction that constitutes LPS below which, the system might be best described and modeled as a solid suspension in liquid. During LPS, the solid particles, liquid and pores in a compact will behave either as a diffusion controlled sintering system or as a suspension of isolated solid particles and pores in a liquid matrix. This implies that there is a minimum solid volume fraction above which the compact can be considered a LPS system and below which the compact is a suspension of solid, and pores in a liquid matrix. German (10) defines this as the critical volume fraction of solid. The critical volume fraction of solid for a system in which the dihedral angle is zero is 0.6 to 0.64, based on observations of random packing of smooth spheres in unit gravity. This would imply a coordination number of about 8, assuming that the spheres are of uniform diameter.

Determination of the volume fraction of solid below which the behavior of the compact will transition from sintering to a suspended solid is critical for determining compact stability. When the critical volume fraction of solid is exceeded, the compact will exhibit dimensional stability. Below this critical volume fraction of solid, the compact will slump and become unstable when processed in unit gravity. In microgravity, on the other hand, such a compact will try to minimize its energy and assume a spherical shape.

The solid particles and liquid will behave as sintered systems until the liquid neck between particles is ruptured. Figure 5a shows two spheres with radius R separated by a distance D. Figure 5b shows spheres separated by distance D when the liquid neck is ruptured. Experimentally, the rupture phenomenon has been observed by Mason and Clark (11). They observed a normalized rupture distance of D/R ranging from 0.1
to 0.3. Based on this normalized rupture distance, assuming uniform spherical spheres and packing with a coordination number of 8, (which was the number for random packing in unit gravity), the critical volume fraction of solid for LPS was calculated to range from 0.54 to 0.60.

![Diagram of solid particle and liquid neck](image)

Figure 5. a) The geometry of the two solid spheres connected by a liquid neck. b) the geometry of two spheres with liquid neck ruptured.

This result indicates that when the volume fraction of the solid in a compact decreases below 0.54, the compact will begin to behave as a suspended solid. Although this is considered globally, instability could also occur locally where the volume fraction of solid is below the critical volume fraction in certain regions of the microstructure. However, shape accommodation and particle size distribution are additional considerations that have to be factored into the equation to derive the critical volume fraction of solid for LPS. Note that gravitational forces are not considered here because of the microgravity environment.

For a first approximation, a critical coordination number can be computed using the equation derived by German (12):

\[
V_s = -0.831 + 0.806N_c - 0.0555N_c^2 + 0.00176N_c^3 - 0.355N_c\cos\phi/2 + 0.00803(N_c\cos\phi/2)^2
\]

where \(V_s\) is the volume fraction of solid, \(N_c\) is the three dimensional coordination number and \(\phi\) is the dihedral angle. This equation was developed using computer simulations of idealized liquid phase sintered microstructures. In this calculation, the critical volume fraction of solid is taken as 0.54 and an approximate equilibrium dihedral angle of 60° is assumed based on the observations in this study. Accordingly, the critical coordination number below which the system may be described as a suspension rather than an LPS system is 4.4. Given that particles are not perfectly spherical and of uniform size, the critical volume fraction for LPS is most likely lower than 0.54 and accordingly, the critical coordination number may also be lower than 4.4.

The application of this result to the present study yields interesting results. The initial decrease in \(N_c\) in the Fe-33wt.%Cu and Fe-43wt.%Cu samples may be attributed to the wetting of Fe particles by liquid copper, thus reducing interparticle contact. There is no indication of instability on any macroscopic scale with \(N_c\) values ranging between 5 and 6. However, there could be localized instability in the areas of the microstructure where \(N_c\) is around 4. With further increase in sintering time, \(N_c\) increases toward an apparent equilibrium value of 6. In the case of the Fe-53wt.%Cu sample, there is a steep initial increase in \(N_c\). It is interesting to note that, after 2.5 minutes of processing of this compact, \(N_c\) is 4.7 which is close to the critical \(N_c\) required for stability. Therefore, it is believed that instability drives the initial increase in \(N_c\) to above 8, indicating an agglomeration of Fe particles. Subsequent processing reduces \(N_c\) toward the apparent equilibrium value of 6. It is important to note that there appears to be an equilibrium value for both the dihedral angle and the three dimensional coordination number. It is therefore possible to determine the apparent equilibrium composition for this system using Equation 2. Substituting 60° for \(\phi\) (the apparent equilibrium dihedral angle, determined experimentally in Figure 2) and 6 for \(N_c\) (the apparent equilibrium coordination number, determined experimentally in Figure 4), the equilibrium volume fraction of solid for the Fe-Cu LPS system in microgravity is 0.75. This implies that the solid particles and the liquid phase in any composition in the Fe-Cu system will undergo rearrangement and grain growth and attempt to reach the equilibrium solid volume fraction of around 0.75. This was particularly clear in the microstructure of Fe-53 wt.%Cu in which large pockets of Cu were dispersed among areas where the localized volume fraction of solid was about 0.75. It must be noted that 0.75 is the idealized equilibrium volume fraction assuming spherical and uniform particles without any grain growth. The equilibrium volume fraction of solid may be lower than 0.75 when there is deviation from these idealized assumptions.

4. Pore Evolution

Processing in a microgravity environment provided the first opportunity to study pore evolution in
LPS systems because, under unit gravity, differences in the densities of the solid and fluid phases cause deformation of the pores and forces the pores to migrate toward the surface of the compact during LPS.

Pore evolution was studied in detail in the Fe-33wt.% Cu samples. Sample #1 was one of eleven specimens sintered in the Consort 4 sounding rocket for 2.5 minutes, sample #2 was one of eleven specimens sintered in the ECLIPSE-HAB1 experiment aboard STS-57 processed for 5 minutes, sample #3 was one of eleven specimens from ECLIPSE-HAB2 (STS-60) processed for 17 minutes and sample #4 was one of eleven specimens from ECLIPSE-HAB3 (STS-63) processed for 66 minutes. Examination of the samples revealed that pores within the microstructure underwent metamorphosis, the long cylindrical pores breaking up into a string of smaller spherical pores as time progressed. SEM micrographs of Sample #1 showed that both individual pores and networked pores were present (Figure 6). The individual pores transformed from the networked state and were irregular in shape at 2.5 minutes. The SEM micrograph of sample #2 (Figure 7) showed that the grains had coarsened considerably, most networked pores had closed, and the pores were more spheroidized. More significantly, several of these individual spherical pores were linearly arranged. This suggests that they were originally part of long cylindrical or ellipsoidal pores that were broken up by an ovulation mechanism (13). Dumbbell shapes were observed as a result of necking, suggesting that these pores were in the process of breaking up. Pore shapes also resemble those observed in pores of solid phase sintered specimens undergoing break up (14-16). Micrographs of sample #3 that was processed for 17 minutes (Figure 8) showed additional pores arranged in linear strings, some of which were dumbbell shaped. The pore shapes were more spherical and much smaller in size. This strongly indicates that pores were breaking up and that the increased processing time resulted in pores of smaller sizes and regular shapes. Micrographs of sample #4 shows that the pore sizes and population did not change much with the processing time increasing from 17 minutes to 66 minutes (Figure 9). These results seem to suggest that the pores that were present after processing for 17 minutes were already too small to break up.

At the onset of LPS in the Fe-Cu system, the solid Fe phase coexists with the liquid Cu phase and pores that are part of the green microstructure. However, the equilibrium solid phase in the Fe-Cu system at the LPS temperature is Fe-10at.% Cu. Accordingly, the initial reaction involves the dissolution of Cu in Fe. The dissolution reaction is followed by coarsening of the equilibrium solid phase (Fe-10at.% Cu). Total energy minimization being the driving force, this coarsening reduces the solid-liquid interfacial surface area and thus, the energy. Energy minimization would also be expected to dictate pore metamorphosis. The liquid phase (Cu) is the medium in which the phases coarsen or break up to reduce the overall energy of the system.

Figure 6 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-33Cu Sample Processed 2.5 minutes

Figure 7 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-33Cu Sample Processed 5 Minutes

In the Fe-33wt.% Cu samples, coarsening of the solid phase is accompanied by break up of long cylindrical pores into smaller spherical pores as described in the previous section. This phenomenon may be explained as
follows. The initial green microstructure would not be expected to include long cylindrical pores and therefore this morphology must be a result of initial pore coalescence at the onset of LPS, during the rearrangement phase. This also appears reasonable because Cu dissolution in Fe has to precede grain growth and therefore, initial minimization of energy has to be accomplished by pore coalescence during the particle rearrangement stage of LPS. The constraints imposed by the large volume fraction of solid is most likely the reason for these pores remaining cylindrical during the early stages of sintering in the Fe-33 wt.% Cu samples. With increasing processing time, these cylindrical pores break up into smaller spherical pores, thus enabling a reduction in the energy of the system together with grain growth. Xue et.al. (6) substantiated this phenomenological explanation by invoking Rayleigh's model (17) for the break up of a liquid cylinder into spherical droplets.

These cylindrical pores would, most likely, have assumed a spherical morphology in the initial stage of LPS had there been less constraint for movement, as might be expected in samples with higher volume fractions of the liquid phase. However, even after 17 minutes of processing, samples of Fe-43 wt.%Cu and Fe-53 wt.%Cu displayed large non-spherical pore configurations (compare Figures 8, 10 and 11). The reason for this behavior is not clear. Most likely, the lower volume fraction of solid reduces capillary forces that could induce pore break up. However, it is clear that pores in the Fe-53 wt.%Cu sample (Figure 11), with its larger volume fraction of liquid, are more spherical than pores in the Fe-43 wt.%Cu sample (Figure 10). This pore distribution is responsible for

Figure 8 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-33Cu Sample Processed 17 Minutes

Figure 9 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-33Cu Sample Processed 66 Minutes

Figure 10 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-43Cu Sample Processed 5 Minutes

the swelling that is observed in these samples in the initial stages of LPS. In Fe-33 wt.%Cu, pore evolution beyond 17 minutes would be dictated by energy considerations where grain growth and pore coalescence
would be the major influence. This is substantiated by the observation of a limited amount of pore coalescence within the processing time associated with this study. Similar energy considerations would apply in the case of Fe-43 wt.%Cu and Fe-53 wt.%Cu samples. In the later stage of sintering in these samples, grain growth and pore break up probably promote densification. A forthcoming publication will address the effect of composition on pore metamorphosis in the Fe-Cu system.

4) When the coordination number in an LPS system in microgravity decreases below its critical coordination number either globally or locally, the resultant instability will attempt to drive the system, through localized agglomeration, toward a higher coordination number.

5) Evaluation of pore metamorphosis as a function of composition reveals that increasing the volume fraction of liquid promotes pore coalescence which affects densification.

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Figure 11 SEM-BEI Microphotograph of a Vertical Cross-Section of Fe-53Cu Sample Processed 5 Minutes

IV. Summary and Conclusion

Fe-Cu samples with varying composition of Cu have been liquid phase sintered in microgravity. The effect of composition and sintering time on densification, dihedral angle, grain contact and pore metamorphosis have been evaluated. The following conclusions can be drawn from this study:

1) There is a critical volume fraction of liquid in the Fe-Cu system in microgravity, above which the powder compact will swell before it undergoes densification. That volume fraction appears to be between 0.3 and 0.4, close to the apparent equilibrium composition.

2) The dihedral angle decreases with time in the initial stage of microgravity LPS in the Fe-Cu system. However, they appear to move towards an equilibrium value of approximately 60°

3) Assuming perfectly spherical particles and uniform sizes, a critical volume fraction of solid for LPS in microgravity has been found to be 0.54, with a critical three dimensional coordination number of 4.4.