Effects of Initial States on the Spinodal Decomposition of Quenched and Melt-Spun Cu-15Ni-8Sn Alloy

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We investigate early stages of spinodal decomposition in a melt-spun Cu-15Ni-8Sn alloy (melt-spun samples) by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and electron diffraction analysis through comparison against a non-melt-spun alloy of the same composition (quenched samples). In XRD measurements, no sidebands of (200) planes are found in the melt-spun sample after aging at 350°C for 120 min, whereas they are found in the quenched sample after a heat treatment at 350°C for 60 min. TEM observations of a quenched sample after aging at 350°C for 60 min indicate the presence of a modulated structure (λ = 5–10 nm) in the matrix, whereas those of a melt-spun sample after the same heat treatment also indicate the presence of a modulated structure (λ: too small to measure). Electron diffraction patterns reveal satellite structures in both samples, although with superlattice reflections from ordering phases visible in the quenched sample. These differences are presumably due to a difference in the size of clusters present in their respective quenched states; in melt-spun samples, cluster size was much smaller as a result of a high cooling rate (≈8 × 10^5°C/s).

Keywords: melt-spin, sideband, copper-nickel-tin alloy, spinodal decomposition, clustering formation

1. Introduction

In spinodal decomposition, clustering is an essential step in a process by which a homogeneous, supersaturated solid solution spontaneously separates into two phases, each with the same crystal structure but different compositions. In contrast to a conventional nucleation process (in which a critical nuclei forms in a solid solution under slight undercooling and/or low supersaturation), spinodal decomposition, particularly its early stage, is initiated by concentration fluctuations. Small concentration fluctuations occurring in a supersaturated solid solution can be easily enhanced, eventually resulting in macroscopic phase separation.

From an experimental viewpoint, the kinetics of spinodal decomposition after a solution heat treatment (solutionizing) are affected by aging parameters, particularly aging temperature. Many investigations have thus focused their attention on relationships between aging temperature and spinodal decomposition, employing X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), electron diffraction analysis, resistivity measurement, magnetic analysis (including the Mössbauer effect) and neutron diffraction analysis.1–20 Here, however, we note that initial states (initial concentration fluctuations) also seem to play an important role in the kinetics leading to phase separation. Nonetheless, few discussions or investigations relevant to the initial states have been carried out.

Let us consider a solutionizing heat treatment, which is usually performed prior to aging. Here, it is assumed that after solutionizing, the sample is rapidly cooled from a high temperature by quenching in cold water or even iced water, thus producing a homogeneous and supersaturated solid solution in which remain high-temperature atomic arrangements and other thermodynamically unstable states. Note, however, that this approach lacks any detailed consideration of whether high-temperature atomic arrangements can be preserved at low temperatures by simply quenching the sample in cold/iced water for a few seconds. It is true that many XRD profiles of various spinodal alloys in the as-quenched (As-Q) condition exhibit no intermediate bands or sidebands, instead exhibiting only high-temperature homogeneous phases. Furthermore, X-ray small-angle scattering (XSAS) and neutron small-angle scattering (NSAS) investigations of As-Q samples do not reveal any characteristic peaks, and thus do not provide evidence of spinodal decomposition. The intensities of NSAS and XSAS in the As-Q condition monotonically decrease with scattering angle,16,21–25 The above suggests that it is practically impossible to clearly detect and precisely measure very fine clusters in As-Q alloy with any measurement apparatus. Nevertheless, we cannot deny the possibility of very fine cluster formation, particularly when we consider that even when quenching in iced water, the cooling rate can be as low as 10^3°C/s.

Let us consider a solutionizing treatment in which a copper-based alloy is soaked at approximately 800°C and then rapidly quenched in iced water (approximately 0°C) for roughly 1 s so as to maintain its high-temperature phases. Using Einstein’s formula of \( \chi = (2D)\sqrt{t} \), we estimate average diffusion distance \( \chi \) over the quenching process to be approximately 1.4 nm. For this calculation, we utilize the diffusion coefficient of Cu at \( T = 550°C \) and set \( t = 1 \text{s} \) (here, we assume that the temperature of specimen will nonlinearly decrease with time during quenching because of the formation of an insulating vapor shroud when it comes in contact with the iced water). Thus, for the duration of the quenching process, we assume the coefficient of diffusion \( D \) to be approximately \( 10^{-14} \text{cm}^2/\text{s} \). From an experimental viewpoint, we infer Gunier’s radius of gyration for Cu-4 mass% Ti in the As-Q condition to be approximately 1 nm,22 from the results of extrapolating the XSAS data.
Accordingly, we infer that small (less than approximately 1 nm) clusters are likely to exist during the solutionizing heat treatment and we suppose that such clusters act keys to promote phase separation, thereby greatly affecting subsequent spinodal decomposition. Since such a small cluster corresponds to a fluctuation in concentration, clusters already existing in the initial state can be considered as a nucleus or trigger that promotes spinodal decomposition.

However, provided that the cooling rate is sufficiently high to produce an amorphous alloy, the initial condition of atomic arrangement can be expected to be utterly different from that in the solutionizing heat treatment. In a melt-spinning apparatus, the cooling rate can be as high as $8 \times 10^5 \text{C/s}$.

Resulting differences in initial condition can be expected to influence the kinetics of spinodal decomposition.

In this study, we determine the effect of initial state on spinodal decomposition by comparing the behavior of a melt-spun Cu alloy (melt-spun samples) and a non-melt-spun Cu alloy of the same composition (quenched samples). Here, we particularly focus on the early stage of decomposition.

We selected Cu-15Ni-8Sn alloy (melting point $\approx 1150^\circ\text{C}$) as our model alloy for this investigation because it is known to exhibit spinodal decomposition before ordering (i.e., pure spinodal decomposition).

On the basis of the time-temperature-transformation (TTT) diagram for this alloy obtained by TEM characterization and electrical resistivity measurement, we determine that at temperatures above $550^\circ\text{C}$, a discontinuous $\gamma$($DO_3$) phase precipitates without spinodal decomposition from an $\alpha$ phase, and at temperatures between $550^\circ\text{C}$ and $300^\circ\text{C}$, spinodal decomposition first occurs without ordering and later, with increasing annealing time, with $DO_{22}$ ordering. This $DO_{22}$ ordering phase (the crystalline structure of which is the same as that of intermetallic compound $Al_2Ti$ or $Ni_3V$), has an ordered tetragonal structure of ($Cu_{1-x}Ni_{x}Sn$) of $a = 0.377$ nm and $c = 0.724$ nm. It precipitates in a needle-like shape, generating various strain fields in the matrix. With further annealing, $L1_2$ ordering appears. This takes the same crystalline structure as $Al_2Cu$ (i.e., a ($Cu_{1-x}Ni_{x}Sn$) structure). The newly formed $L1_2$ phase nucleates at the $DO_{22}/fcc$ interface with a spherical or cuboidal shape, relaxing the strain fields in the matrix. Finally, mixed $L1_2+DO_{22}$ phase structures become dominant. At temperatures below $300^\circ\text{C}$, spinodal decomposition occurs first and then mixed phases of $L1_2+DO_{22}$ structures simultaneously appear afterward.

From a commercial viewpoint, we note that this alloy, developed by Bell Laboratories in the 1970s as a substitute for potentially hazardous Cu-Be alloys, finds wide industrial application to bushings, bearings, springs and electronic connectors. We thus think it worthwhile to focus on its kinetic mechanisms, particularly with an emphasis on initial state, to promote further commercial use.

2. Experimental Procedures

In this study, small pieces of oxygen-free high-purity copper, 99.999% purity nickel and 99.999% purity tin were charged into a high-frequency furnace at a weight ratio of Cu-15 mass% Ni-8 mass% Sn and then melted together under argon gas shielding. To prepare quenched samples, specimens (9 mm x 9 mm square, 0.6 mm thick, 3 gr mass) were cut from solidified alloy and annealed at $840^\circ\text{C}$ for 60 min before quenching in iced water. Following this heat treatment (i.e., solutionizing and quenching), the specimens were aged at $250^\circ\text{C}$ for 20 min, 40 min or 60 min, or at $350^\circ\text{C}$ for 20 min, 40 min or 60 min.

To prepare melt-spun samples, specimens were fabricated under an argon gas atmosphere using a single roller melt-spinning apparatus. As with the samples for quenching, the specimens for melt-spinning had a mass of 3 gr. These samples were quenched from liquid at a temperature of about $1250^\circ\text{C}$ at a surface velocity of approximately 42 m/s and a blow-off pressure of 0.6 atm. The melt-spun samples thus obtained were about 50–60 µm thick and 1–1.5 mm wide. They were subsequently aged at $250^\circ\text{C}$ for 20 min, 40 min or 60 min, or at $350^\circ\text{C}$ for 20 min, 40 min, 60 min or 120 min.

XRD analysis with a Cu-K radiation source was conducted to investigate sidebands and/or new ordered phases formed during aging. Particularly with regards to sidebands of (200) planes, step scanning was conducted from about 47° to 53° at a scanning speed of 0.3°/min, which we consider appropriate in light of the scanning speed of 0.25°/min reported by Findik.

For TEM, we selected quenched and melt-spun samples that had been aged for 0 min (As-Q) or 60 min at $350^\circ\text{C}$ in order to identify and classify any structural differences between them. TEM specimen discs (diameter: approx. 3 mm) were punched from the samples and polished by ion milling. We next utilized a JEOL-JEM2010 high-resolution transmission electron microscope to observe microstructure and perform selected area diffraction pattern (SADP) analysis.

3. Results and Discussion

3.1 XRD analysis

XRD measurements of both quenched and melt-spun samples from 20° to 80° revealed that no intermetallic phases formed during aging. Instead, only (111) and (200) diffraction profiles from Cu were observed. Step-scan results are illustrated in Figs. 1 and 2. Here, Fig. 1 shows (200) diffraction profiles of quenched samples aged at $250^\circ\text{C}$ for 0 min (i.e., as-quenched (As-Q)), 20 min, 40 min or 60 min. Figure 2 shows (200) diffraction profiles of melt-spun samples produced under the same heat treatment conditions. In both figures (i.e., in both the quenched and melt-spun samples), we note an absence of any clear sidebands.

In an SADP study by Zhao and Notis in which they examined the spinodal decomposition kinetics of a quenched sample, pure spinodal decomposition without ordering is reported to occur in a quenched sample even upon aging at $225^\circ\text{C}$ for 10 min. Also, the ordering process was found to become dominant with a further progression of spinodal decomposition. Accordingly, the spinodal decomposition inferred from Figs. 1 and 2 presumably remains in the initial state without ordering (or, in other words, as pure spinodal decomposition). Thus, the wavelength and amplification are considered to be very small, meaning the results indicate that X-ray intensities of sidebands are very weak and that the shift from the fundamental Bragg peak tends to become large. This

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seems to be the main reason why XRD results show no sidebands in Figs. 1 and 2.

Figure 3(a) shows step-scan results or, more specifically, (200) diffraction profiles of quenched samples aged at 350°C for 0 min (As-Q), 20 min, 40 min or 60 min. Figure 3 (b) shows a magnification of results for the sample aged for 60 min.

Figure 4(a) shows step-scan results or, more specifically, (200) diffraction profiles of melt-spun samples aged at 350°C for 0 min (As-Q), 20 min, 40 min, 60 min or 120 min. Figure 4(b) shows a magnified view of results for the samples aged for 60 min or 120 min.

In contrast to Figs. 1 and 2, Fig. 3(b) shows that a sideband is clearly apparent for the quenched sample aged for 60 min. No sidebands are apparent even in the melt-spun sample aged for 120 min (Fig. 4(b)).

For the quenched sample aged for 60 min, we evaluate the wavelength $\lambda$ of spinodal decomposition using the Daniel-Lipson formula

$$\lambda = \frac{a_0}{h^2 + k^2 + l^2} \delta \theta$$

where $\theta$ is the Bragg angle of the fundamental cubic peak and $\delta \theta$ is the distance of the angle between the sideband and the Bragg peak. Further, $a_0$ is a lattice parameter of the matrix alloy corresponding to its state before spinodal decomposition (i.e., the initial state). The parameters $h$, $k$ and $l$ are the Miller indices of the Bragg peak (in this case, $h = 2$ and $k = l = 0$). From the above equation, we obtain $\lambda \approx 6.0$ nm using the values of $a_0 = 0.3638$ nm, $\theta = 25.08^\circ$ and $\delta \theta = 0.81^\circ$.

For the quenched sample, a peak shift to a smaller angle is observed upon aging at 350°C for 20 min. This shift, apparent...
Maximum of the (200) diffraction profile in Fig. 3(a), is probably attributable to a slight deviation from lattice parameter $a_0$. A small change in lattice parameter may result from the progression of spinodal decomposition. Using RIETAN-2000,37) we determined the lattice parameters of $\alpha$ phase in the AS-Q, 20 min, 40 min and 60 min aged specimens (with a 20 min lattice extension annealing) to be 0.3638 nm, 0.3652 nm, 0.3647 nm and 0.3645 nm, respectively.

As stated in the introduction, DO$_{22}$ ordering phase appears after the pure spinodal decomposition, which generates tensile stress; thus, the lattice extension is attributed to such precipitation of the DO$_{22}$ phase. However, L$_{12}$ phase precipitates at the DO$_{22}$/fcc interface with a spherical or cuboidal shape and this presumably reduces the extension stress in the matrix, resulting in the peak shift to a larger angle with annealing time.

Based on the above discussion, we infer that the split in the (200) peak in the quenched sample aged at 350°C for 60 min (as apparent in Fig. 3 (a)) is associated with precipitation of L$_{12}$ phase, although we cannot yet provide a detailed explanation of this split.

Figure 5 shows the dependence of full width at half maximum of the (200) diffraction profile $\Gamma$ on annealing time for the quenched and melt-spun specimens. Here, $\Gamma$ is at a maximum when the quenched samples are aged at 250°C or 350°C for 20 min. In contrast, $\Gamma$ seems to be constant in the melt-spun samples regardless of annealing temperature and time.

As mentioned in the introduction, the precipitation of the DO$_{22}$ phase from the matrix probably generates various strain fields in the matrix (namely, strain fields under various tensile stresses), leading to higher disorder. Considering that $\Gamma$ tends to increase with degree of disorder and that precipitation of the DO$_{22}$ phase from the matrix probably occurs at 20 min aging, $\Gamma$ reaches a maximum at this time when the DO$_{22}$ phase precipitates. However, as pointed out in the introduction, the transformation of DO$_{22}$ to L$_{12}$ proceeds with longer annealing times, resulting in the relaxation of strain fields in the matrix and leading to a decrease in $\Gamma$.

Additionally, the average grain size of samples fabricated by melt-spinning is usually considered to be very small (about 0.4–0.5 µm in diameter).38) Since $\Gamma$ tends to broaden with decreasing grain size, the large $\Gamma$ of the melt-spun samples in the As-Q condition ($\Gamma \approx 0.35^\circ$) can therefore be attributed to the smaller grain size of such samples relative to that of the quenched samples ($\Gamma \approx 0.24^\circ$).

We next discuss the experimental results of XRD analysis. From Figs. 3 and 4, we note that that a sideband is only observed in a quenched sample. No sideband is detected in the melt-spun samples even upon annealing at 350°C for 120 min. This difference is presumably due to the initial conditions.

In the quenched samples, concentration fluctuations (which are thought to form small clusters) were introduced by the solution heat treatment and triggered spinodal decomposition. This presumably leads to the distinct sidebands apparent in the quenched sample aged for 60 min. Regarding the size of the clusters, Einstein’s formula and an extrapolation of XSAS data relevant to as-quenched Cu-4 mass% Ti alloy22) lead us to infer a diameter of less than 1 nm.

In contrast, the initial conditions seem markedly different in the melt-spun samples. Atom migration is presumably very slight when the samples are quenched from a liquid state with a melt-spinning apparatus at a high cooling rate ($\approx 8 \times 10^5^\circ$C/s), and indeed there appear to be no clusters likely to promote spinodal decomposition in the As-Q condition. For these samples, it would presumably take considerably more time for a further progression of spinodal decomposition to produce a distinct sideband.
From the above discussion, we should be able to detect a sideband in the melt-spun sample if further annealing is performed. Evidence in support of this assertion is straightforwardly given in Fig. 6, which is a magnified view of a (200) diffraction profile for the melt-spun sample aged at 350°C for 300 min. In the figure we can detect the presence of a sideband. This said, the intensity of the sideband appears to be weak in comparison to that of the quenched sample aged for 60 min (Fig. 3(b)), which experimentally demonstrates that much more than 300 min is necessary to produce a distinct sideband in a melt-spun sample. We can interpret this to mean that melt-spinning inhibits spinodal decomposition.

### 3.2 TEM observations and electron diffraction

Next we examine the microstructure of this alloy with TEM observation and electron diffraction. Figure 7 shows TEM bright-field (BF) micrographs of quenched and melt-spun samples (quenched sample are shown in Figs. 7(a0) and (a1), and melt-spun samples are shown in Figs. 7(b0) and (b1)). Note that 0 min aging indicates the As-Q condition (Figs. 7(a0) and (b0)). The two remaining samples (Figs. 7(a1) and (b1)) are both aged at 350°C for 60 min.

TEM observations of the samples in As-Q condition do not reveal any distinct differences (e.g., modulated structures). This result is not unexpected. The initial concentration fluctuations (clusters) are present within the samples prior to annealing. They are very small (less than 1 nm) and amplitudes from such small fluctuations seem to be very weak. It would thus be difficult to detect any marked differences in the As-Q samples.

In Fig. 7(a1), a modulated structure specific to spinodal decomposition is apparent within this quenched sample. From this figure, wavelength $\lambda$ can be roughly estimated to be about 5–10 nm, which seems to be in good agreement with the analytical result of 6.0 nm obtained from eq. (1). Such a modulated structure in the matrix area was also reportedly observed by Zhao and Notis. Although their reported images (for a specimen aged at 475°C for 10 min) appear similar to Fig. 7(a1), there exists no discontinuous precipitate in our case (instead we see only a fully modulated structure). Such a difference is probably attributable to aging temperature. An aging temperature of 475°C may be sufficiently...

![Fig. 6](image6.png)

**Fig. 6** Magnification of (200) diffraction profile for melt-spun sample aged at 350°C for 300 min.

![Fig. 7](image7.png)

**Fig. 7** TEM bright-field (BF) micrographs of quenched and melt-spun samples: (a0) quenched sample aged at 0 min (As-Q state), (a1) quenched sample aged at 350°C for 60 min, (b0) melt-spun sample aged at 0 min (As-Q state) and (b1) melt-spun sample aged at 350°C for 60 min.
high to promote spinodal decomposition even when the aging time is as short as 10 min.

In contrast to Fig. 7(a1), it is difficult to find a modulated structure in Fig. 7(b1). This said, a very fine structure with a small wave length \( \lambda \) does seem to exist. Presumably, such a structure would not show sidebands.

Figures 8(a) and (b) show SADPs of the quenched sample aged at 350°C for 60 min, which corresponds to Fig. 7(a1). Figure 8(c) shows an SADP of the melt-spun sample aged at 350°C for 60 min, which corresponds to Fig. 7(b1). Figure 9 shows the diffraction patterns of the fcc matrix, DO\(_{22}\) and L\(_{12}\) ordering reflections reported by Zhao and Notis.\(^27\)

Figures 8(a) and (b) cover different areas. Thus, their electron diffraction patterns are thought to be somewhat different too (although the exposure time of 5 s is the same). Satellites attributed to structure modulation are apparent. In Fig. 8(b), \{001\} and \{011\}-type reflections from L\(_{12}\) ordering can be seen, indicating the presence of L\(_{12}\) precipitation. As shown in Fig. 9, there are overlaps between L\(_{12}\) and DO\(_{22}\) superlattice reflections (i.e., \{001\} and \{011\} reflections from DO\(_{22}\)). Hence, both phases are considered to coexist. The TTT diagram\(^27\) obtained from TEM and electrical resistivity measurements suggests a coexistence of L\(_{12}\) and DO\(_{22}\) ordering under 350°C aging for 60 min; thus, we would expect to see a coexistence of both ordering phases. However, the intensities of \{0 1/2 1\} reflections of DO\(_{22}\) ordering (which originated from only DO\(_{22}\) ordering) appear weak and rather indistinct. Accordingly, the proportion of DO\(_{22}\) in the matrix may be relatively small. Furthermore, by considering the above results together with the detection of the satellites formed by structure modulation (Fig. 8(a)), the spinodal decomposition with L\(_{12}\) and DO\(_{22}\) ordering seems to proceed in the quenched samples.

In contrast to Figs. 8(a) and (b), Fig. 8(c) shows satellites formed by structure modulation with no superlattice reflections. In the melt-spun samples, this result indicates that spinodal decomposition takes place during 350°C/60 min aging without ordering. In other words, pure spinodal decomposition occurs in the melt-spun sample, although it is difficult to determine spinodal decomposition from the BF image shown in Fig. 7(b1) or the X-ray diffraction profile shown in Fig. 4. Considering this result along with the slow progression of spinodal decomposition, we can conclude that spinodal decomposition remains in the initial state even when melt-spun sample is aged at 350°C for 60 min.
4. Conclusion

From the results of X-ray diffraction (step scanning) and TEM observation (both BF imaging and SADP), we reveal that spinodal decomposition progresses more slowly in the melt-spun sample aged at 350°C for 60 min than in the corresponding quenched sample. The reason why spinodal decomposition is dependent on fabrication method is probably attributable to differences in initial conditions.

As pointed out in the previous section, there exist concentration fluctuations (clusters on the order of less than 1 nm) in the quenched samples. These clusters are introduced to the samples during solution heat treatment, and the progression of spinodal decomposition is likely to be triggered by these concentration fluctuations. Here, we note that distinct sidebands are observed in the quenched sample aged for 60 min.

In contrast, concentration fluctuations existing in the melt-spun samples are presumably too small to promote spinodal decomposition. Because of the high cooling rate to which such samples are subjected, much time is required to induce spinodal decomposition. That is, the formation and growth of initial concentration fluctuations in melt-spun samples are presumably too small to promote spinodal decomposition. In the quenched samples, for instance, as illustrated in Fig. 6, a long annealing time (300 min) is required to produce a sideband in a melt-spun sample.

We conclude that early stage spinodal decomposition is affected by initial conditions (i.e., the size of clusters introduced into the sample prior to aging). However, in this report, we do not consider the As-Q conditions of both sets of samples (i.e., quench and melt-spun samples) in detail. For melt spun samples, which are notable for a very low rate of spinodal decomposition, the extent of initial concentration fluctuations (i.e., those in the As-Q samples) remains to be determined. It is probably safe to say that the fluctuations in those samples will be less than in the quenched samples, but their precise size remains unknown. For the quenched samples as well, uncertainty remains. Einstein’s formula and an extrapolation of XSAS data relevant to the As-Q state of Cu-4 mass% Ti lead us to infer an initial cluster size of less than approximately 1 nm. However, because of a small wavelength and weak amplitude, we could not verify this experimentally. Here, we think that further investigations are required, particularly those focusing on the precise determination of initial cluster sizes within both types of samples by XSAS, NSAS and TEM.

REFERENCES