The Early Stages of GP Zone Formation in Naturally Aged Al-4 Wt Pct Cu Alloys

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The early stages of the room temperature decomposition of supersaturated solid solutions of Al-4 wt pct Cu alloys have been investigated. Diffuse satellites have been found to flank fundamental reflections in electron diffraction patterns prior to the formation of the platelike GP zones. These are herein interpreted as evidence for the occurrence of spinodal decomposition at room temperature. The development of GP zones from the modulated microstructure is documented by the bright field and weak beam dark field techniques. This continuous formation of GP zones is then interpreted in terms of Cahn's later stage spinodal theory.

THE decomposition process in Al-Cu alloys is one which has received an unusual amount of attention. The independent works of Guinier[1] and Preston[2] were the first to show that coherent platelets of copper (now called GP zones) form on the {100} planes of the aluminum matrix prior to the formation of the metastable θ'' and θ' phases.

The sequence of these reactions has been reviewed frequently (see *e.g.* Ref. 3). In this paper we shall only consider the processes which occur before and during the formation of the GP zones during natural aging (*viz* room temperature aging).

After Cahn published his initial work on spinodal decomposition,[4] workers in the field began to speculate that the GP zones may form via the spinodal mechanism. Indeed, the final microstructure was observed to be somewhat similar to that predicted by the theory,[5] having particles that were aligned along the elastically soft directions, and somewhat periodically spaced. However, the composition profiles for GP zones are step functions of narrow width (about one atomic plane thick), whereas the early stage linear theory of spinodal decomposition predicts rather diffuse, periodic modulations. Clearly, the GP zone formation *could* be preceded by spinodal decomposition. However, there was no experimental evidence that it was. If spinodal decomposition does precede the formation of the GP zones, satellites in reciprocal space (or sidebands on Debye-Scherrer diffraction patterns) present because of modulations of composition in real space, should be observed. Until recently, no such observations were reported.

Nevertheless, workers continued to report "hints" that the formation of GP zones may occur in a continuous manner. Asana and Hirano[6] for example found anomalies in electrical resistivity measurements at and below 40°C (313 K). Some calorimetry work[7] showed that abnormal changes occurred in the rate of release of heat below the coherent GP solvus. And finally, the recent X-ray work of Naudin[8,9] and coworkers has shown that satellites apparently occur near the fundamental reflections in Al-Cu alloys.

This work was undertaken to ascertain if satellites in the Al-Cu system are observable by transmission electron microscopy, and if so to ascertain if they are due to composition modulations or if they are due to the intersection of the Ewald sphere with diffuse ⟨110⟩ rel-rods, as has been reported in the Cu-Be system.[10] Furthermore, the mechanism and sequence of the development of GP zones from the modulated microstructure was to be investigated.

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EXPERIMENTAL PROCEDURE

High purity aluminum 4 wt pct copper alloys were solution treated in an argon atmosphere in a tube furnace at 540°C (813 K) for 5 h. The specimens were quenched in water at room temperature and aged for various times at room temperature.

Discs 3 mm diam were punched out of the sheet, and thin foils were prepared by the double jet electropolishing technique, using a one-third nitric acid, two-thirds methanol solution at −25°C (248 K).

A JEM 100B electron microscope equipped with a double tilt stage was used to observe the alloys. The shortest aging time possible at room temperature was about ten minutes, because of the time needed to transport the sample to the polishing solution, and from the polishing solution to the microscope.

Weak beam photographs[11] were taken by satisfying the (020) Bragg reflection, and tilting the reflection into the axis of the column. This resulted in the (060) reflection being satisfied. The s value for this condition, in Al-Cu alloys is about 0.9×10^{-1} nm^{-1}. Throughout the paper this condition will be referred to as the (020), (060) weak beam condition. Exposure times varied from 15 to 60 s. Diffraction patterns were taken with a well defocused condenser lens, for times of 30 to 150 s.

RESULTS

The as-quenched, solution-treated samples showed no evidence of decomposition. Strong two-beam bright field microscopy as well as weak beam dark field microscopy (**g** = (020), (060)) failed to detect GP zones or modulations. The diffraction patterns consisted only of spherical fundamental reflections. No satellites or ⟨100⟩ streaks were detected (see Fig. 1).

Aging at room temperature caused the supersaturated solid solution to decompose. The first evidence of this decomposition occurred after five hours of aging, and was detected by the observation of diffuse satellites at all fundamental reflections. These are shown in Fig. 2. These satellites in reciprocal space imply the existence of real space modulations. The satellites are absent from reflections when $\mathbf{g} \cdot \mathbf{S}_S = 0$, where $\mathbf{S}_S$ is the vector from $\mathbf{g}$, the fundamental reflection, to the satellite position in question. This means they arise from strain modulations[12] which are present because of composition modulations. Their diffusiveness corresponds to modulations of wavelength varying from 4.0 to 8.0 nm. The lack of a ⟨100⟩ streak in reciprocal space, as well as the lack of observation of GP zones in bright field and weak beam mode shows that the zones are as yet not present.

The fact that the relative intensities of the satellites increase with $\mathbf{g}$ (*cf* those at (040) to those at (020) in Fig. 4) is also indicative of their origin, as only satellites which arise from modulations in strain follow this pattern. Care must be taken however when interpreting relative intensities since the intensity of the satellites is also somewhat dependent on the crystal orientation.

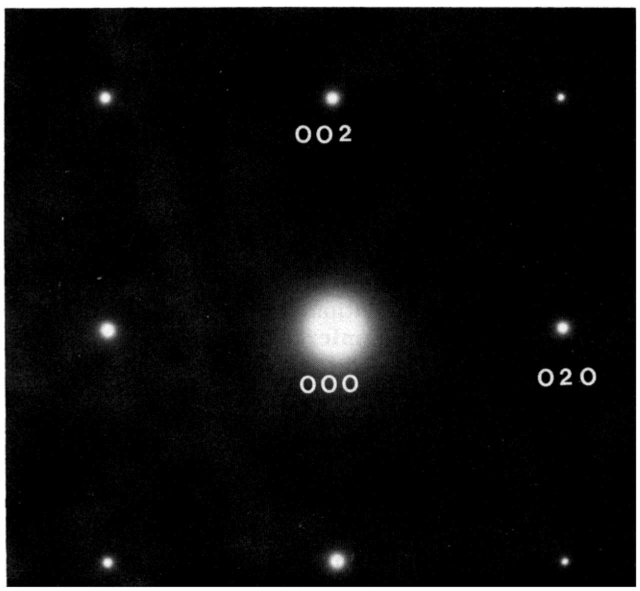


Fig. 1—The [100] diffraction pattern of an as-quenched Al-4 wt pct Cu alloy. The fundamental reflections are round, showing no evidence of satellites or ⟨110⟩ rel-rods. ⟨100⟩ streaks are also absent.

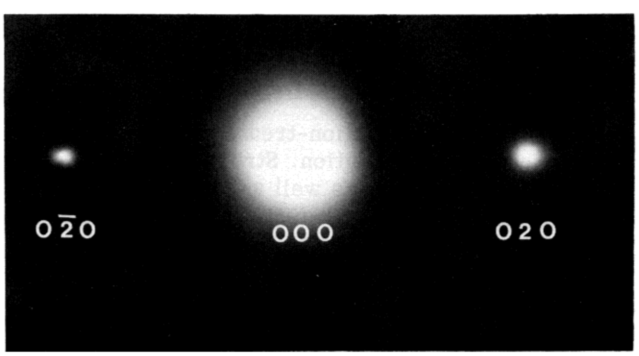


Fig. 2—A section of the [100] diffraction pattern of an Al-4 wt pct Cu alloy aged for 5 h at room temperature. Notice diffuse satellites at the (0$\bar{2}$0) reflection.

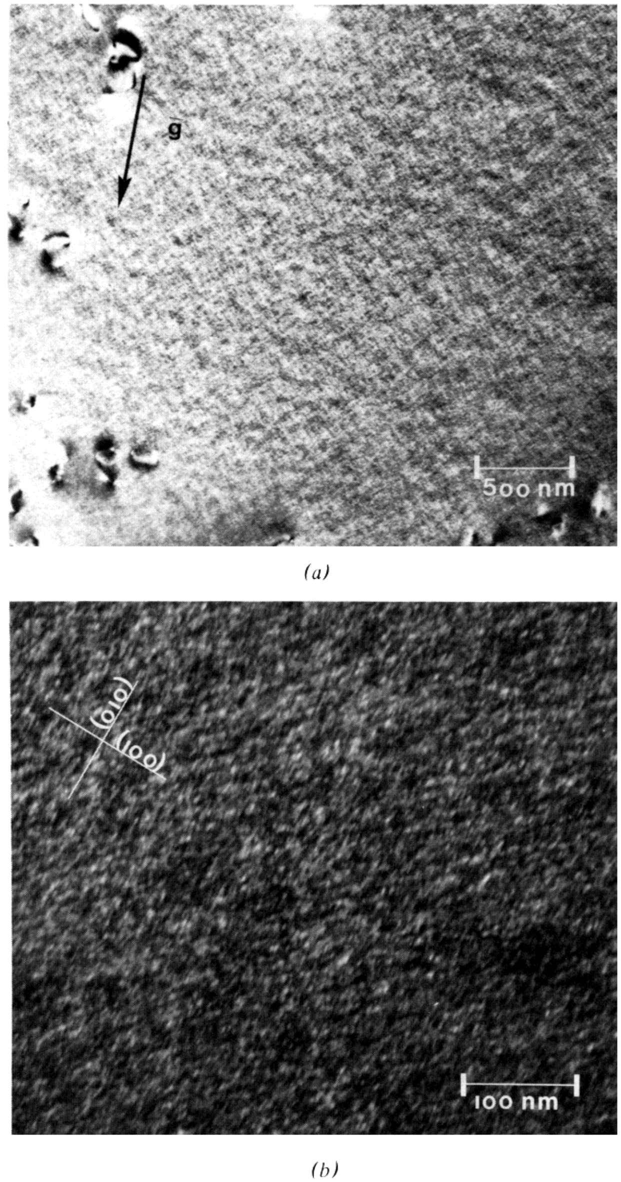


Fig. 3—The microstructure of an Al-4 wt pct Cu sample aged for 168 h at room temperature. (*a*) Bright field, $\mathbf{g}$ = (020), showing ⟨110⟩ tweed; (*b*) weak beam dark field, s = 0.09 nm^{-1} ((020), (060) case). The GP zones show up as bright regions in the weak beam photographs. Zone axis near [100].

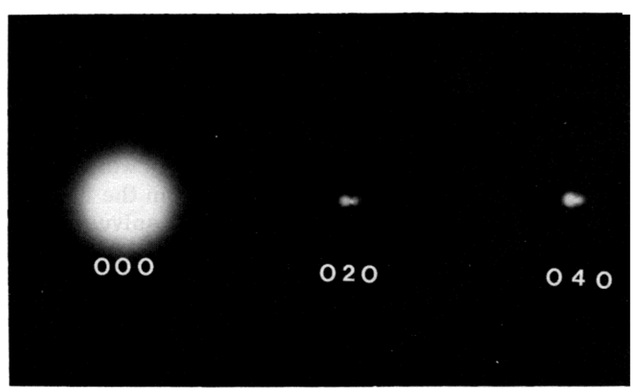


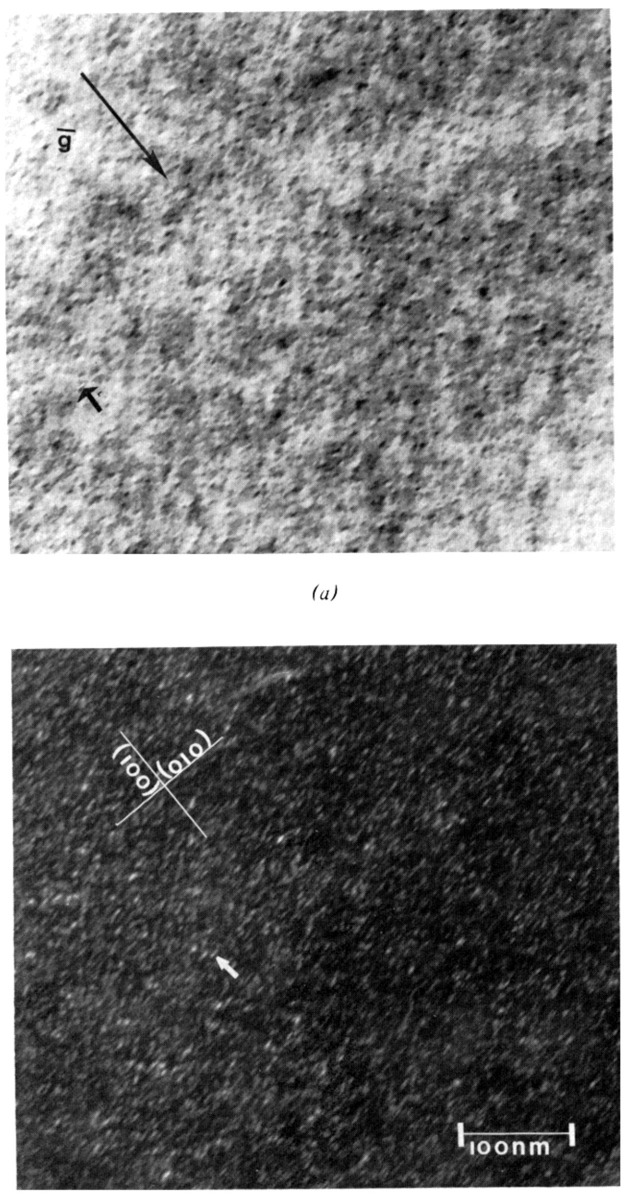
Fig. 4—The [100] diffraction pattern of an Al-4 wt pct Cu alloy aged for 672 h at room temperature. The intensity of the satellites has increased. See the (020) reflection and compare with the (0$\bar{2}$0) of Fig. 2.

Another striking feature of the satellites is their marked intensity asymmetry (*cf* the two satellites flanking the (040) in Fig. 4). This can be explained by noting that the Cu depleted regions probably contain more strain than the Cu enriched regions. Since the intensity of a strain-induced satellite is proportional to the value of the strain squared, the regions with the greater strain (*viz* Cu depleted ones) should give rise to the more intense satellite. These Cu depleted regions have a greater average lattice parameter; hence the low angle satellites are more intense.

After aging for one week at room temperature faint ⟨110⟩ tweed is observed in the bright field mode (Fig. 3(*a*)). This contrast has been said to arise from elastic interactions due to tetragonally distorted regions (as of GP zones) aligned in a stairstep fashion.[13] The 3.0 nm GP zones are shown in Fig. 3(*b*), as imaged by the weak beam technique. The white regions correspond to the zones.

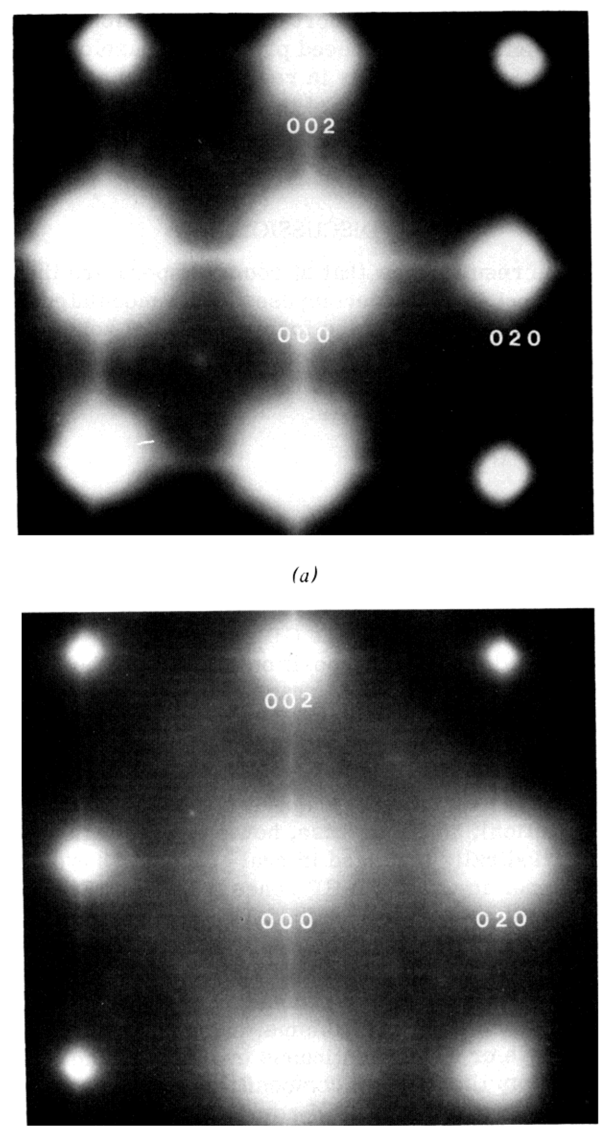
Aging four weeks at room temperature resulted in a large increase in intensity of the satellites (see Fig. 4). Also, GP zones become more readily observable, for example at the arrows of Fig. 5(*a*) and (*b*). The zones are very small, ~3 to 8 nm in diam. They are best seen by the weak beam technique (Fig. 5(*b*)). Yoshida, Cockayne and Whelan[14] have recently shown that GP zones 3.5 to 10 nm are visible by this technique. These results reaffirm their conclusions. Our results differed from theirs somewhat though, in that the GP zones appeared almost exclusively as single bright lines, whereas in their work, pairs of bright lines were more frequently observed.

The ⟨100⟩ streaks in the diffraction pattern for the alloy also show the GP zones are present. They are diffuse, because of the small GP zone diameter. The



(*b*)

Fig. 5—The microstructure of Al-4 wt pct Cu aged at room temperature 672 h. (*a*) Bright field, **g** = (020), showing small (~ 3 nm) GP zone platelets. Notice the black-white contrast; (*b*) weak beam dark field, $s = 0.09\ nm^{-1}$ ((020), (060) case). GP zones show up as bright lines. Zone axis near [100].



(*b*)

Fig. 6—[100] diffraction patterns of Al-4 wt pct Cu alloy. (*a*) Aged 1128 h at room temperature. Notice diffuse ⟨100⟩ streaks; (*b*) aged 130° for 16 h. Notice sharp ⟨100⟩ streaks.

broadening exists in the reciprocal lattice directions which correspond to the radial directions of the real space zones, that is in $\{100\}$ planes. These diffuse streaks are best observed in Fig. 6(a) which is a diffraction pattern of a sample aged for 1128 h at room temperature. The diffuseness should be compared with the sharp streak observed in samples aged at 130°C (403 K). See Fig. 6(b) and discussion below.

Extra reflections appear in the diffraction pattern shown in Fig. 6(a). The diffuse reflections at the (011) positions are intersections of the [100] streaks with the reflection sphere. The other two diffuse reflections are from Al_2O_3 oxide, which forms epitaxially on the surface of the specimens.

With further aging at room temperature the satellites remain, and for times up to four months the well known transition phases of θ'' and θ' do not appear in bulk samples (*i.e.* samples of thickness on the order of 0.01 in. (250 μm) thick).

The samples were carefully examined for the existence of $\langle 110\rangle$ rel-rods in reciprocal space. They were not observed, giving support to the conclusion that the diffuse satellites are indeed present because of diffuse composition modulations in real space, and not because of the intersection of the Ewald sphere with $\langle 110\rangle$ rel-rods, as is the case in the similar Cu-Be system.[10]

DISCUSSION

These results show that at room temperature the Al-4 wt pct Cu alloy decomposes into a modulated microstructure *before* the formation of GP zones. This implies that the alloy may have decomposed by the spinodal mechanism. This initial decomposition process may be written as:

$$\alpha' \rightarrow \alpha_{Al} + \alpha_{Cu} \qquad [1]$$

where

α' is the supersaturated solid solution,
α_{Al} is the Al-enriched regions of the matrix and
α_{Cu} is the Cu enriched regions of the matrix.

Following this process, the GP zones form.

The details of the composition profiles in the Cu-enriched regions (*viz* α_{Cu}) can not be obtained by conventional TEM techniques. Thus the regions may be similar to the "Guinier zones"[15] (not to be confused with GP zones), or they may have a continuous composition variation throughout (as in spinodal decomposition). In either case, however, the regions are periodically arranged in real space as shown by the manner in which the GP zones form (*e.g.* Fig. 5). Thus it appears that spinodal decomposition has occurred.

The appearance of the platelike GP zones *after* the initial decomposition process can be accounted for by two distinct mechanisms, namely by nucleation and growth or by the continuous evolution of the plates from the existing composition modulations. These two mechanisms will now be qualitatively discussed.

Clearly the solute enriched regions could act as sites for easy nucleation of the pure Cu platelet GP zones. The build-up of solute in the regions minimizes the need for solute diffusion to the sites. This mechanism is fairly straight-forward, and does allow for the existence of the "semiperiodic" array of GP zones that results.

However the diffuseness of the $\langle 100\rangle$ streak does suggest that the zones could be forming continuously from the initial modulated structure. GP zones that form at 130°C (403 K) give rise to very sharp $\langle 100\rangle$ streaks in reciprocal space. This is to be expected if they form above the spinodal, where they nucleate directly as plates. However, if the modulated microstructure continuously transforms to the GP zone microstructure, we would expect the $\langle 100\rangle$ streaks to appear gradually, their initial appearance being rather diffuse. Such is the case. (See Fig. 6(a), which is the diffraction pattern which corresponds to a sample aged for 1128 h at room temperature. *cf* Fig. 6(b).) We conclude therefore that such a mechanism is the more likely.

This continuous change of the early stage microstructure into the later stage GP zone microstructure, can not however be explained by the linear theory of spinodal decomposition. This theory predicts[5] that the final microstructure will consist of particles of the solute-enriched phase that are more or less cuboidal in nature. The previous studies on Cu-Ni-Fe[16,17] and Ni-Ti[18–20] follow this very closely. One exception is found in the Cu-Ti case, where the particles of Cu_4Ti terminate as "elongated" cuboids.[21–23] This however is a coarsening effect, and is related to the fact that the Cu_4Ti has tetragonal symmetry, as opposed to the cubic symmetry in the Ni-Ti and Cu-Ni-Fe cases.[24] The particles elongate along their c-axis in order to minimize the coherency strains.

In Al-Cu, however, the exception is more pronounced. The cuboidal regions collapse to platelike regions during the later stages of the spinodal decomposition process. In terms of Cahn's later stage solution to the nonlinearized diffusion equation,[25] the higher order anharmonic terms have an exaggerated effect on the final microstructure. Specifically, the second and third harmonics, which come about by expanding the expression (Eq. [3] of Ref. 15)

$$\frac{M}{N_v}\left\{\frac{\partial^2 f}{\partial c^2} + \frac{2\eta^2 E}{1-\nu}\right\} \qquad [2]$$

about the average composition are of great importance in the Al-Cu system. In the above expression, $\partial^2 f/\partial c^2$ is the second derivative of free energy with respect to composition, η is the fractional change in lattice parameter per unit composition change (*viz* $(1/a) \times (da/dc)$), E is Young's modulus (assumed isotropic), ν is Poisson's ratio, M is the diffusional mobility and N_v is the number of atoms per unit volume.

The second harmonic amplifies the composition of the GP zones at the expense of the matrix, and limits their spatial extent.[25] The third harmonic sharpens the interface between the zone and the matrix,[25] ultimately yielding the one atomic layer thick GP zone (often called GP I). The reason for the unusually strong composition dependence of Expression [2] is not certain. It probably is related to the fact that Al and Cu have a large atomic disparity (about 9 pct). This makes it energetically unfavorable to build up 3-

dimensional regions of pure Cu in the Al matrix. However, the details of this relationship have not yet been worked out.

Thus, while the decomposition process starts out as predicted by the linear theory of spinodal decomposition, the higher order harmonic terms soon take on a predominant role in the development of the microstructure. It must be emphasized that these conclusions are based on room temperature aging experiments. At higher temperatures (*e.g.* 130°C (403 K)) the zones nucleate directly from the supersaturated solid solution without any prior decomposition. Satellites are not observed prior to the formation of GP zones at 130°C (403 K).

CONCLUSIONS

From the results and the discussion we conclude the following:

1) Al-4 wt pct Cu initially decomposes into solute enriched and solute lean regions. We interpret this to show that spinodal decomposition occurs at room temperature. This is first observed after 5 h.

2) GP zones were first resolved after about 1 week at room temperature.

3) The GP zones form continuously from the early stage modulated microstructure as a result of the dominance of the second and third harmonic terms of the solution to the nonlinearized diffusion equation.

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