The Microstructure of Metastable Phases in Ag-Cu Alloys Generated by Continuous Laser Melt Quenching

DAVID G. BECK, S. M. COPLEY, AND M. BASS

A scanning high power CW CO_2 laser with an average power density of 13.4 MW cm^{-2} was used to produce metastable phases in three Ag-Cu alloys; Cu 25 at pct Ag, Cu 50 at pct Ag, and Cu 75 at pct Ag. Scanning, at traverse rates of 10 to 115 cm s^{-1}, was performed in an inert atmosphere to prevent oxidation. Inspection of the trails by scanning electron microscopy showed the microstructure to be either cellular dendritic or featureless. X-ray examination of the trails verified the presence of extended metastable solid solutions. After etching, the transverse section showed alternating light and dark bands perpendicular to the local growth direction. Through the use of energy dispersive X-ray analysis, it was shown that there was a significant increase in the Ag concentration in the light bands.

BY "splat cooling," Duwez *et al* were the first to produce metastable extended solid solutions in the Ag-Cu system.[1] Subsequently, the Ag-Cu system has often been used in the examination of new techniques for non-equilibrium phase formation. It exhibits a simple eutectic phase diagram (Fig. 1), with the supersaturated solid solutions' lattice parameters showing an almost linear dependence on composition.[1] Recently, Elliot *et al* produced metastable extended solid solutions in Ag-Cu alloys by self-substrate quenching small regions melted with a pulsed Nd:glass laser.[2] We have previously demonstrated the feasibility of forming continuous trails of metastable extended solid solutions melted by scanning a CW CO_2 laser beam along the surface of Ag-Cu alloy specimens.[3] In this paper, we present the results of a detailed investigation of the constitution and microstructure of continuous melt trails in Ag-Cu alloys containing 25, 50, and 75 at. pct Ag. These compositions were chosen so that a direct comparison could be made with the microstructures observed in earlier experiments employing a pulsed Nd:glass laser.[2]

SAMPLE PREPARATION AND OPERATING CONDITIONS

Starting with 99.995 pct purity silver and 99.9999 pct purity copper, three alloys were formed; 25, 50, and 75 at. pct Ag. The samples were repeatedly mixed with an arc button melter to promote homogenization, turning over the cast buttons before each individual melting process was begun. The buttons were cold rolled and then annealed at 725 °C for approximately one month. A low speed abrasive saw was employed to slice individual specimens. To enhance absorption, the scanned surfaces were coated with a trichloroethane suspension of graphite. Prior to coating, the top surfaces were polished in order to insure uniform surface roughness. Full details of sample preparation were previously presented.[4]

The laser, operating at a wavelength of 10.6 μm in the TEM_{oo} mode, had an output power of 1250 W and an incident power of 1050 W. After coating, the samples absorbed an average of 26 percent as calculated using a melting efficiency approach. Focussing with a 63.5 mm focal length lens, an average power density of 13.4 MW cm^{-2} was achieved. Sample translation rates ranged from 10 to 115 cm s^{-1} with an inert atmosphere being employed to prevent oxidation reactions from occurring. The laser beam was oriented at normal incidence to the samples.

MICROSTRUCTURE

Figure 2 (a) through (c) show cross-sectional views of a trail in each composition range. A low speed abrasive saw was used to section the trails which were then mechanically polished down to a finish of 0.3 μm alumina. The etching solution was made up of 7.6 gm CrO_3, 5 ml H_2SO_4, and 1 liter H_2O, which had previously been observed to attack Cu-rich material more strongly than Ag-rich material.[3] As opposed to an earlier report[4] in which trails from several rates were studied, in this investigation, only 10 cm s^{-1} trails were examined in detail. These samples had sufficiently large trails to

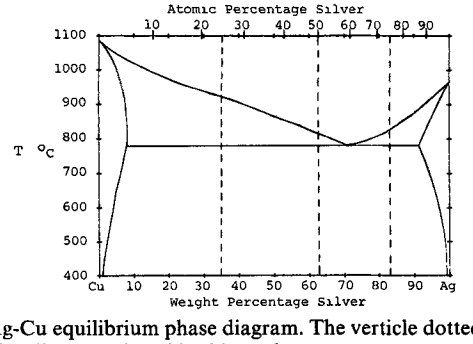

Fig. 1—Ag-Cu equilibrium phase diagram. The verticle dotted lines indicate the alloys employed in this study.

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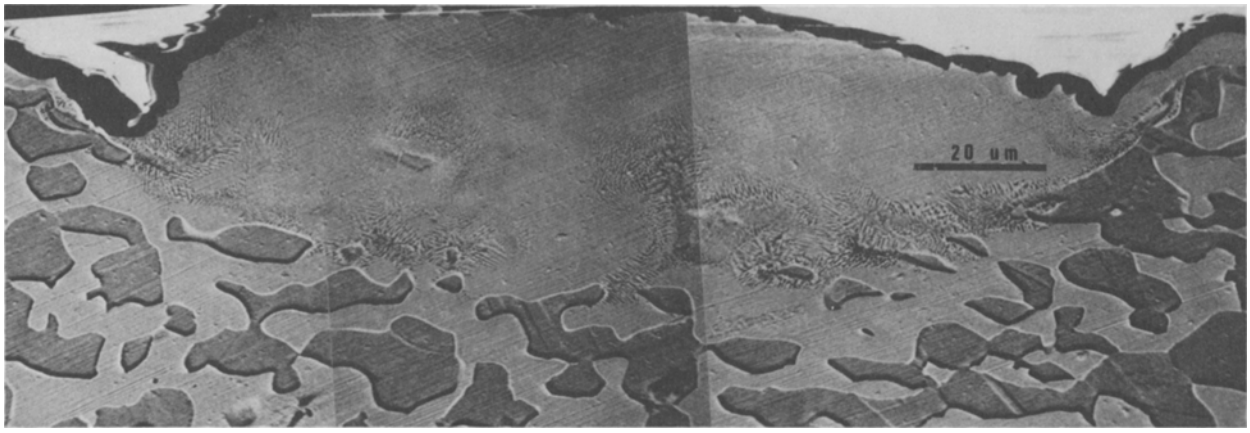
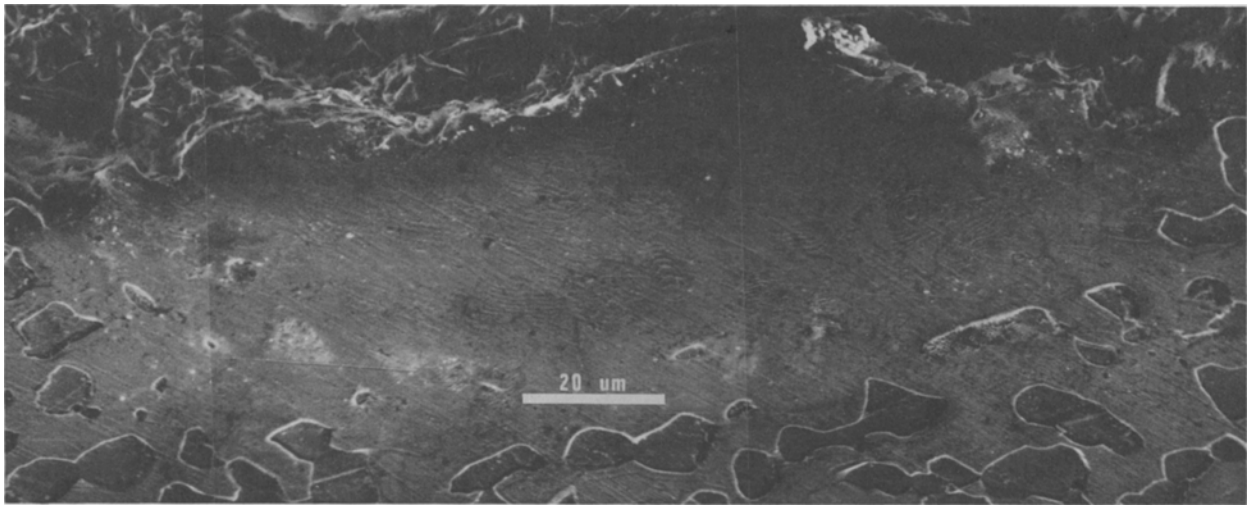
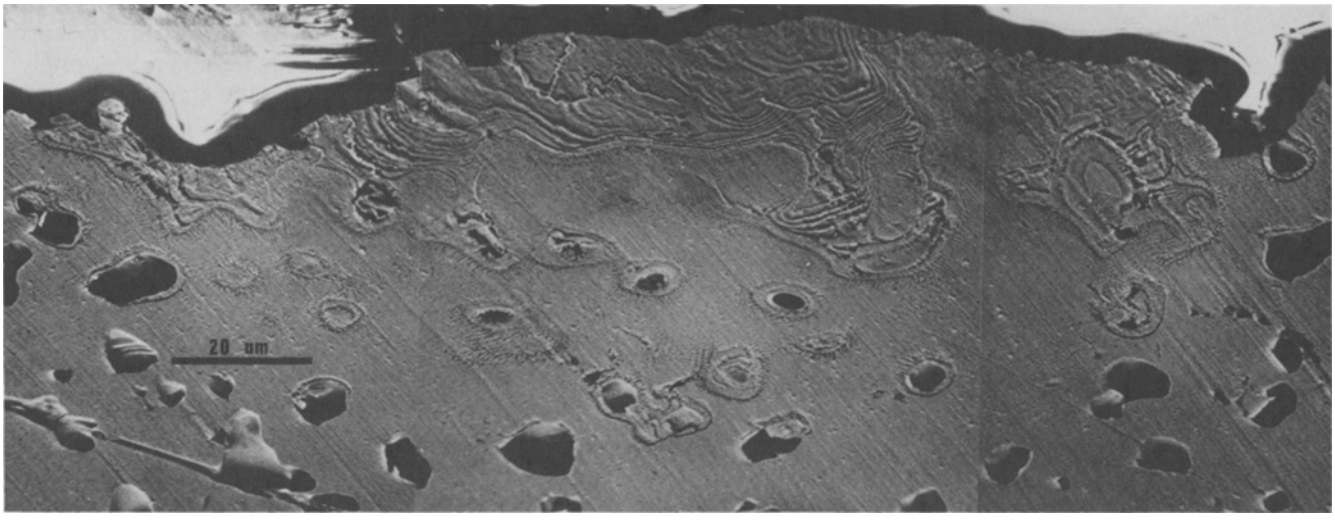
facilitate characterization while still exhibiting the same phenomena found in the higher rate samples. In the lower regions of Fig. 2 (a) through (c) the coarsened eutectic microstructure of the unmelted parent matrix can be seen; the dark areas corresponding to the Cu-rich phase. Except for the banding structures discussed in greater detail in the next section, the bulk of the melt zones in the Cu 25 at. pct Ag and Cu 50 at. pct Ag samples appear to be featureless at magnifications of up to 30 K. For the SEM used, structures ranging



(a)



(b)



(c)

Fig. 2—(*a*) Cross section of a Cu 25 at. pct Ag sample. (*b*) Cross section of a Cu 50 at. pct Ag sample. (*c*) Cross section of a Cu 75 at. pct Ag sample.

from 200 to 300Å (the variance due to the exact operating conditions used) are resolvable. In previous work[3] at lower power densities (5.7 MW cm^{-2}) as well as slower scan speeds (0.7 to 2.1 cm s^{-1}), areas of fine eutectic plates with approximately 450 to 750Å spacing were observed at the same magnification (Fig. 3). It was not possible, however, to resolve any form of structure in the 'featureless zones' of the current samples.

In the Cu 75 at. pct Ag alloys, while some areas were featureless, others had a cellular dendritic structure. These dendrites as well as a series of bands can be seen in Fig. 4, showing the very top of a melt zone. Even under extreme etching, bands and Ag-rich dendrites were never observed in the same region.

BANDING PHENOMENA

In all three compositions etching of transverse sections revealed bands running approximately normal to the local heat flow as seen in Fig. 2. This suggests that in Fig. 5, a heavily etched portion of a Cu 50 at. pct trail, the light, elevated bands are Ag-rich while the dark, depressed bands are Cu-rich.

To determine in a more quantitative way to what extent composition was varying between bands, energy dispersive X-ray analysis was employed involving a two step analysis of incoming X-ray spectra. Initially a multiple least squares analysis technique was applied to obtain accurate measurements of peak intensity in the presence of both continuum and peak overlaps. Next a theoretical correction procedure was undertaken to correct for atomic number, absorption, and fluorescence (*i.e.*, ZAF correction factor). To statistically determine the difference, if any, in silver concentration between bands, a null hypothesis two-tailed test was applied where the null hypothesis to be tested was that adjoining bands have, on the average, the same concentration of silver. In order to compensate for the effects of any overall compositional gradients, the data was paired before analysis. This gives a positive correlation between the concentrations found in the two bands.[5] Figure 5 indicates the pairs used in one such analysis with Table I giving the concentrations found for this set of points. For this area, using 99.9 percent confidence limits, it was concluded that the Ag-rich bands contained a significant increase in silver concentration. This confidence level shows that there is less than 1 chance in a 1000 that the above null hypothesis is actually true. The mean increase in silver concentration was 1.1 at. pct. It should be noted, however, that this is only the 'apparent' mean increase, and quite likely to be less than the actual difference in silver concentrations. This is due to the sampling volume being approximately 1 μm in diameter, due to the depth of penetration, while the bands being studied are less than 1 μm in width. Thus the determined silver concentration in the Ag-rich bands will be reduced while the silver concentration in the adjoining Ag-depleted bands will be increased. Therefore the mean increase in silver concentration between bands which was found in this study should be treated as the lower limit in difference, rather than the actual difference in silver concentration.

Occasionally the bands were observed to be nonparallel to the local heat flow direction but rather to be distorted as in Fig. 6. A point to point energy dispersive X-ray analysis revealed not only the alternating concentrations between light and dark bands but also the decreasing copper concentration as the radial distance was increased. This phenomena could best be explained by the presence of a partially dissolved Cu particle lying just beneath the surface. The high concentration of Cu would be expected to raise the melting point of the liquid surrounding the particle. This suggests that the bands mark a position of the melt-solid interface during

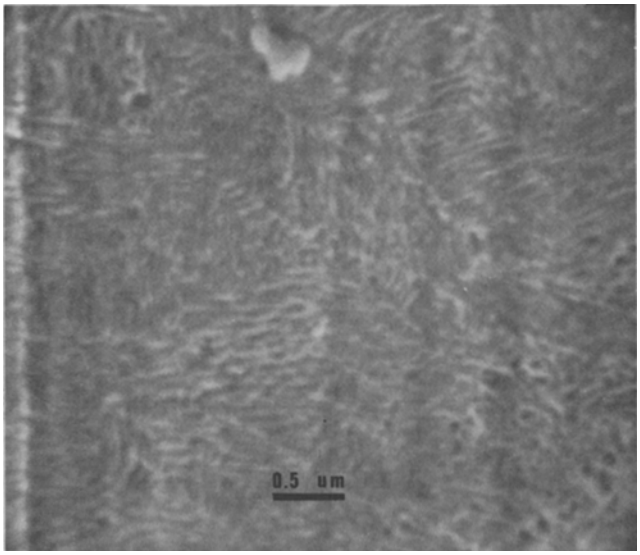


Fig. 3—Fine eutectic plates as observed in earlier work.

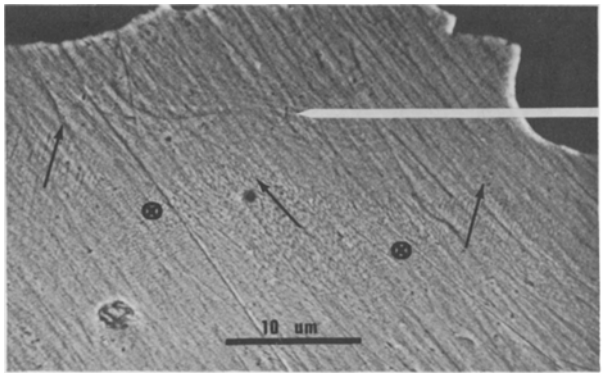


Fig. 4—The top of a melt zone in a Cu 75 at. pct Ag sample. Arrows indicate dendrite growth. In areas marked ⊗ the dendrite growth is not parallel to the plane of the section.

solidification rather than conforming to the local direction of heat flow.

Bands similar in appearance to ours have been seen in identical compositions by Elliot *et al*,[2] who employed a pulsed Nd:glass laser. They suggested that power spikes in the laser pulse were causing variations in solidification rates resulting in the bands. The observation of such bands in our trails produced by a laser operated in the CW mode appear to rule out this explanation and support the hypothesis that they are a feature inherent in the solidification process. Bands such as these have been seen in one form or another in other types of crystal growth.[7] They have been attributed to growth rate fluctuations and melt composition variations, both of which are likely to be present in laser produced melt trails. Growth rate fluctuations may occur due to temperature variation in the melt pool resulting from surface tension driven convection. It has been shown that such convection is often present in laser melt pools.[8,9] Close examination of Fig. 2 (a) through (c) reveals the presence of partially dissolved Cu-rich particles indicating variations in melt composition. Therefore the occurance of bands, although not a fully understood phenomenon, is not surprising.

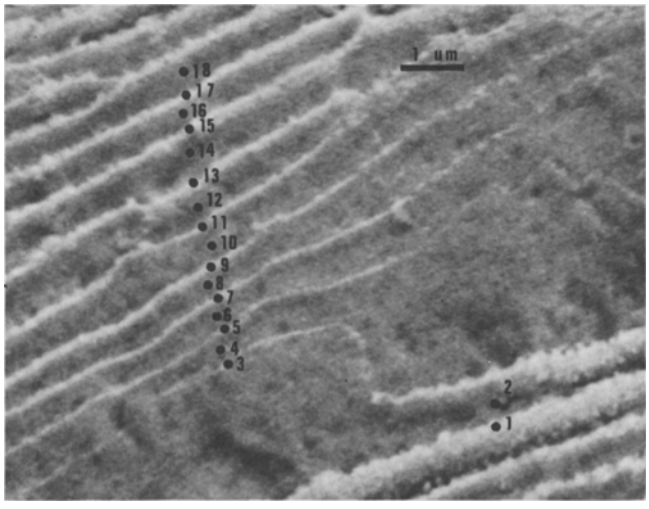


Fig. 5.—Heavily etched bands—Cu 50 at. pct Ag.

Table I. Concentrations Found For Points In Figure 5

Pair Number (Points)	Ag Concentration	
	Light Band	Dark Band
1 (1&2)	80.3	78.6
2 (3&4)	71.0	70.1
3 (5&6)	71.8	70.1
4 (7&8)	71.6	70.2
5 (9&10)	69.7	69.3
6 (11&12)	70.0	70.0
7 (13&14)	71.2	69.9
8 (15&16)	71.7	69.9
9 (17&18)	69.9	69.2
10 (19&20) (off picture)	79.4	78.1

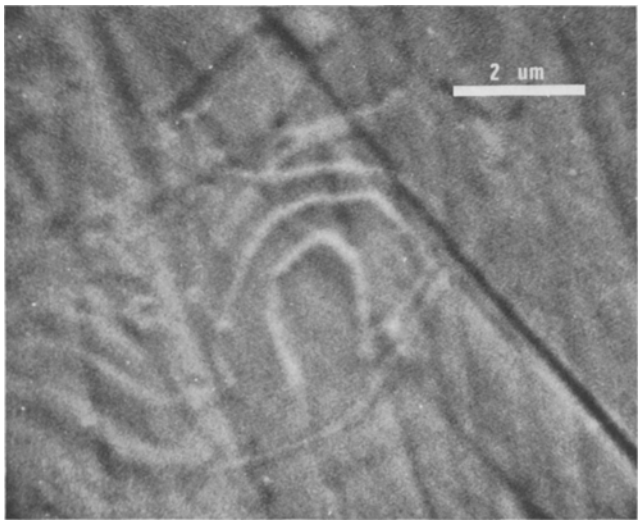


Fig. 6—Bands flowing around a Cu-rich particle lying just below the surface.

ANNEALING

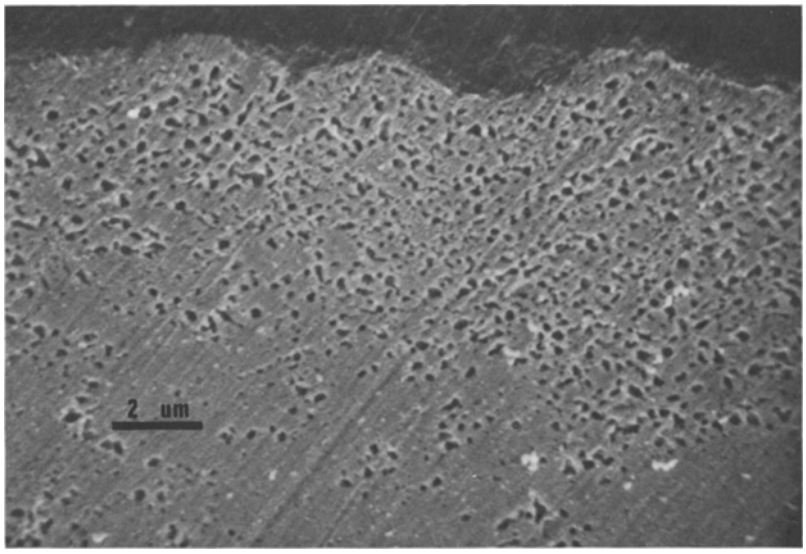
A section of a Cu 50 at. pct Ag sample scanned at 10 cm s^{-1} was annealed in an argon atmosphere for 1.75 h at 390 °C and then air cooled. Figure 7(a) shows a centered section encompassing the top fourth of the trail in this sample. The structures observed in this micrograph were also seen in the other two compositions, although the eutectic concentration was lower and the dendritic concentration was higher. Etched out regions about 0.1 μm in diam, presumably marking Cu-rich precipitates, were observed throughout the trail. Interspersed about the melt zone, and seen at the bottom of Fig. 7(a), are regions which appear featureless at low magnification. Figure 7(b) is one such area under high magnification, demonstrating the presence of an extremely fine eutectic. Evidently these areas were there prior to annealing, but had too fine a structure to be resolved by the SEM. During annealing precipitation occurs rapidly in the metastable phase due to the large driving force while the more stable eutectic phase only undergoes gradual coarsening. The final size of the eutectic, ranging from a plate spacing of 450 to 1700Å, is dependent upon its initial size. The area under view in Fig. 7(b) has a plate spacing of approximately 0.14 μm.

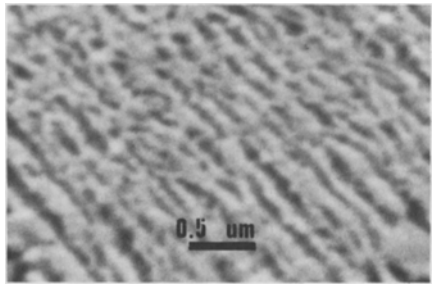
X-RAY RESULTS

A full discussion of the X-ray methods used for this work were reported earlier.[4] As previously stated, the trail made up only 3 to 4 pct of the diffracting volume, thus the diffraction lines due to the metastable phases were

Table II. Determined Lattice Parameters for the Three Compositions Under Investigation

		Composition		
		25 Ag/75 Cu	50Ag/50 Cu	75 Ag/25 Cu
Lattice Parameter (Å)	α	4.0688	4.0688	4.0688
	β	3.6290	3.6290	3.6290
	γ	3.7407	3.9081	3.9924





(b)

(a)

Fig. 7—(*a*) Annealed Cu 50 at. pct Ag sample. (*b*) Fine eutectic region.

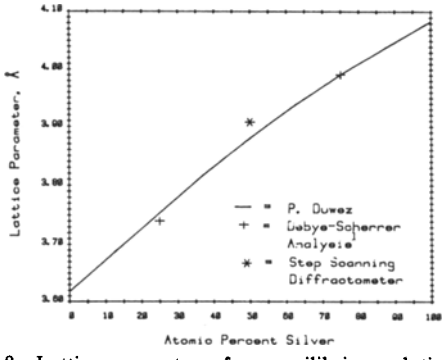


Fig. 8—Lattice parameters of nonequilibrium solutions.

very light in contrast to the α (silver-rich) and β (copper-rich) diffraction lines.

For all three compositions, metastable solid solutions were indicated by a modified Debye-Scherrer camera, the resultant lattice parameters being given in Table II. Figure 8 compares these results with those obtained by Duwez through the use of a splat cooling technique.[1]

CONCLUSIONS

1) Continuous trails containing significant amounts of metastable extended solid solutions have been formed at the surface of Ag-Cu alloy samples melted with a scanning CW CO_2 laser.

2) In the Cu 75 at. pct Ag alloy, the region occupied by the metastable phase has a cellular dendritic structure. In the Cu 25 at. pct Ag and Cu 50 at. pct Ag samples this region is featureless.

3) For all three compositions, alternating light and dark bands lying approximately perpendicular to the local growth direction were observed. These bands had a minimum local variance in composition averaging 1 at. pct.

4) For all three compositions, annealing at 390°C for 1.75 h resulted in precipitation in some regions of the trail. It is suggested that these regions are occupied by the metastable phase.

5) Lattice parameters for the metastable phases of the three compositions were determined and were found to lie quite close to the lattice parameters determined by Duwez[1] in splat cooled specimens of the same composition.

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