assuming that weak contrast was indicative of  $\mathbf{g}.\mathbf{b} = \mathbf{0}$ . It was found that in the majority of cases the term m was greater than 0.1 and for those cases where it was lower complete invisibility could be obtained if care was taken to establish the best possible two beam conditions. This is illustrated in Fig. 1 which shows an example of the contrast corresponding to high and low values of m. As long as these precautions were taken, it was found possible to unambiguously identify the presence of the Burgers vector  $\frac{1}{3}$  (1 1  $\overline{2}$  3). Although the importance of the term m explains the difficulty that is encountered in obtaining invisibilities, it does not provide a reason for the frequent observation of multiple images. The most common cause of this type of behaviour is the failure to obtain exact two-beam diffraction conditions which causes non-systematic reflections to contribute to the image. The effect of these non-systematic reflections can be eliminated by the use of complementary bright- and dark-field electron microscopy. Of the many instances of multiple images that we have observed, none were indicative of a dislocation dissociation since the multiple image was always lost in dark-field conditions. A typical example of this type of behaviour is shown in Fig. 2a and b which shows the same area imaged for both bright and dark field conditions. It is also worth noting that when the dislocation is imaged close to the Bragg condition it is also quite possible for a symmetrical double image to result from an undissociated dislocation.

From these results it is apparent that the difficulties encountered by other workers in identifying the  $\frac{1}{3}$  (1 1  $\overline{2}$  3) Burgers vector is a result of contrast effects caused by the nature of the dislocations. Although the variation of dislocation image contrast with dislocation character is a well known effect it is worth stressing its special significance to many ceramic materials. This arises from the fact that many ceramics possess large unit cells, often containing several atoms of different elements, which often results in large Burgers vectors. It is therefore obviously necessary when using transmission electron microscopy to determine Burgers vectors to take both full account of the effect that this can have on the dislocation images and to exercise extreme care in the setting of the experimental conditions.

## Acknowledgements

The authors wish to thank the Directors of Pilkington Bros Ltd and Dr D. S. Oliver for permission to publish this letter.

## References

- 1. A. G. EVANS and J. V. SHARP, J. Mater. Sci. 6 (1971) 1292.
- 2. E. BUTLER, Phil. Mag. 21 (1971) 829.
- 3. R. KOSSOWSKY, J. Mater. Sci. 8 (1973) 1603.
- A. G. EVANS and J. V. SHARP, "Electron Microscopy and Structure of Materials" (California Press, 1972) p. 1141.

Received 25 August and accepted 10 September 1976

> P. M. MARQUIS Department of Physical Metallurgy and Science of Materials, University of Birmingham, Birmingham, UK

E. BUTLER Pilkington Bros Research Laboratories, Latholm, Lancashire, UK

# Reply to "A discussion of flip-flop decomposition"

In offering a description of a possible mode of decomposition within miscibility gaps, it is my contention that the proposed model is not in agreement with the usual interpretation of Cahn's analysis but this is not intended to imply that the model is not consistent with Cahn's Equation 18 [1]. We did refer to the process as spinodal 426 decomposition, but with some reservations because this term has been so widely and loosely used as to be almost devoid of meaning. They correctly point out that Hillert [2] had already considered this model, a point which we unfortunately failed to note. While the model would include the case where the initial particles formed during cooling this is, we feel, unnecessarily restrictive.

If, as we believe, Cahn's Equation 18 [1] is applicable to the model in question then its

© 1977 Chapman and Hall Ltd. Printed in Great Britain.

numerical solution in the direction normal to the plate growth would yield a rate of growth and the period of the structure. But in the absence of such a solution, the relation between plate thickness, driving force, and chemical gradient energy is truly unknown. The concept of a geometric series of composition fluctuations does not directly lead to a unique plate thickness.

Our interpretation of their comments is that the proposed model is in agreement with the concept of a solution corresponding to the superposition of sine waves of time dependent amplitude. We question this because in the first place the composition fluctuations are occurring in only one of the three possible directions in the region of growth. Further, we are concerned primarily only with harmonics of the fundamental wave length and all waves share a common phase relationship within the decomposed region.

Their contention that the model is described by the theory but, when put to the test in the Fe–Al system, does not work, would appear to pose an interesting dilemma for them. It poses no such problem for us, since we reject the test for the following reason.

Based upon the phase equilibria data and the limited thermodynamic data, we are reasonably confident that the thermodynamics of the Cu-Ti system is approximately as shown in Fig. 1a. The fact that the two free-energy curves are distinct and always concave upwards indicates that spinodal decomposition cannot occur in these alloys. We also believe that the same argument is applicable to the Fe-Al system. Thus, we consider that any observations of these systems have no bearing on questions of spinodal decomposition. There are, however, other common precipitation systems, the Al-Cu and Al-Ag systems, where spinodal decomposition may indeed take place because of the presence of a real, metastable, skewed miscibility gap (Fig. 1b). The precipitate also orders, as indicated by the second free energy curve, although for the Al-Ag system the temperature must be below 190° C. Interestingly enough, the initial precipitate in the Al-Cu system, the G.P. zones, consist of very thin plates of Cu<sub>3</sub>Al rather than the supposedly pure copper.

Their comment that electron microscopy failed to establish the plate-like character at the end of the decomposition and prior to growth is particu-

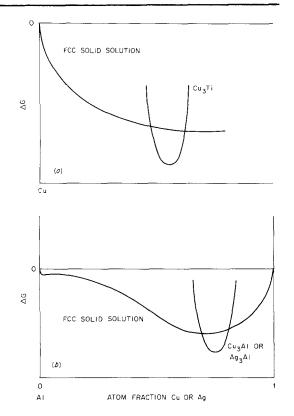


Figure 1 Free-energy curves for (a) the Cu-Ti system (b) the Al-Cu and Al-Ag systems.

larly interesting. The investigations on CuNiFe which were referenced were concerned with growth [3, 4], not the decomposition. In the one case the decomposition was essentially complete after the first ageing while in the second, the decomposition occurred during the quench. What these studies clearly show is that electron microscopy is not a definitive tool for studying spinodal decomposition.

We have not claimed, nor is it believed, that all structures which exhibit side bands, are highly regular plate-like structures. Nor is it necessary to have spinodal decomposition to develop structures which will exhibit side bands, the Cu-Ti system being a good example of normal precipitation leading to side bands.

Their claim that particles which are cubes can give rise to side bands is not, in our opinion, fully substantiated. Presumably we are concerned here with the Ni-Al system which does show side bands and in which the initial decomposition produces a product has been described as a more or less random collection of cubes of  $Ni_3$  Al. We seriously doubt that such a random collection would give side bands, but if the cubes existed in a cubical array, as they are known to do after growth, then side bands might result. But such an array would also give additional diffraction features which have not been so far reported.

We support the claim that those structures which give the best defined side bands consist of highly regular parallel plates of the type which the model would generate. It is known that a sine variation of a single wave length does result in very sharp side bands. However, we are not aware of how such a structure could be obtained by either spinodal decomposition or precipitation.

We wish to put forward the following point which relates to the origin of plate-like structures during spinodal decomposition. There are two coherent miscibility gaps. The upper has the minimum strain energy and consists of a microstructure of parallel plates on that habit plane which minimizes the strain energy. The lower gap has the maximum strain energy corresponding to both phases being isotropically strained to a common lattice parameter. The Swiss cheese structure might approximate this strain system, but in any case, the Fe-Cr system is an excellent example of a real system where this strain system is closely approximated [5]. Because the strain energy is typically 2.5 times greater for the isotropic case compared to the first, the critical

temperature is suppressed 2.5 times as far. This means that, for systems which exhibit large coherency energies, the initial composition fluctuations might run in all directions so long as the composition fluctuations were small but, as the fluctuations become large, there will be an interaction which causes a single direction normal to the plates to be locally preferred. Thus, only a plate-like structure is possible between the gaps and it remains energetically favoured inside the lower gap.

# Acknowledgement

Research sponsored by the Energy Research and Development Administration under contract with the Union Carbide Corporation.

#### References

- 1. J. W. CAHN, Acta Met. 9 (1961) 795.
- 2. M. HILLERT, *ibid* 9 (1961) 525.
- 3. E. P. BUTLER and G. THOMAS, *ibid* 18 (1970) 347.
- 4. R. T. LIVAK and G. THOMAS, *ibid* 19 (1971) 497.
- 5. R.O. WILLIAMS and H.W. PAXTON, JISI 185 (1957) 358.

Received and accepted 27 August 1976

R. O. WILLIAMS Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA