

## Letters

### *A discussion of flip-flop decomposition*

In a recent letter to this journal [1] Williams describes a decomposition process which he terms "flip-flop decomposition within miscibility gaps". This process of decomposition is said to explain how a degree of regularity higher than that obtained by spinodal decomposition can be obtained in a single phase alloy that is decomposing into two separate phases. As such, it is presented as an alternative mechanism to the process that has been called spinodal decomposition [2, 3]. In fact, he goes on to state that the microstructure of sideband alloys "must arise from flip-flop decomposition since we do not believe that decomposition which occurs more or less uniformly throughout the matrix can lead to the required degree of regularity".

It is the purpose of this note to point out (1) that Williams' mechanism is nothing more or less than a qualitative description of a special case of spinodal decomposition and (2) that the discrepancies that Williams sees between the spinodal theory and actual experimental observations are not discrepancies at all, but rather conclusions based on a misunderstanding on his part of the experimental observations.

Williams begins with an A-rich nucleus and lets it grow depleting the matrix A. With normal diffusion in the matrix, the depleted zone of this surrounding particle should expand indefinitely or until the diffusion field overlaps the depleted zones of the other nucleated particles. Instead, Williams proposes that the A-depleted matrix now acts as a B-rich nucleus enriching the zone of remaining matrix in A until it becomes a new A particle. At every stage this is uphill diffusion and therefore, in a binary, spinodal decomposition. His free energy curve shows that he even uses some of the concepts of spinodal decomposition. He uses "chemical gradient energy", but claims that the relationship of it to the thickness of plates is "presently unknown".

The idea that a particle rather than random fluctuations are present at the beginning of the spinodal decomposition is not new, since nucleation can occur during the quench before the

spinodal is crossed. Spinodal decomposition in the presence of a particle was treated quantitatively by Hillert [4, 5] whose Fig. 7 [4] shows the calculated result of what Williams depicts qualitatively in his Fig. 1. In the theory the composition profile of such a particle is an initial condition of the diffusion problem. It is described by a wave packet of sine waves that fit the profile and interfere with each other everywhere else. After more rapid growth of sine waves near certain wavelengths, this interference is removed and waves surround the initial particle in the manner shown by Hillert. We are thus in complete agreement with Williams' qualitative description of the operating decomposition process, but see no reason to change its name.

We now move on to criticizing the reasons that promoted him to develop his "new" model. He has based his "flip-flop" model on two misunderstandings about sideband alloys:

(1) he states that sidebands arise from "a regular arrangement of parallel coherent plates", and

(2) that a high degree of regularity exists. Both of these statements conflict with experimental observations of the early stages of decomposition in sideband alloys.

Sidebands need not arise from plates; they may arise from regions that are more or less cubic in

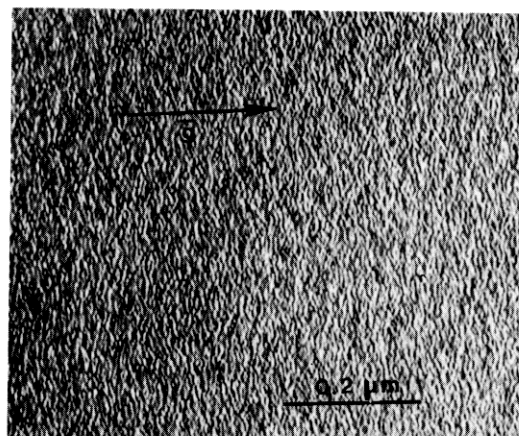


Figure 1 Cu 5 wt % Ti alloy solution treated at 900° C and aged at 400° C for 5 min. Foil normal near [110],  $g = (002)$ .

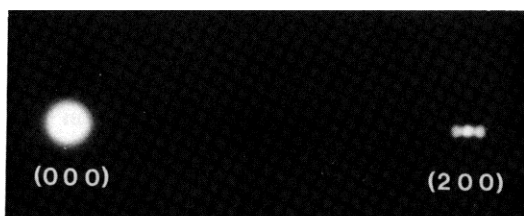


Figure 2 Cu-5 wt% Ti alloy solution treated at 900° C and aged at 400° C for 1 min. Diffuse satellites visible at the (200) reflection.

nature, or even from regions that appear sinusoidal (see Fig. 1). Almost all the electron microscopy on sideband alloys [6–10] has shown that early in the process, before distinct particles appear, sidebands are present. Furthermore, even after particles are present, they tend to be more cubic than plate-like. In some systems (e.g. Cu–Ni–Fe [6, 7]) plates are observed, but they are observed late in the decomposition process, after coarsening has begun. Thus, plates are not part of the initial decomposition microstructure.

Furthermore, Williams has overestimated the regularity of the microstructure of sideband alloys. Early in the process the sidebands are quite diffuse (see Fig. 2, and cf. with Fig. 1). This can only be interpreted as showing that a range of wavelengths are present in the decomposing alloy. In the example shown in Fig. 2, the wavelengths giving rise to the satellites range from 4.5 to 8.5 nm. Williams has confused the later-stage microstructure with the microstructure that is obtained during the original decomposition process (namely, before coarsening). If a microstructure is to clarify the mechanism of transformation, it must be that microstructure which exists *during* the process.

It is possible to create in the Fe–Al system the initial state that Williams would like and thereby examine experimentally just what morphology occurs. Antiphase domain walls in the B2 ordered phase near the tricritical point are diffuse sheets of material enriched in iron broad enough to be resolvable by ordinary transmission electron microscopy. When the temperature of such a sample is lowered just into the two-phase B2 plus disordered iron-rich  $\alpha$  region, such antiphase boundaries act as barrierless nucleation sites for

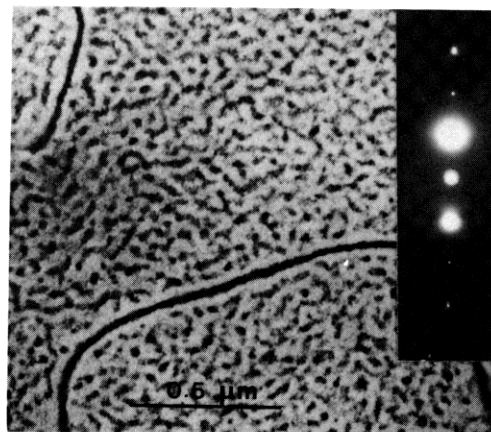


Figure 3 Fe–24% Al heated for 1 h at 625° C to create a large domain size in single phase B2, followed by 5 min at 570° C to form  $\alpha$  + B2.

the  $\alpha$ . At greater undercooling, a continuous phase separation occurs and the original iron-rich boundary should then, according to Williams, lead to a regular set of parallel sheets of the phases on both sides of the original domain wall. Fig. 3 is a transmission electron micrograph of such an alloy using a superlattice reflection of FeAl for imaging. FeAl is bright,  $\alpha$  is dark. There is some alignment of  $\alpha$ -precipitates adjacent to the walls, but the structure is random within a few particle spacings. Williams's regularity is simply not present.

Thus, Williams has not presented any compelling reasons to make a new model for the formation of periodic microstructures. In fact, since his model is identical to that of spinodal decomposition in the presence of an existing particle, any experimental observations that conflict with the spinodal model conflict with the "flip-flop" model.

Qualitative theories, since they do not make precise predictions, can more easily and often erroneously be claimed to be consistent with experiment. Wrong qualitative theories often survive contradictory experiment, because of their imagined successes in rationalizing some qualitative observations. We have in Williams' note an example of a proposal to reject the quantitative theory in favour of the same theory restated qualitatively and thus with less precise predictions, thus avoiding imagined shortcomings of the original theory.

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**The influence of hydrogen in the nitriding gas on the strength of reaction sintered silicon nitride**

Reaction sintered silicon nitride is usually prepared by heating silicon compacts in an atmosphere of nitrogen which is maintained at a pressure slightly above atmospheric pressure in order to minimize the possibility of air leaking into the furnace. In order to conserve nitrogen, "static" gas systems are used [1, 2] and nitrogen is supplied to the furnace at a rate determined by the rate of consumption of the gas by the reacting silicon compacts. Recent evidence has indicated that whilst contamination of the nitriding atmosphere with oxygen and water vapour has little influence on strength [3], gas flow during nitriding has a significant effect [2]. When nitrogen is allowed to flow through the furnace even at very slow rates the structure of the product is modified, much larger critical defects are formed and small but significant changes in elastic moduli and the surface energy for fracture initiation result [4]. It has been suggested [2] that undetected leaks in nominally "static" nitriding systems could produce sufficient gas flow to adversely affect the strength of the product and that this was a reason for occasional weak batches of reaction-sintered silicon nitride. The detection and elimination of small leaks in large furnaces operating at

temperatures up to about 1400°C is a difficult practical problem.

We are studying the influence of hydrogen in the nitriding gas on the strength of reaction sintered silicon nitride and some important preliminary results are reported here. A batch of silicon powder (Table I) was isostatically pressed at 185 MN m<sup>-2</sup> and the compact heated for 4 h at 1175°C in argon. Test bars 4.57 mm × 4.57 mm × 30.0 mm were machined from the compact and nitrided to various degrees of conversion at temperatures from 1200 to 1350°C under "static" conditions or in a gas flow of 100 ml min<sup>-1</sup> using either high purity nitrogen or gas mixtures by volume of 99 N<sub>2</sub>/1 H<sub>2</sub>, 98 N<sub>2</sub>/2 H<sub>2</sub>, 95 N<sub>2</sub>/5 H<sub>2</sub> and 90 N<sub>2</sub>/10 H<sub>2</sub>. Nitriding conditions were

TABLE I Characteristics of starting silicon powder

Median particle size* (μm)	13
Maximum particle size* (μm)	60
Specific surface area† (m <sup>2</sup> g <sup>-1</sup> )	1.5
<i>Impurity content (wt %)</i>	
Iron	0.87
Aluminium	0.20
Calcium	0.27
Titanium	0.08
Other cations	0.05
Oxygen‡	1.0

\* Measured by Coulter Counter.

† Measured by BET.

‡ Measured by neutron activation analysis.