Letters

Flip-flop decomposition within miscibility gaps

A number of metallic solutions decompose to give distinct X-ray diffraction effects in which there are sharp maxima on both sides of the Bragg peaks. Such structures must consist of a regular arrangement of parallel coherent plates of alternating composition. The plates may be as thin as 20 Å. The diffraction effects arise from the differences in scattering power of the two regions and from the coherency strains. Such structures sometimes arise from decomposition within miscibility gaps in which case the process is termed spinodal decomposition. Cahn's treatment of spinodal decomposition [1, 2] predicts some degree of regularity but fails to predict the high degree of regularity which is observed. This note provides an alternate description of the decomposition process.

We consider an equiatomic alloy cooled into a miscibility gap (Fig. 1), and we suppose that there is an A-rich nucleus. If of sufficient size, this region will continue to become richer in A, thus causing the adjacent region to be enriched in B. Ultimately this region approaches the equilibrium composition, and now the B-rich regions are analogous to the original nucleus and would now become B-rich plates. Thus the decomposition will proceed by this flip-flop type of growth without any subsequent nucleation, as illustrated in Fig. 1. The interfacial or chemical gradient energy will determine the thickness of the successive plates, but the relationship is presently unknown.

In the case of significant anisotropic effects, either strain energy or interfacial energy, this model will lead to a series of uniform plates (Fig. 2a). A prediction of the growth rates would require the solution to a complex diffusion problem, but it seems reasonable that the average distance of diffusion at an edge is half that normal to the plates. This leads to an edge growth rate four times the lateral growth rate. In an isotropic system one might expect an onion structure (Fig. 2b); however, if our conclusion about the growth rate is approximately correct, the advancing interface is unstable to perturbations, which leads to a structure of two intermeshing phases, a Swiss cheese structure (Fig. 2c).

We claim that this decomposition process cannot be avoided within a coherent miscibility gap. That is, having obtained a supercritical nucleus, it must lead to flip-flop growth if the surrounding matrix is essentially unchanged.

The usual interpretation of Cahn's model is that the degree of decomposition is essentially uniform throughout the sample, whereas for the present model we consider that the sample

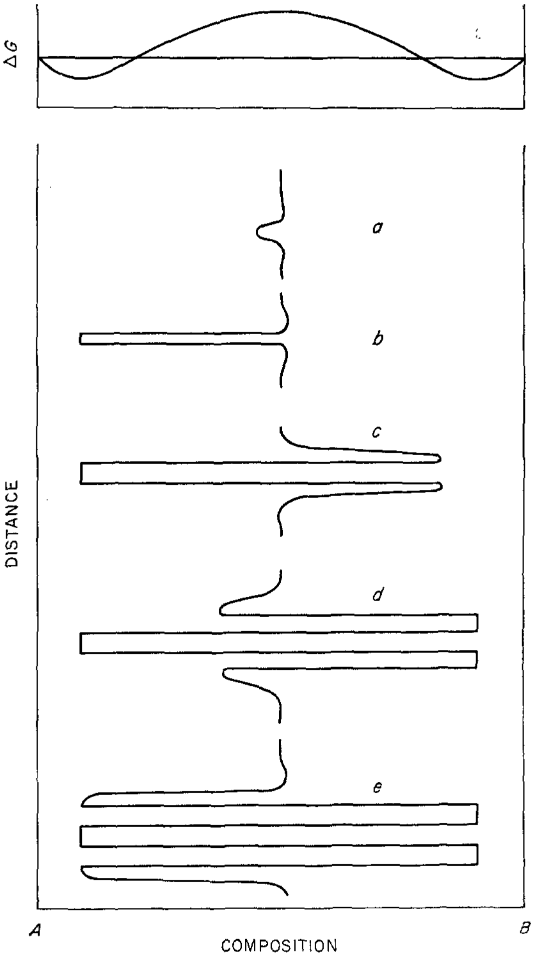

Figure 1 Successive stages in flip-flop decomposition. If of sufficient size the A-rich region will continue to be enriched in A, thereby depleting the adjacent regions which ultimately reach a size where they, in turn, start to deplete the matrix of B. The continuation of the process leads, ideally, to a uniform structure consisting of alternating regions of the equilibrium phases.

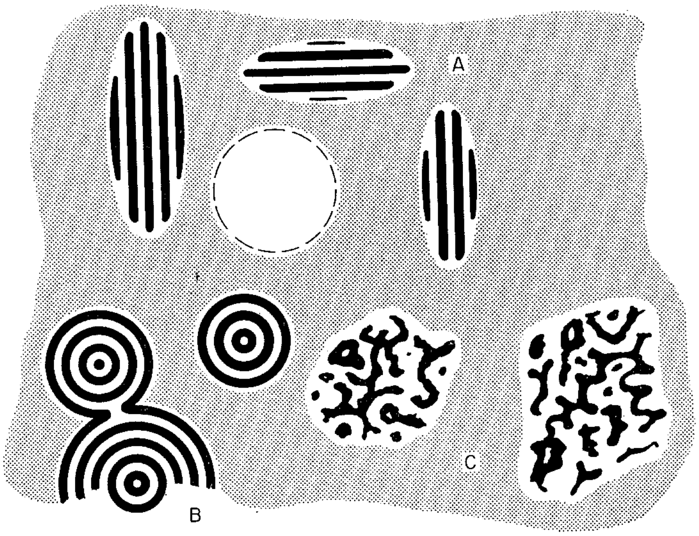

Figure 2 Possible structures from flip-flop decomposition. Case A results if there are significant anisotropic effects. The ideal structure in the absence of anisotropic effects is given in B but if, as believed, the advancing interface is unstable then the structure becomes irregular, C.

consists of distinct regions which are either decomposed or not decomposed. As the density of nucleation increases the present model merges into Cahn's model.

The numerous cases where one obtains well-defined side bands on the diffraction lines are considered as strong support for a structure consisting of uniform, parallel plates. We believe that such a structure 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. In contrast, there is no structural feature associated with the Swiss cheese structure which provides a clue as to whether or not flip-flop decomposition occurred. The X-ray intensity will obey a simple rule of mixtures during decomposition if the scale of the decomposition is sufficiently coarse, thus providing a method of distinguishing between the two models. The recent results of Agarwal and Herman [3] on the decomposition in the Al–Zn system would appear to obey a rule of mixtures such that the system could have undergone flip-flop decomposition.

Another interesting feature of the systems with side bands is that on continued annealing, the side bands move into the associated diffraction peak, which means that the plates are becoming

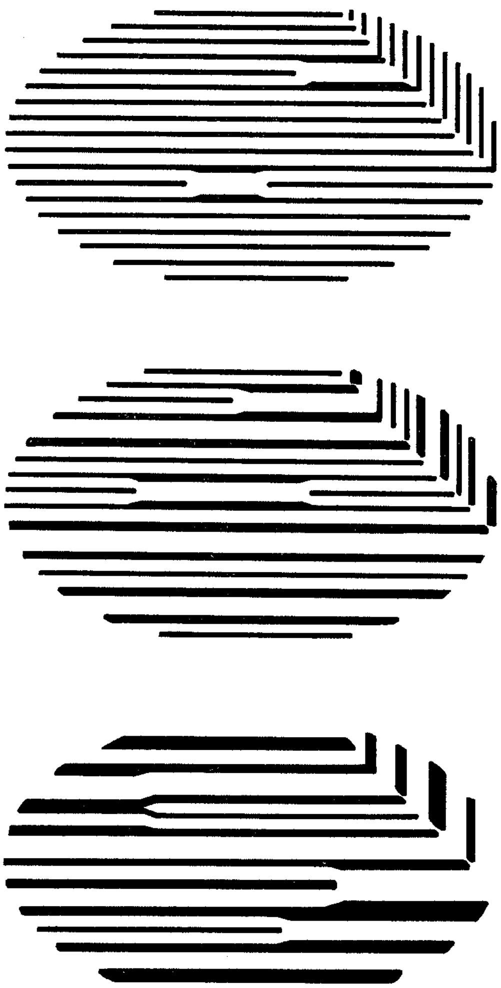

Figure 3 Model for plate coarsening. Starting from a local perturbation a plate may be assimilated by its neighbours, a process continuing with the thinner plates being consumed so as to retain the overall plate structure.

thicker. Obviously this does not result from bulk transport of complete plates but by a process of plate elimination as shown in Fig. 3. Certain plates are consumed by their immediate neighbours, a process being initiated by local perturbations. This mode of growth does require some variation in the plate thicknesses, possibly of a greater degree than existed originally, but the degree of variation is not sufficiently great to conflict with the observations.

Acknowledgement

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References

1. J. W. CAHN, *Acta Met.* **9** (1961) 795.
2. *Idem, ibid* **10** (1962) 179.
3. S. AGARWAL and H. HERMAN, *Scripta Met.* 7 (1973) 503.

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

The effect of voids on the brittle failure of polystyrene

Owing to the technological importance of high impact polymers, there has been much work on the role of small elastic particles in modifying the properties of thermoplastics [1, 2]. The work described here, which was largely incidental to a study of hole growth in polymers [3] has been useful in examining a limiting case of this problem, that of a thermoplastic containing voids.

Spherical voids, 0.20 mm radius and occupying a volume fraction of 0.189, were produced in 4 mm thick sheets of polystyrene by degrading the material by an annealing treatment of 30 min in air at 393 K. The number average molecular weight as determined by the conventional G.P.C. techniques was found to be 68 000 compared with a number average molecular weight of 72 700 before degradation. The similarity of these molecular weights suggests that large quantities of monomer or dimer were not being produced, and this is borne out by the fact that the observations of monomer production have generally been made at temperatures between 580 and 775 K [4, 5]. A likely process is the production of steam from absorbed water vapour or the degradation of excess catalyst which remains in the polymer. Such reactions would not significantly change the molecular weight, which is an important factor in determining the strength of polymers. The effect of this variable has been investigated by Vincent [6]; and using his data it may be concluded that molecular weight changes such as occur in the present case have a negligible effect on the fracture of polystyrene. It is thus proposed to attribute any difference in the behaviour of the degraded and undegraded material to the effect of the voids in the latter.

At room temperature polystyrene is a hard brittle solid which at the strain rate used in the work (6.6×10^{-4} sec^{-1}) behaves in an approximately elastic manner up to fracture. The introduction of small spherical cavities by degradation produces sites of stress concentration to which the analyses by Southwell and Gough [7] and also Goodier [8] may be applied. Using the usual cylindrical co-ordinate system with the notation of Southwell and Gough in which a uniaxial stress is applied along the Z axis, the greatest stress concentration occurs on the equator of the void where $\sigma_{ZZ} = 2\ 1/16\sigma^{\infty}$, $\sigma_{rr} = 0$, and $\sigma_{\theta\theta} = 3/16\sigma^{\infty}$ (taking Poisson's ratio as 1/3 and σ^{∞} as the applied stress). It is at this point that the crazes are nucleated and begin to grow radially as shown in Fig. 1. Owing to the concentration of stress, craze nucleation occurs at significantly lower overall applied stresses than in the undegraded material. Despite this fact, the fracture stress of the undegraded material is comparable with the original. In fact, if the average stress on the matrix is considered and the fracture stress of the degraded material raised by a factor of $(1 - f)^{-1}$ where f is the volume fraction of holes, its fracture stress becomes significantly greater than that of the undegraded specimens as shown in Fig. 2.

Examination of the fracture surface showed the usual features which have been discussed by Hull and Murray [9], and Fig. 3a emphasizes the