

reptation model provides a schematic picture of how this works (see figure): at each change in field orientation, both ends of the chain move off in the new direction. Only after a certain time, dependent on the length of the chain, is a molecule completely oriented in the new direction; this process must be completed before further net progress is made. Thus longer molecules are retarded more than shorter ones. This mechanism does not explain all the experimental results, particularly those in which the field is periodically reversed.

The simulations of Deutsch and Madden contain some artificial features: they are conducted in two rather than three dimensions (which may not be serious), and the rectangular array of

CRYSTALLIZATION

## Views of interfacial ephemera

A. Lindsay Greer

QUANTITATIVE measurement of crystallization kinetics in alloy systems has become possible in recent years through the annealing of metallic glasses. In the glasses the atomic mobility is sufficiently low for the rates of crystal nucleation and growth to be measurable and for the sample temperature to remain uniform during the reaction. These are conditions which do not apply in the more common case of crystallization from a liquid. Newly reported work by Sutton *et al.*<sup>1</sup> shows that important information on the structural changes during crystallization of a metallic glass may be lost if the experiment is not conducted in real time during the anneal. The transient interfacial phases suggested in the new work merit further study because of their potential significance in understanding crystallization kinetics not only in glasses, but also in liquids.

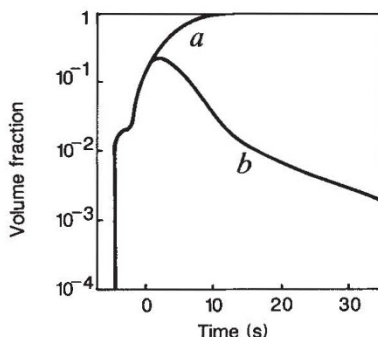
In conventional structural studies of the crystallization of metallic glasses, X-ray diffraction experiments are performed at room temperature after annealing. In contrast, Sutton *et al.*<sup>1</sup> use synchrotron radiation to study the transformation *in situ*, with time resolution of 3 ms. The study is of the formation of the body-centred tetragonal phase of NiZr<sub>2</sub> from metallic glass of the same composition. Diffraction patterns from the partially transformed samples cannot be reproduced by superposing the patterns from the initial amorphous phase and from the final NiZr<sub>2</sub>, so that the authors postulate there is a precursor phase. It has broad diffraction maxima and is a transient structure existing at the interface between the growing-crystal phase and the amorphous phase. As shown in the figure, the phase is most noticeable in the early stages of the transformation. It is found only during anneals at higher temperature when the transformation is more rapid.

obstructions cannot correctly mirror the true structure of the gel, which is largely unknown. Further work should ameliorate these difficulties and also suggest what happens when the direction of the field is changed. Nevertheless, it is hoped that these insights and observations will stimulate experimentalists to devise methods of resolving longer and longer DNA chains. □

Ted Richards, formerly at King's College London, is now at 2 Peckham Wood, London SE26 6RX, UK.

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That metallurgical transformations can proceed through intermediate stages (rationalized, for example, by Turnbull's step-entropy rule<sup>2</sup>) is well appreciated, and is exploited in the conventional practice of quenching and annealing, as in the production of precipitation-hardened alloys. The annealing is stopped before



The time dependence of the total crystalline volume fraction (a) and the volume fraction of intermediate crystalline phase (b) for an anneal of NiZr<sub>2</sub> metallic glass at 680 K (redrawn from ref. 1).

the final equilibrium is reached, to preserve the intermediate microstructure which is technologically useful.

But the possibility of an intermediate phase that exists only during the reaction and that cannot be preserved by cooling is not commonly considered. Such a concept is related to the activated-complex or transition state used in considering the mechanisms and rates of chemical reactions. For crystallization, a first-order transformation, any intermediate state must be associated with the interface between the two phases. One instance where a transient interfacial phase has previously been postulated<sup>3</sup> is the explosive crystallization of thin films of an amorphous semiconductor, such as germanium, which is explicable only if

there is a thin layer of metallic liquid, maintained by the release of latent heat, at the interface between the solid amorphous and crystalline phases, both of which have covalent tetrahedral bonding.

The nature and origin of the possible transient phase in the crystallization of Ni–Zr glass must be very different, but likewise it may be significant in analysing crystal growth. The attachment of atoms to a crystal growing in a liquid or amorphous phase may involve diffusive jumps, leading to a maximum, diffusion-limited growth velocity of around 10 m s<sup>-1</sup>. But measurements of dendrite velocities in undercooled melts led Turnbull<sup>2</sup> to suggest that for pure metals, the crystal growth rate may be limited only by the collision rate of atoms with the interface. The collision-limited growth rate would then be near the speed of sound, about 200 times the diffusive speed. From pulsed laser experiments, there is firm evidence for each type of growth; collision-limited for pure metals<sup>4</sup>, but diffusion-limited for intermetallic compounds<sup>5</sup>. The transition from one type of growth to the other as the solute content is increased has not yet been satisfactorily analysed.

Sutton *et al.*<sup>1</sup> suggest that the transient phase is a poorly ordered version of the final crystalline structure. Thus there is evidence for growth proceeding in two stages, crystallization followed by chemical ordering, in a manner consistent with the step-entropy rule. Diffusion-limited growth may arise when there is a need for rearrangement of the atomic short-range order at the interface, and just such a process may be revealed by the *in situ* study. The transition between types of growth may be elucidated by studies of the same type on growth of extended elemental solid solutions and of intermetallic compounds with different structures.

The greater fraction of intermediate phase detected at higher temperatures could reflect, as the authors suggest, the higher nucleation frequencies and greater interfacial areas during the transformation. On the other hand, it is possible that it could be associated with the ordering lagging further behind the faster interface. A transition from growth of an ordered phase to growth of a disordered intermediate could affect not only the growth rate, but also the degree of faceting of the crystal through the well-known link with entropy change across the interface<sup>6</sup>. □

A. Lindsay Greer is in the Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK.

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