THE FORMATION AND NATURE OF THE AMORPHOUS SOLID STATE

The rapid growth of research on amorphous solids during the past three decades has been motivated, partly by the scientific challenge posed by highly disordered systems, following notable advances in the understanding of well ordered solids; partly by the discovery of glassy or amorphous solid forms of materials (e. g. metallic alloys) which were thought incapable of existing in such forms; and partly by demonstrations that some of these new materials may prove to be very important technologically. With the discovery, by the late Pol Duwez and his students, that certain metals can be melt quenched to glasses, it is now clear that amorphous solid formation is not limited by the nature of the cohesive forces *per se* but can be exhibited by materials bound by any type of such force——whether it be covalent, ionic, van der Waals or metallic.

Experience shows that all materials are less stable in amorphous solid than in some crystalline form, which may be homogeneous or phase separated. Therefore, for an amorphous solid to form and persist a thermodynamically preferred crystallization process must be bypassed and suppressed.

The general procedure for forming a configurationally frozen metastable state, such as an amorphous solid, might be described as a sequence of the following three steps: (1) energization of a material by, e. g., melting, dissolution, irradiation, or cold working; (2) deenergization of the material by quenching or by some condensation process; and (3) further deenergization to kinetically trap the metastable state, if formed. The deenergizing step may expose several thermodynamic options and to appear a metastable state must be kinetically preferred to the more stable one. Actually, experience indicates that metastable states usually are kinetically preferred and they are often the states with entropy nearest to that of the initial one. It is the step of least entropy change which will generally require the least reconstruction and it is, thus, likely to be most favored kinetically. We might say that a principle of "minimum reconstruction" usually dictates kinetic preference in structural evolution.

Since an amorphous solid can form by structural collapse, while crystallization is generally reconstructive of the atomic short range order, it seems by the minimum reconstruction principle that the amorphous should always be kinetically preferred to the crystalline solid. However the amorphous solid often may be hard to form because it is difficult to trap kinetically or the thermodynamic factors favoring crystallization may be too large.

The models which have emerged for describing the structures of the different classes of amorphous solids-covalent, semiconducting, and metallic are remarkably parallel; they are of three types: microcrystallite, continuous random——e. g. the continuous random network (CRN) and dense random packed (DRP), and amorphous cluster models. A major stumbling block to acceptance of the microcrystallite models is that the crystallization of melts and glasses always occurs by crystal nucleation and growth rather than by grain coarsening. Further, glass forming melts must be deeply undercooled before homogeneous nucleation becomes measurable, though crystal growth generally proceeds at easily measurable rates at small undercooling. The high crystal nucleation resistance of melts, even monatomic ones, strongly suggests that 3-dimensional crystallization generally must be attended by some essential reconstruction of the atomic short range order in the melt or glass, as would be needed for crystallization of continuous random or amorphous cluster structures. Also the pair distribution function of glasses, deduced from diffraction data, are generally in much better accord with the latter than with the microcrystallite type models.

The structural relaxation and melt → glass transition--as exhibited rheologically, thermally, and volumetrically—behaviors of the

several types of amorphous solids are also quite similar. Theory indicates and experience generally confirms that the kinetic resistance of melts to crystallization increases sharply with the sealed melt → glass transition temperature, defined by $T_{rg}=T_g/T_l$, where T_g is the actual transition temperature and T_l is the thermodynamic crystallization point. In the metastable range between T_l and T_g crystal growth rates are usually appreciable and often high, so to quench a melt to a glass it is essential that the nucleation frequency be negligible throughout this range. The common glasses——e. g. silica based, chalcogenides——formed by the slow cooling of large liquid masses exhibit T_{rg}'s of 0.65 or more. In contrast, metallic glassforming melts are much more susceptible to crystallization, reflecting that their T_{rg}'s are usually considerably lower; those reported range from 0.45 to a high of 0.67. Also, in contrast with nonmetallic glasses, considerable homophase impurity admixture has proven essential to the formation of metallic amorphous solids, either by melt quenching or condensation. There is much evidence that crystal growth in pure amorphous metals is quench insuppressible. Thus, a thermodynamic requisite for impurity redistribution, by partitioning or local reordering, which is quench suppressible, is a necessary condition for amorphous solid formation by metals. Also, metal glass formation is favored by those impurity additions which markedly depress the liquidus temperature; the general effect of such depression is to elevate T_{rg} since T_g is usually only weakly dependent on impurity concentration.

While the distinguishing characteristics of the amorphous solid state are quite similar for the different types of materials, the technological uses of amorphous solids vary considerably with material type. Covalent insulating glasses are heavily used because of their remarkable transparency, as well as for their insulating behavior. Amorphous semiconductors, such as chalcogenides and amorphous silicon, are very useful because of their optical-electro responses. The ferromagnetic metallic glasses are exceptionally soft magnetically and are finding important applications as transformer core materials. Some also have shown exceptional corrosion resistance, presumably due to their structural and compositional homogeneity. These properties, in combination with the exceptional mechanical strength with some ductility of most of the alloys, suggest that the technological importance of metallic glasses will continue to grow.