FIZIKA 2 Suppl. 2 (1970) 25.1

CRITERIA FOR FORMATION OF AMORPHOUS PHASES

R. W. Cahn

Materials Science Division, School of Applied Sciences,
University of Sussex, Brighton BN1 9QT, England

The paper reviews various criteria, structural and kinetic, which have been put forward for distinguishing materials which can be obtained in a glassy form from those which cannot.

Introduction

One of the most intriguing features of alloys ultra-rapidly cooled from the melt is the prevalence of amorphous alloys. A whole range of these have now been reported, and have been surveyed in several reviews by Duwez, in whose laboratory many of them were discovered. Apart from Duwez's own survey in the present volume, the most recent survey of some experimental facts about amorphous alloys is in an article by Giessen and Willens (1). Apart from the recognition that amorphous phases are normally found only in the vicinity of eutectic compositions, and the further recognition that the alloy systems concerned almost invariably involve a metalloid (Si, Ge, P) as one constituent, the rationale underlying the formation of these phases is still very much open to argument. The purpose of this paper is to outline the principal hypotheses that have been advanced to make sense of the formation of glasses, not only in alloys but also in oxide mixtures and other inorganic materials. Oxide glasses have been studied for much longer than amorphous alloys, and because of their industrial importance a great deal of thought has been devoted to the criteria for the formation of oxide glasses in particular. Some of these criteria, though certainly not all, may well prove to be applicable to alloy systems as well. Long-chain polymers are not included in this survey, since their chemistry is so distinct that they cannot be expected to confer much insight into the behaviour of inorganic materials.

What is a Glass?

The terms "amorphous", "non-crystalline" and "glassy" are commonly used interchangeably. However, Bagley, Chen and Turnbull (2) have pointed out that the word "glass" is normally reserved to "amorphous solids formed by continuous solidification of a liquid". There are also a whole range of other methods of making metastable amorphous phases. Roy (3) has classified those methods as follows: (a) amorphized solids, made by mechanically shearing, irradiating or chemically reacting a solid; (b) glasses made by cooling a melt or by chemically reacting liquids to form a desiccated gel; (c) polymers made from liquid or vapour; (d) amorphous layers made by condensation of vapours (by various forms of evaporation, sputtering or vapour-phase pyrolysis). He might have added electroless plating, as applied for instance to Ni-P. He also reserves the word "glass" for cooled, congruently transformed liquids, including of course those which have been splat-cooled.

Bagley et al. point out that a glass often differs from an amorphous phase prepared by some other method not only in its mode of formation but also in possessing a glass transition, i.e. a continuous transition (preferably repeatable) between the metastable liquid and glassy states, as revealed for instance by measurements of viscosity or density. This, in the view of Bagley et al., serves as a good test to distinguish truly amorphous materials (which includes glasses as defined above) from others which may in fact be microcrystalline; though they recognise that some vapour-deposited phases are in fact truly amorphous, and therefore propose that the description "glass" should be applied to all phases showing the transition amorphous solid◄► glass. On this criterion, a number of phases, for instance in the Au-Si-Ge (2), Pd-Si (4), and Pd-Si-Au (4,5) systems, are true glasses. The term "glass" will be used loosely, in a wider sense, in this paper.

In this paper, both glasses made from the melt and amorphous phases made by evaporation will be considered: these can be distinguished, following Suryanarayana and Anantharaman (6), by the terms liquisol-quenching and vaposol-quenching respectively.

Materials Capable of Forming Amorphous Phases

To help establish the facts to be explained by any general theory of glass-formation, a brief list of some of the most important materials that can form amorphous phases now follows:

(A) By cooling from the melt at slow rates:

(1) Oxide glasses. The most important are based on SiO_2 as network-former, with Na_2O, K_2O, Li_2O, CaO, B_2O_3, Al_2O_3, TiO_2 and other oxides as network-modifiers.

(2) Other inorganic compound glasses. These include principally glasses made from mixtures of nitrates, halides, chalcogenides. Groups (1) and (2) are very thoroughly reviewed in an excellent book by Rawson (7).

(3) Organic monomers. These include substances such as glycerol, sucrose, etc. (7, p. 42)(8).

(B) By ultra-rapid cooling from the melt (liquisol-quenching)

(1) Oxide melts. Very few attempts have been made to extend the range of glass-formation by rapid cooling, or make glasses from liquids which crystallise on slow cooling. Sarjeant and Roy (9, 10) extended the glassy range in $MgO-Al_2O_3$, and produced glassy forms of V_2O_5, TeO_2, MoO_3 and WO_3 by liquisol-quenching. Frank and Liebertz (11) used a novel form of liquisol-quenching to extend the glassy range in $CaO-Al_2O_3$ and to make glasses in $SrO-Al_2O_3$ and $BaO-Al_2O_3$.

(2) Alloys. These include, inter alia, phases in Pd-Si, Au-Si, Pd-Ge, Pt-Si, Pt-Ge, Pb-Sb, Te-base alloys, ternaries such as Au-Si-Ge, Pd-Si-Au, Pd-Si-Ag, Pd-Si-Cu, Fe-P-C. Elementary Se and Ga can also be made amorphous.

(C) By evaporation

This method was pioneered by Hilsch, Buckel and their collaborators (12), when they made amorphous films of Bi and Sn-Cu alloys, and was extensively

applied by Mader (13-15). All evaporations were made on to substrates cooled in liquid helium. From among a number of alloys investigated (13), Mader found amorphous phases in concentrated alloys in Cu-Ag, Cu-Mg, Au-Mg, Co-Ag and Co-Au. Fujime (16) has made amorphous films of Fe and W by the same method, and recently Bosnell (17) has made films of Fe (provided a very good vacuum was maintained). Bosnell also made amorphous films of Ni and Ni-Fe alloys which remained amorphous on warming up to room-temperature; Ni is the only truly metallic element to behave in this manner, though amorphous Si and Ge are readily prepared and are stable to room-temperature (18).

(D) By electroless plating

Amorphous films of Ni-P and Co-P solid solutions are made for electronic applications (e.g. [19,20]) by an electroless chemical plating process from aqueous solution. Amorphous Ge has also been made by electrolytic deposition (18).

Structural Criteria for Glass Formation

Attempts to explain which substances can form glasses have fallen into two main categories - structural criteria and kinetic criteria. The distinction is one of convenience rather than of deep significance, since any criterion based on chemical bonding, coordination or electronic structure merely implies, indirectly, that particular structural characteristics inhibit nucleation or growth, or both, of crystalline phases. Many of the structural theories are outlined in chapter 2 of Rawson's book (7). A complementary treatment can be found in a book by Scholze (21).

The first attempt to formulate a structural criterion was Zachariasen's network hypothesis and set of rules, published in what is arguably the most influential paper in the history of glass science (22). With respect specifically to oxide glasses, he formulated the notion of a continuous three-dimensional network of metal-oxide polyhedra as a condition for glass-formation. The network might be modified and weakened by added oxides which by themselves cannot form glasses, but only in proportions which left a continuous network in existence. Zachariasen's rules are: (a) No oxygen atom may be linked to more than two metal atoms; (b) the number of oxygen atoms surrounding a

metal atom must be small (he believed that 4 was the maximum feasible); (c) the oxygen polyhedra share corners with each other, but not edges or faces; (these first 3 rules imply that only oxides A_mO_n were $n/m \geq 2$ can be glass network-formers); (d) at least three corners of each polyhedra must be shared. Underlying the whole model was the hypothesis that polyhedra such as the SiO_4^{4-} tetrahedron maintain their geometrical identity in a glass. This basic tenet was soon confirmed by Warren's X-ray analysis of silica glass, an analysis which has very recently been repeated in much subtler detail, 33 years after Warren's original classic paper (23).

Zachariasen's hypothesis has been very fruitful in stimulating research on glasses, but can no longer be sustained in detail. Thus, the existence of invert glasses, SiO_2-Na_2O-K_2O-CaO-BaO mixtures containing only 40% SiO_2 (24) break the first three rules and exclude a continuous 3-dimensional network, while Zarzycki (25) has recently proved by X-ray analysis that titania-rich glasses such as $2TiO_2.K_2O$ contain 6-coordinated Ti ions, which infringes rule (b). Other criticisms are outlined in Rawson's book (7), p. 18. Rawson also gives a good account of the "boric oxide anomaly" (p. 109), which also implies that Zachariasen's correlation between continuity of the network and glass-stability is not valid.

Another purely geometrical approach is in terms of ionic radii, an approach which has been highly successful in interpreting the choice of crystal structure of ionic compounds (26). Goldschmidt judged that glass-forming oxides are those for which the metal/oxygen radius ratio was in the range 0.2-0.4. The radius-ratio is intimately related to cation coordination and Goldschmidt's purely empirical criterion was based on the then prevalent, but erroneous, belief that tetrahedral coordination was necessary for glass-formation.

However, the radius-ratio approach has proved helpful in understanding formation of amorphous phases by evaporation (vaposol-quenching). By a systematic investigation of a number of alloy systems, Mader (13) showed

that amorphous phases were formed by vaposol-quenching on to a substrate at $4^{o}K$ only if the constituents are close-packed, the phase diagram shows limited primary solubility in both constituents, and the atomic radii of the constituents differ by more than 10%. This last empirical condition was effectively interpreted by means of a pin-table model in which balls of two different sizes were "alloyed" in an imitation of vaposol-quenching (27); it was shown that if the ball radii were sufficiently different, random arrays were formed and proved resistant to "crystallization".

Mader's criteria are related to Polk's (28) structural model for amorphous metallic alloys. Unlike Zachariasen's and Goldschmidt's criteria (which relate to covalently or ionically bonded polyhedra), Polk starts out from Bernal's model of dense random packing of hard spheres with undirected bonds (29,30) - a model which has had impressive support from tests with spheres (e.g. 31) and very recently has also been supported by detailed computer-simulation, by Finney (32). (Finney's structural computation fits excellently with G. S. Cargill's X-ray data for amorphous Ni-P: Harvard Ph. D. thesis, 1969). Polk's model consists of a Bernal structure which is primarily metallic, with a metalloid solute filling some of the larger holes inherent in the random packing. (The model really applies only to liquisol-quenched amorphous alloys, which normally require a metalloid solute, though Polk does not actually say so). For details his paper should be consulted, but the conclusion is that the role of the metalloid solute atoms is to fill the larger holes and thereby mechanically stabilise or "jam" a solvent structure which is already fairly stable mechanically. To achieve this extra stabilization, both the size of the solute atoms and their concentration must be right. Hence metalloid solutes are necessary, and their concentration must be enough to fill all the larger holes but not enough for them to start occupying less formable, de-stabilizing sites in the Bernal array.

We turn now to attempts to establish a relationship between glass-formation and chemical bond type. These various ideas are particularly well and critically surveyed by Rawson (7) and a brief outline will suffice here. Smekal (33) proposed that mixed chemical bonding is a precondition for glass-formation. Examples are SiO_2 (mixed covalent/ionic bonding), elements such as Se or organic compounds (mixed covalent/van der Waals bonding). Scholze (21) points out (p. 279) that with the aid of Pauling's electronegativity approach the degree of ionicity in substances with mixed covalent/ionic bonding can be estimated. The differences among different glass-formers are so great (As_2S_3 ~10% ionic, SiO_2 ~50% ionic, BeF_2 ~ 80% ionic) that Smekal's rule has very little interpretative power.

Stanworth (34), however, has pursued the analysis of bond types in oxide glasses in terms of electronegativities and on the basis of the degree of ionicity estimated by this means has successfully distinguished between network formers, network modifiers and oxides which can fulfil either function. His principal success - and in this he is almost unique along theorists of glass-formation - was to predict a hitherto unknown family of glasses, based on TeO_2. TeO_2 has the same electronegativity as P_2O_5, which was known to form glasses readily, and the prediction followed from this. In spite of this success, Rawson points out the unreliability of Stanworth's criteria, especially if one attempts to extend it beyond the realm of oxide glasses.

Yet another gloss on bond types is Winter's (35) p-electron criterion: he proposed, empirically, that the ability to form glass is related to the average number of p-electrons in all the atoms (including oxygen): this number should be in the range 2-4, 4 being best. Winter checked his ideas carefully and found good agreement, not only for oxide glasses. However, he leant heavily on the reported formation of glasses by O_2 and Al_2O_3, but neither of these is now believed to form glasses (ref. 21, p. 281).

A further set of criteria relates to bond strength, rather than bond type. Sun (36) pointed out that the bond strengths in glass-forming oxides are often especially high. These strengths, derived from thermochemical data, are systematically higher for network-formers than for network-modifiers, but the principle is of little use for molecular glass-formers of mixed bond type, such as CO_2, where the action of van der Waals bonds is vital. Rawson (37) modified Sun's approach, in pointing out that glass-formation depends on how difficult it is to break bonds at the thermodynamic freezing (= melting) temperature, T_m, and this depends not only on the mean bond strength but also on the thermal energy, kT_m, available to do the breaking. He therefore attempted, with considerable success, to relate glass-forming ability to the ratio of bond strength to the absolute ideal melting-point. In particular, on this basis the extremely high glassiness of boric oxide becomes understandable. (This is virtually equivalent to Turnbull and Cohen's (38) correlation of glass-formation in simple organic liquids to T_b/T_m, where T_b, the boiling-point, is for such liquids a measure of cohesion). Rawson's modification of Sun's criterion leads directly to the corollary that deep eutectic compositions are particularly favourable for glass-formation, and this accords well with empirical findings, not only for oxide glasses but for alloys too.

It is to be noted that, by introducing kT_m into consideration, Rawson has taken the essential step of converting a purely structural approach into what is implicitly a kinetic approach. We now turn to explicitly kinetic theories of glass-formation.

Kinetic Theories of Glass-Formation

Weyl and Marboe (39-41) devoted much disputational energy to combating the notion that considerations of bond type or strength have any bearing on glass-formation, and concentrate their attention on the structure of liquids, which they categorise into 3 types (Bernal, Frenkel, Stewart) according to

the degree of instantaneous bond rupture and associated viscosity. Any given liquid at a given temperature, in their view, can be located in a ternary diagram of liquid type, and accordingly the tendency to glass-formation can be systematised. Liquid type changes with temperature and bond strength, so that Weyl and Marboe's ideas are very closely related to Rawson's approach, outlined at the end of the preceding section. To pursue these very involved ideas further, Weyl's concise summary of his ideas (41) should be consulted in the first instance. It is unlikely that his ideas will have much relevance to alloy melts, since (in his terminology) these should be of Bernal type at all temperatures.

The only systematic, explicit attempt to relate the tendency to glass-formation to the kinetics of nucleation and growth of the equilibrium crystalline phase(s) is due to Turnbull and Cohen (38, 42, 43). An admirably clear account of this approach is to be found in chapter 3 of Rawson's book (7), so only a summary of the principal conclusions is given here. Turnbull and Cohen point out that their theory should be more nearly applicable to "simple liquids", which presumably includes alloys, than it is to complex mixtures of oxides.

The nucleation rate $N = ke^{-W/RT} e^{-\Delta G'/RT}$. Here $W(\propto \sigma^3/\Delta G^2)$ is the "thermodynamic barrier to nucleation", σ is the specific liquid/solid interfacial energy, ΔG is the crystallisation energy per grain-molecule, while $\Delta G'$ is the "kinetic barrier to nucleation", which is limited by the diffusion rate in the melt.

If we take $\Delta G \propto \Delta T$, where ΔT is the degree of supercool, we find that $N \propto e^{\sigma^3 T_m^2/(\Delta T)^2 . RT} . e^{-\Delta G'/RT}$. This represents an extremely steep increase with falling temperature, because of the first term, until eventually the second term takes over.

The rate of crystal growth, u, is given by $u = e^{-\Delta G/RT} e^{-\Delta G''/RT}$, where ΔG is again the energy of crystallization (here it constitutes the "thermodynamic term") and $\Delta G''$ is another kinetic factor. For simple liquids, Turnbull

and Cohen take $\Delta G''$ to be closely related to the activation energy for viscosity, η, and $u \propto \frac{RT}{\eta} e^{-\Delta G/RT}$. They now go on to specify permissible limits for N and u if glasses are to form. If T' is the temperature at which N = 1 nucleus/cm^3.sec, then a glass will form (a) if no temperature T' exists (i.e., N is never as high as the specified figure), or (b) if T' does exist and $u < 10^{-5}$ cm/sec at T'. This pair of conditions is ultraconservative - i.e. it would permit glass to form even for very slow cooling-rates.

If these conditions are now examined in terms of the equations outlined above, then it turns out that condition (a) is equivalent to the requirement that $\Delta G' \geq 40\ RT_m$; condition (b) is equivalent to the requirement that $\Delta G''$ and $\Delta G'$ both $\geq 30\ RT_m$ - i.e. the principal component of the activation energy for <u>either</u> nucleation <u>or</u> growth exceeds $30\ RT_m$. For simple liquids, it appears to be an acceptable rough extrapolation of this condition that an activation energy for <u>viscosity</u> near T_m greater than $30\ RT_m$ should predispose a melt to glass-formation.

If now one postulates a more realistically rapid rate of cooling than is implied by the above condition, then it suffices for $\Delta G'$ or $\Delta G''$ to $\geq 20\ RT_m$; for splat-cooling rates, of course, this condition would be further relaxed. However, Turnbull and Cohen gave only very scant attention to this crucial factor of cooling-rate, perhaps because in connection with oxide-glasses this is rarely regarded as an important factor.

Turnbull and Cohen also attempt to relate the various activation energies to structural features of the melt, but for details of this the reader should refer to their papers or to Rawson's summary.

It is instructive to apply this analysis to alloy systems. Since energies ΔG, $\Delta G'$ and $\Delta G''$ are only known for a few pure metals, the simplest (though very rough and ready) approach is to examine activation energies for viscosity of metallic melts near T_m. Information about these activation

energies, E_η, and about the actual viscosity, η, at $T_m + 50^oK$, is collected in tables 24 and 27 of Wilson's review of the structure of liquid metals and alloys (44). It is striking that both η and E_η are mostly higher for the metals (Cu, Ag, Au, Fe, Co, Ni) which are the solvents in amorphous alloy phases formed either by liquisol-quenching or by vaposol-quenching, than for other metals, such as the alkali metals, which do not. (However, Al and Mg have high values of E_η though as solvents they do not form amorphous phases). No information on viscosity of Pd or Pt is listed. The highest E_η is 12.0 kcal/mole for Ni, and most values for the solvents in the glass-forming category are in the range 5-10 kcal/mole. The alkali metals have E_η only just above 1 kcal/mole. Unfortunately the information about eutectics in Wilson's paper is inadequate for the present purpose.

The information available is not sufficient to compare E_η for the <u>alloys</u> capable by splat-cooling to form amorphous phases, with our version of Turnbull and Chen's criterion, that $E_\eta \geq 20\ RT_m$ (perhaps $\sim 10\ RT_m$ for ultrarapid cooling?). On this basis, E_η should be typically in the region of 30-40 kcal/mole, which is still substantially greater than the values listed above for the <u>pure metals</u> near their T_m.

Turnbull and Cohen (43) have developed their model further to formulate a semiquantitative criterion for glass-forming tendency. This tendency they take to increase as the <u>reduced</u> absolute melting temperature $\tau = RT_m/H_\upsilon$, where H_υ is the molecular heat of vapourization. This criterion is tested against a number of oxide melts for which H_υ has recently been measured (21, p. 285), confirming the applicability of Turnbull and Cohen's criterion at least to these melts.

The principal criticism to be made of Turnbull and Cohen's very careful theoretical analysis is that they pay inadequate attention to cooling-rate as a variable. The only systematic attempt to do this is due to Sarjeant & Roy (45). Unfortunately - but probably inevitably in view of the extreme complexity of the problem - their approach contains so many crude approximations that it can be regarded as only a very rough guide. They assess the effective cooling

rates for splat-quenching thin foils of various substances (SiO_2, $MgAl_2O_4$, NaCl, Pb, H_2O, etc.) then calculate a diffusional relaxation time for the various melts at T_m, starting either from experimental figures for viscosity or from dielectric relaxation, and go on to calculate, very roughly, critical cooling-rates for glass-formation for their various substances. These are approximately consistent with their observations on glass-formation or its absence at a cooling-rate of $\sim 10^6$ deg K/sec. Thus $MgSiO_3$, Mg_2SiO_4, $BaTiO_3$ were obtained wholly or partly in glassy form.

As the next step in the attempts to understand glass-formation in a range of materials, and more particularly alloys, it is highly desirable that Sarjeant and Roy's calculations of critical cooling-rates should be put on a somewhat more rigorous basis, more comparable with Turnbull and Cohen's approach; this will prove to be a very challenging but worth-while task.

In conclusion, it would be interesting to analyse whether any of the kinetic analyses outlined above can be applied to amorphous films quenched from the vapour. No attempts have as yet been made to extend the kinetic approach to these films, and hitherto only structural theories, in terms of solvent/solute radius ratios, have been attempted. Moreover, the very powerful vapour-to-solid route to making amorphous solids has been very much neglected in comparison with the liquid-to-solid route, effective though that has been, and this imbalance deserves to be put right in future experimental work.

References

1. B. C. Giessen and R. H. Willens, in "Phase Diagrams: Materials Science and Technology" (ed. A. M. Alper), vol. 3 (Academic Press, New York & London, 1970), p. 129.

2. B. G. Bagley, H. S. Chen and D. Turnbull, Mater. Research Bull., 3, 159 (1968).

3. R. Roy, J. Non-Cryst. Solids, 3, 33 (1970).

4. H. S. Chen and D. Turnbull, Acta Met., 17, 1021 (1969).

5. A. Eisenberg and R. Reich, Proc. Third Internat. Conf. on Physics of Non-Cryst. Solids, Sheffield, Sept. 1970; to be published.

6. C. Suryanarayana and T. R. Anantharaman, J. Mater. Sci., 5, 992 (1970).

7. H. Rawson, Inorganic Glass-Forming Systems (Academic Press, New York & London, 1967).

8. A. R. Ubbelohde, "Melting and Crystal Structure" (Clarendon Press, Oxford, 1965), p. 294.

9. P. T. Sarjeant and R. Roy, J. Appl. Phys., 38, 4540 (1967).

10. P. T. Sarjeant and R. Roy, J. Amer. Ceram. Soc., 50, 500 (1967).

11. B. Frank and J. Liebertz, Glastechnische Berichte, 41, 253 (1968).

12. R. Hilsch, in "Non-Crystalline Solids" (ed. V. F. Frechette) (Wiley, New York, 1960), ch. 15. A review of earlier work.

13. S. Mader, J. Vac. Sci. & Tech., 2, 35 (1965).

14. S. Mader, in "Recrystallization, Grain Growth and Recovery", (Amer. Soc. Metals., Metals Park, 1966), p. 523.

15. S. Mader and A. S. Nowick, Acta Met., 15, 203, 215 (1967).

16. S. Fujime, Jap. J. Appl. Phys., 5, 1029 (1966); 6, 305 (1967).

17. J. R. Bosnell, Thin Solid Films, 3, 233 (1969).

18. H. S. Chen and D. Turnbull, J. Appl. Phys., 40, 4214 (1969). This paper gives references to earlier work.

19. J. S. Judge et al., J. Electrochem. Soc., 113, 547 (1967).

20. A. W. Simpson and D. R. Brambley, Phys. Stat. Sol., 43 (Jan. 1971)

21. H. Scholze, "Glas", (Vieweg, Braunschweig, 1965), p. 276.

22. W. H. Zachariasen, J. Am. Chem. Soc., 54, 3841(1932).

23. R. L. Mozzi and B. E. Warren, J. Appl. Cryst., 2, 164 (1969).

24. H. J. L. Trap and J. M. Stevels, Glastechnische Berichte, 32K, 31 (1959).

25. J. Zarzycki, J. Mater. Sci., 6 (Jan. 1971).

26. R. C. Evans, "Crystal Chemistry" (Cambridge University Press, second edition, 1964.

27. A. S. Nowick and S. Mader, IBM J. Res. & Dev., 9, 358 (1965).

28. D. E. Polk, Scripta Met., 4, 117 (1970).

29. J. D. Bernal, Nature, 185, 68 (1960).

30. J. D. Bernal, Proc. Roy. Soc., A280, 299 (1964).

31. M. H. Cohen and D. Turnbull, Nature, 203, 964 (1964).

32. J. L. Finney, Proc. Roy. Soc., A319, 479, 495 (1970).

33. A. Smekal, J. Soc. Glass Technol., 35, 411T (1951).

34. J. E. Stanworth, J.Soc.GlassTechnol., 36, 217T (1952).

35. A. Winter, J.Am.Ceram.Soc., 40, 54 (1957).

36. K.H.Sun, J.Am.Ceram.Soc., 30, 277 (1947).

37. H.Rawson, "Proc.4th Internat. Congress on Glass", (Imprimerie Chaix, Paris, 1956), p. 62.

38. D. Turnbull and M.H.Cohen, in "Modern Aspects of the Vitreous State", ed. J.D.Mackenzie, (Butterworth, London, 1960), p. 38.

39. W. A. Weyl and E.C.Marboe, Glass Industry, 41 (1961); 42 (1962): numerous short papers.

40. W.A.Weyl and E.C.Marboe, "The Constitution of Glasses. A Dynamic Interpretation", (Interscience, New York and London, 1962-5), vol. 1.

41. W. A. Weyl, "Symposium on Nucleation and Crystallization in Glasses and Melts", (Amer.Ceram.Soc., Columbus, Ohio, 1964), p. 39.

42. D. Turnbull and M.H.Cohen, J.Chem.Phys., 29, 1049 (1958).

43. D. Turnbull and M.H.Cohen, Nature, 189, 131 (1961)

44. J.R.Wilson, Metallurgical Reviews, 10, 381 (1965).

45. P.T.Sarjeant and R.Roy, Mater.Research Bull., 3, 265 (1968).