

Glass ... Current Issues

Edited by

A.F. Wright and J. Dupuy

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PREFACE

Glass... Current Issues is the proceedings of a NATO Advanced Study Institute held in Puerto de la Cruz, Tenerife between the 2nd and 13th April 1984. The objectives of the School were twofold. Firstly to inform participants of actual and developing technological applications of glassy materials in which fundamental science makes a strong contribution, and secondly to bring together scientists from the widely different backgrounds of glass science and technology to promote mutual understanding and collaboration.

The amorphous state has for more than a decade now been a renaissance of scientific and technological activity extending beyond traditional glass technology research. Striking developments of amorphous materials have been made in fields such as metallurgy, electronics and telecommunications and even in disciplines until recently less concerned by materials science, such as colloid chemistry, medicine and agriculture. The physical and chemical properties brought into application here result from the interaction between the glass composition and its non-crystalline structure. One rôle of the basic research is to understand this interaction, which in time through development, helps to extend the range of properties and applications. In this meeting we hoped to sensitize participants to the vast range of applications of amorphous materials which exploit their unique properties, and thus broaden future investigation.

The program was organised around seven topics, signposts of scientific and technological activity in the 1980's : optical materials, amorphous metals, crystallisation phenomena, electronic and electrical devices, sol-gel preparative methods, composite materials and long-term applications. The latter included glass

for nuclear waste storage, and applications in medicine and biology. In addition active discussion sessions were held and participants were invited to contribute to a permanent poster exhibition.

An excellent example of the complementarity of basic and applied research can be found in the development of optical waveguides. Early work of fibre optic communications centred on SiO_2 based glass because of its promising optical qualities and known fibre drawing behaviour. Processing experience gained with SiO_2 or $\text{SiO}_2\text{-GeO}_2$, has given fibres with a best loss figure of 0.2 dB.km^{-1} at $1.55 \mu\text{m}$. This excellent value, close to the intrinsic minimum imposed by multiphonon absorption and Rayleigh scattering is sufficient for many applications, but still imposes a requirement for frequent repeater stations. The need to displace the multiphonon edge to higher wavelength has led to further development of chalcogenide and fluoride glasses. The optical window in the former extends to $10 \mu\text{m}$ and these glasses find use in the optical components of IR cameras, night vision and thermal surveillance systems. Fluoride glasses (based on ZrF_4) exhibit a broad optical window from 0.3 to $7 \mu\text{m}$, but more importantly have the ultra low loss potential of $10^{-3} \text{ dB.km}^{-1}$ at $3 \mu\text{m}$. Many processing problems must be overcome however, since these glasses have poor fibre drawing properties, are prone to crystallisation and are sensitive to water, but the enormous potential merits the development efforts.

The interdisciplinary nature of the meeting brought many physicists and materials scientists together for the first time with chemists working on sol-gel preparative techniques. This mixture of polymer chemistry, colloid science and ceramics technology is advancing extremely rapidly to produce novel amorphous oxides with unique physical properties. The method opens up applications ranging from electrically conducting films to optical fibres as well as refractory monolithic materials which are impossible to make by classical melt-quench procedures. For many years a domain dominated by its chemistry, sol-gel methods of glass formation have now reached a stage where these new materials are readily available in modest quantity. We can expect in the next few years growing interest in measurement of the physical properties and structure as a function of preparation variables. The aim here will be to improve reproducibility in the development programs.

Similar observations to these outlined above can equally well be drawn from the texts of the other topics which contributed to the 55 lectures delivered. We would encourage the reader to take account of the wide range of disciplines presented. This reflects the current broad scientific and technological base of amorphous materials, which motivated us to organise the meeting

and suggests a bright future for glasses.

We address our sincere thanks firstly to Jean-Pierre Causse, who, in spite of his heavy work-load as Directeur Général Adjoint of Saint Gobain Research accepted the role of co-director of the A.S.I. and contributed in many ways and over a very long period to the success of the meeting.

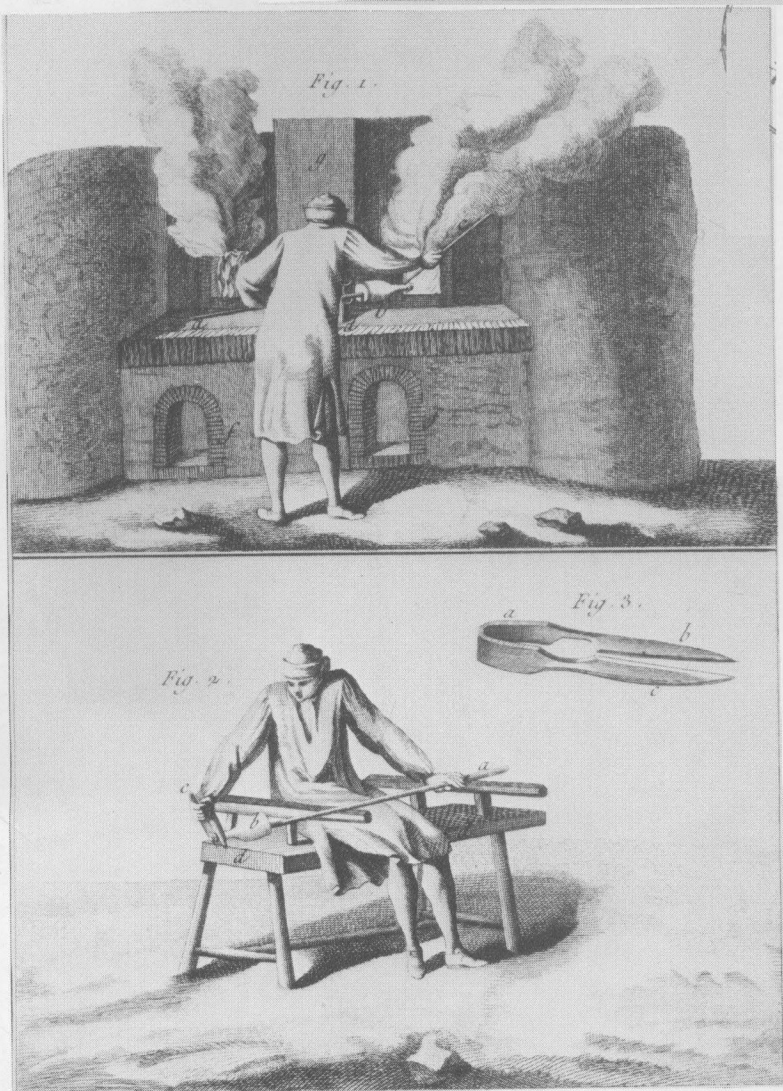
We thank all the chairmen lecturers and participants who, cooperated so fully in the discussions and exchanges, on the one hand between different disciplines, and on the other between applied technologies and basic research. We were only too aware of the difficulty to achieve this type of exchange. That many lively and spontaneous discussions continued until late in the evenings was a credit to the far-sightedness and understanding of the participants.

We thank all those organisations who generously supported the meeting :

- NATO, Scientific Affairs Division provided 50 % of the funds under the framework of the NATO double jump programme, the aim of which is to generate closer collaboration between industry and basic research organisations of the member countries.
- The industrial and national organisations below responded most admirably, ensuring the remaining support, either by direct financial aid or by providing one or more key lecturers according to our wishes and at their own expense for such an extended period : Compagnie Saint-Gobain, U.S. Air Force, (EAORD, London), D.R.E.T., Allied Corporation, Institut Laue-Langevin, C.N.E.T., C.E.A., Schott Glasswerke, Pilkington Brothers, C.N.R. (Italy), and N.S.F.
- We are also very grateful to Mr. Gobin for his assistance and support through the Ministère de l'Industrie et de la Recherche.
- Finally we express our personal gratitude for the continued devotion of the secretariat over many months : Danielle de Baere and France Parisot.

J. DUPUY, Lyon
A.F. WRIGHT, Grenoble.

May 1984.



'Dawn of glass technology'
From a eighteenth century encyclopedia
by Diderot d'Alembert

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CHAPTER I: NUCLEATION AND CRYSTALLIZATION

NUCLEATION AND CRYSTALLIZATION IN GLASS-FORMING SYSTEMS

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I. INTRODUCTION

The present paper will attempt in a brief space to summarize the present state of knowledge and outstanding problems in the area of nucleation and crystal growth in glass-forming liquids. It is intended to provide background for the papers on crystallization phenomena to follow at this meeting. Specifically, it will not address applications of controlled crystallization to form glass-ceramic materials, which will be considered by Beall; and it will not address the often-subtle effects of thermal history near and below the glass transition, which will be considered by Wright.

The combined effects of nucleation and crystal growth are important in the formation of glasses as well as in the development of glass-ceramic materials with desired combinations of properties; and an attractive approach to treating glass formation will be briefly discussed. This will be followed by separate considerations of nucleation and crystal growth processes in both single-component and multi-component systems, with emphasis on developments of the past decade. Finally, consideration will be given to differences expected in the nucleation and crystal growth behavior of metal alloys, familiar oxide systems, and sol-gel derived oxides.

II. TRANSFORMATION KINETICS AND GLASS FORMATION

The kinetics of overall crystallization in an initially amorphous material are generally described using a form of analysis introduced by Avrami (1, e.g.). The most widely-used form of this analysis represents the volume fraction crystallized, V_c/V , as a

function of time under isothermal conditions:

$$\frac{V_c}{V} = 1 - \exp\left(-\int_0^t I_v \left[\int_{t'}^t u d\tau\right]^3 dt'\right) \quad (1)$$

Here I_v is the nucleation rate per unit volume and u is the crystal growth rate.

In evaluating V_c/V as a function of time, it is thus necessary to know the time dependence of both I_v and u . For the simple but frequently applicable case where the nucleation rate and growth rate are independent of time, Eqn. (1) reduces for isotropic growth to:

$$V_c/V \approx \pi/3 I_v u^3 t^4 \quad (2)$$

This formalism can be used to describe volume crystallization and glass formation by constructing time-temperature transformation (TTT) curves (2). Such curves define the loci of times at various temperatures required to form a given volume fraction crystallized. To obtain a reasonable estimate of the cooling rate required to form a glass, it is useful to assume a minimum detectable V_c/V and construct a continuous cooling (CT) curve corresponding to that value of V_c/V . Such constructions are carried out following the approach of Grange and Kiefer (3, 4).

In considering glass formation, a minimum detectable V_c/V of 10^{-6} has been assumed (2). This seems reasonable as a definition of glass in light of the detection limits of established experimental techniques. From first principles, it may be useful to consider only glasses whose thermal stability is independent of the conditions (cooling rates) used in their formation. In such cases, the critical V_c/V would be about 10^{-10} (5). Use of 10^{-10} rather than 10^{-6} as the volume fraction crystallized would increase the critical cooling rates by about an order of magnitude.

Examples of TTT and CT curves corresponding to $V_c/V = 10^{-6}$ and 0.5-0.9 are shown in Fig. 1 for a lunar composition containing 35.5 wt. % SiO_2 , 3.7% Al_2O_3 , 14.3% TiO_2 , 23.5% FeO , 11.6% MgO , 11.1% CaO and 0.2% Na_2O . The constant rate cooling curves shown in the figure indicate a critical cooling rate to form $V_c/V=10^{-6}$ of about 10^2 K min^{-1} .

A preferred description of glass formation and the development of partial crystallinity is provided by the analysis of crystallization statistics (6). The analysis introduces a crystal distribution function, $\psi(r,t,R)$, defined such that $\psi(r,t,R)dVdR$ is the number of crystals in a volume dV at position r with radii

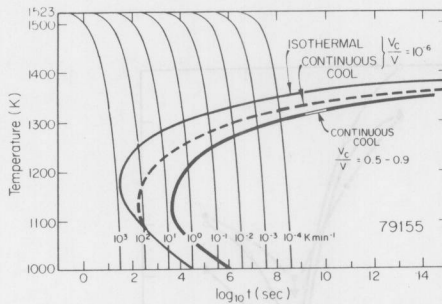


Figure 1 - TTT and CT curves for lunar composition 79155

between R and $R+dR$. Using this approach, it is possible to evaluate the detailed statistics of the number and size distributions of crystallites in a sample as a function of temperature and thermal history. In estimating the critical cooling rate for glass formation, one calculates the time and temperature where V_c/V reaches the value of interest.

With this approach, the volume fraction crystallized is expressed:

$$\frac{V_c}{V}(t_j) = 1 - \exp \left\{ - \sum_{i=1}^j \frac{4\pi}{3} R_i^3(t_j, t_i) I_{vi}(t_i) \Delta T \right\} \quad (3)$$

where $V_c/V(t_j)$ is the volume fraction crystallized at time t_j ; $I_{vi}(t_i)$ is the nucleation frequency at time t_i ; and $R_i(t_j, t_i)$ is the radius at time t_j of crystals nucleated at time t_i . This may be represented:

$$R_i = R_i^* + \sum_{k=1}^j u_k(t_k) \Delta t \quad (4)$$

where R_i^* is the radius of the critical nucleus at t_i and u_k is the crystal growth rate at time t_k .

Using this approach, it is possible to predict cooling rates required to form glasses which are in excellent agreement with measured values. Examples of this agreement are shown in Fig. 2 for a series of $\text{Na}_2\text{O}-\text{SiO}_2$ glasses. The minimum in critical cooling rate corresponds closely with the eutectic seen in the phase diagram for this system. The lower calculated curve in the figure represents predictions of a simplified model of glass formation to predict critical cooling rates (7).

Using the analysis of crystallization statistics, it is also possible to describe the effects of complicated thermal histories on crystallization behavior, including cooling a liquid to the glassy state at a given rate and reheating it at the same or different rates. It is also possible to describe the competition