Bioceramics: Research and Development Opportunities

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I. Introduction

The objectives of this paper are to provide a brief review of the scientific status of the field of bioceramics and its application in the medical and dental field and to discuss the research and development needs of the next decade which will satisfy the growing need for improved replacement parts for the musculo-skeletal system.

The emphasis in this paper will be on future needs since recent reviews provide an extensive discussion of the literature of bioceramics. Special attention is called to reviews by Hench (1991), Gross et al. (1988), Hulbert el ai. (1987), and books edited by Ducheyne and Lemons (1988), Yamamuro, Hench and Wilson (1990) and Davies (1991).

II. Types of Tissue Response

In order to understand the success and failure of prosthetic implant materials, regardless of whether they are ceramic, metal or polymer, it is essential first to understand the types of implant/tissue response that can occur in the body. Table I lists the four primary types of interfacial response between an implant and its host tissue. The advantages of bioceramics as implant materials is related to the fact that certain types of ceramics, such as dense alumina or zirconia are especially biologically inactive. Other bioceramic materials are biologically active and form an interfacial bond with tissues. Specific compositions of bioceramics can dissolve in the body over a period of time and be replaced by the growth of surrounding tissues. This makes the four types of bioceramics, which are listed in Table II. A type of attachment of each category of bioceramic and an example of a material that achieves such attachment is also given in Table II.

The nature of the interface between a material and its host tissue can also vary depending upon the form of the biomaterial. For example, a bioactive material in the form of a powder may dissolve several weeks after implantation and be replaced by host tissues, whereas the same composition of material in the form of a bulk implant may form a stable interfacial bond and remain as a structural device. Therefore, it is important to recognize that the interface of an implant material changes with time and the kinetics of that change may depend upon the surface area of the material which, of course, is substantially higher for powders or rough or porous surfaces than for polished bulk materials.

Table I – Types of implant-tissue response

1) If the material is toxic, the surrounding tissue dies.
2) If the material is nontoxic and biologically inactive (nearly inert), a fibrous tissue of variable thickness forms.
3) If the material is nontoxic and biologically active (bioactive), an interfacial bond forms.
4) If the material is nontoxic and dissolves, the surrounding tissue replaces it.

Bioceramics are produced in four general forms: (1) bulk implants, (2) coatings on higher strength substrates, (3) composites, or (4) powders. Other implant variables in addition to form of the material are factors such as interfacial gradients for coatings, relative volume fraction of the two phases for composites and the mean size and size distribution of powders. Understanding the long term behavior of bioceramics, which will be discussed later, or improving the biological response to bioceramics takes into account these variables in the designs and testing of the material.

III. Applications

Bioceramics in general, are used in the repair and/or reconstruction of the musculo-skeletal system. Thus, bioceramic materials are in contact with either hard tissues such as bone or soft connective tissues such as tendons, ligaments, muscle, and subcutaneous tissues. In numerous applications a bioceramic may be in contact with hard tissues at one portion of the surface, such as the root of the tooth implant, and also be in contact with soft tissues, such as the gingival tissues, in the same implant site. The attachment of prosthetic implant materials is also an important application of

Table II - Types of bioceramics-tissue attachment and bioceramic classification

Type of Bioceramic	Type of Attachrnent	Example
(1)	Dense, nonporous nearly inert cerarnics attach by bone growth into surface irregularities by cementing the device into the tissues, or by press-fitting into a defect. (Termed Morphoiogicai Fixation)	Al_2O_3 (Single Crystal and Polycrystalline)
(2)	For porous inert implants bone ingrowth occurs, which mechanicaliy attaches the bone to the material. (Termed Biological Fixation)	Al_2O_3 (Porous Polycrystalline) Hydroxylapatite coated Porous Metals
(3)	Dense, nonporous surface-reactive ceramics, glasses, and glass-cerarnics attach directly by chemical bonding with the bone. (Termed Bioactive Fixation)	Bioactive glasses Bioactive glass-cerarnics Hydroxylapatite
(4)	Dense, nonporous (or porous) resorbable cerarnics are designed to be slowly replace by bone.	Calcium Sulphate (Plaster of Paris) Tricalcium Phosphate Calciurn-Phosphate Salts

bioceramics. Examples include the repair of joints such as hips or knees. These are called total joint replacements and the attachment of the implant to the remaining bone stock must be stable for the implant to survive. Recently, novel compositions of glasses and glass ceramics have been developed for therapeutic use in medicine. Examples include the use of radioactive glass beads for the treatment of tumors, pioneered by Professor Delbert Day and colleagues at the University of Missouri at Rolla, and the use of magnetic bioactive glass-ceramics for treatment of bone tumors, developed by Professors Yamamuro and Kokubo and colleagues in Kyoto, Japan. Table III summarizes the wide range of clinical applications of bioceramics.

IV. Problems

As discussed in the reviews cited, bioceramics offer many potential advantages in the fields of medicine and dentistry. The materials are either substantially more chernically inert than are metals such as stainless steel, cobalt chrome alloys or titanium alloys which is a decided advantage sirice there is no danger of metalloses due to metal corrosion. Also, bioactive ceramics offer the unique potential of forming a stable interfacial bond between the implarit material and living tissues. This concept was proven as early as 1969, with papers, published in 1971 and 72 by the author and colleagues at the University of Florida. These special compositions of glasses which bond to living tissues, are now termed bioactive glasses (and tradernarked Bioglass®). The compositional range of bioactive bonding has been expanded considerably by studies by Professor Gross and colleagues at the Un versity of Berlin in Germany on the bioactive glass-ceramic Ceravital® and the important advance of a substantially higher strength bioactive glass-ceramic, termed A/W Glass Ceramic, developed by Professor Yamarriuro and Kokubo and colleagues at Kyoto University in Japan.

However, problems in the use of all types of bioceramics for long term stable replacement of the musculoskeletal system still remain. These problems for the most part relate to the fact that the ceramics tend to mechanical failure under tensile stresses in the presence of a reactive chemical environment. The phenomena of slow crack growth, static and cyclic fatigue, stress corrosion and deterioration of toughness with time are all of serious concern for the long term use of bioceramics for loadbearing prostheses. For these reasons, aluminum oxide bioceramics are restricted to use in the ball of total hip replacements whereas the loadbering stem of the device is metallic.

Another important limitation in the use of bioceramics in the body is the limited range of elastic modulus of ceramics. Table IV compares the elastic modulus of alumina ceramics and partially stabilized zirconia ceramics with those of cortical bone and cancellous bone. Other mechanical properties of bone are compared as well. The data show that there is an elastic modulus mismatch between bone and ceramic of a factor of ten or more. A consequence of this mismatch is that a ceramic implant will shield a bone from mechanical loading. This is a serious disadvantage because the bone must be under a certain amount of load in order to remain healthy. Bone that is unloaded or loaded in compression will undergo a biological change which leads to resorption. The loss of bone stock at the interface of an implant weakens the bone and eventually the interface can deteriorate and fail. Thus, stress shielding of bone is a disadvantage of high elastic modulus bioceramics.

A third area of concern is the rate and type of fixation of bioceramics to the musculo-skeletal system. Bioinert ceramics, such as alumina and zirconia, do not bond to bone and therefore must be cemented into a bone by the use of self polymerizing, polymethyl

Table III – Present uses of bioceramics

ORTHOPEDIC LOAD BEARING APPLICATIONS Al_2O_3 Stabilized Zirconia Polyethylene H A Composite	COATINGS FOR TISSUE INGROWTH (Cardiovascular, *Orthopedic,* Dental & *Maxillofacial Prosthetics)* Al_2O_3
COATINGS FOR CHEMICAL BONDING *(Orthopedic,* Dental & *Maxillofacial* Prosthetics) HA Bioactive Glasses Bioactive Glass Cerarnlcs	TEMPORARY BONE SPACE FILLERS Tricalclum Phosphate (TCP Calciurn and Phosphate Salts
DENTAL IMPLANTS Al_2O_3 HA Bioactive Glasses	PERIODONTAL POCKET OBLITERATION HA HA - PLA Cornposite Tricalcium Phosphate (TCP) Calcium and Phosphate Salts Bioactive Glasses
ALVEOLAR RIDGE AUGMENTATIONS Al_2O_3 HA HA - Autogenous Bone Composite HA - PIA Composite Bioactive Glasses	MAXILLOFACIAL RECONSTRUCTION Al_2O_3 HA HA - PLA Composite Bioactive Glasses
OTOLARYNGOLOGICAL Al_2O_3 HA Bioactive Glasses Bioactive Giass Ceramics	PERCUTANEOUS ACCESS DEVICES Bioactive Glass-Ceramics Bioactive Glasses HA
ARTIFICIAL TENDON AND LIGAMENT PLA - Carbon Fiber Composite	ORTHOPEDIC FIXATION DEVICES PIA - Carbon Fibers PLA - Calcium/Phosphorous-Base Glass Fibers
ARTIFICIAL HEART VALVES Pyrolytic Carbon Coatings	SPINAL SURGERY Bioactive Glass-Ceramic HA

Table IV – Physical characteristics of alumina and partially stabilized zirconia (PSZ) bioceramics

	High Alumina Ceramics	ISO Alumina Standard 6474	PSZ	Cortical Bone	Cancellous Bone
Content (% by weight)	$Al_2O_3 > 99.8$	$Al_2O_3 \geq 99.50$	$ZrO_2 > 97$		
Density (g/cm^3)	>3.93	≥3.90	5.6-6.12	1.6-2.1	
Average Grain Size (um)	3-6	<7	1		
Surface Roughness, Ra (um)	0.02		0.008		
Hardness (Vickers. HV)	2300	>2000	1300		
Compressive Strength (MPa)	4500				2-12
Bending Strength (MPa) (after testing in Ringer's Solution)	550	400	1200	50-150	
Young's Modulus (GPa)	380		200	7-25	.05-.5
Fracture Toughness (K_{1c}) MPa $m^{-1/2}$)	5-6		15	2-12	
Slow Crack Growth (unit)	10-52		65		

methacrylate (PMMA) bone cement. This is a similar procedure to that used for metallic and polymeric prostheses. The major disadvantage of this approach to fixation of the device is the incompatibility of the cement with bone. Bone cement interfaces deteriorate with time and loosen. An attractive alternative to the use of bone cement is bioactive fixation, which is achieved by use of bioactive glasses and glass-ceramics such as those listed in Table V and by hydroxyapatite coatings on metal substrates.

The bioactive materials form a bond with bone and thus the stress is transferred more naturally across the interface. However, the rate of formation of the bond is very slow compared with the almost immediate interfacial fixation that is obtained with PMMA cement. Several weeks may be necessary for bioactive materials to develop sufficient interfacial strength to withstand full, loadbearing weight on the interface, Many months are required before an interfacial strength develops which is equivalent to that of bone cement. Thus, the long term prognosis for bioactive fixation may be better than for cement. However, short term loading, which is needed for rapid recovery and healthy bone repair, is not so good for good for bioactive implants. This compromise between long terrn and short term fixation must be recognized and dealt with during the next decade.

Another prob'em area in the field of bioceramics is the lack of data on the effects of age, metabolic state, disease states, etc. on the behavior of biocerarnics. Most of the investigations reported involve short term test on healthy an mals. Most mechanical tests are done on unloaded and nonfunctional devices. In contrast the human need is long term (> 15 years) mechanical stability of the device and interface under loaded conditions in aged and often arthritic bone. There is an enormous contrast between the testing conditions and were conditions and use conditions for bioceramics. The consequrnce of this disparity is the failure of some bioceram cs implants, of certain types, after several years of clinical use. The failures are often attributes to the biomechanics of the application which are not correct because the animal testing was too short term and did not provide the loading necessary to establish the biomeclianical performance for the implant.

V. R&D Opportunities: Short Term

These problems also indicate the opportunities for research and development in the field of bioceramics. Several areas of opportunity may be pursued in the short term, 2-5 years, of development.

Advanced Composites

Composites with low elastic moduli that match cortical bone, with high toughness and rapid rates of interfacial bonding are needed. Studies led by Professor Willian Bonfield at Queen Mary and Westfield College, University of London, indicate that this approach may succeed. The goal is to obtain a material that bonds rapidly, without the use of PMMA cement, and achieves a bond that is sufficiently strong so that the interface will not fail and the load is carried by both the prosthetic material and the living bone. The material must have sufficient toughness and mechanical strength to be equivalent to that of the natural bone stock that it replaces. In order to achieve a rapid rate of bonding the composite must contain a bioactive phase at its surface that is able rapidly to integrate with repairing bone following surgery.

In order to achieve such advanced composites additional, comprehensive understanding of the following variables are required:

a) The effect of volume fraction and orientation of phases on mechanical properties, toughness, fatigue, interfacial inhibition of crack propagation, and effects of the environment on crack growth and toughening mechanisms. Such understandings have been generated in the field of structural composites for aircraft and the general principles need to be extended and applied to the field of bioceramics.

b) Gradient modulus structures need to be developed. Potential advantages of composites include the opportunity to use anisotropy of structures to optimize the properties of a device so that loads more nearly equivalent to that of the anisotropic structures of bone are transmitted. A material with a gradient modulus across the device and longitudinal stiffness in the center of the device may be better able to prevent stress shielding and at the same time provide sufficient toughness to avoid progressive mechanical deterioration.

c) It may be necessary to combine bioactive coatings with composite structures. This could yield fast bonding at the interface with the primary mechanical function provided by the underlying composite structure. Developing coatings on composites with strong interfacial adherence between the coating and the underlying substrate is an area that has been neglected in the past and where there is substantial opportunity for development in the future.

Bioactive Cements

To achieve rapid short term fixation it is desirable to have an in *situ* polymerizing cement. However, it is not desirable to have a cement with the chemical and interfacial disadvantages of PMMA. Consequently, a bioactive cement that establishes interfacial fixation through a bioactive bond may be the ideal. Recent progress in this area has been reported by Professors

Table V – Bioactive glasses and glass-ceramics (wt%)

	45S5 Bioglass®	45S5.4F Bioglass®	45B15S5 Bioglass®	52S4.6 Bioglass®	55S4.3 Bioglass®	KGC Ceravital®	KGS Ceravital®	KGy213 Ceravital®	A-W-GC	MB-GC	S45P7
SiO_2	45	45	30	52	55	46.2	46	38	34.2	19-52	45
P_2O_5	6	6	6	6	6				16.3	4-24	7
CaO	24.5	14.7	24.5	21	19.5	20.2	33	31	44.9	9-3	22
$Ca(PO_3)_2$						25.5	16	13.5			
CaF_2		9.8							0.5		
MgO						2.9			4.6	5-15	
MgF_2											
Na_2O	24.5	24.5	24.5	21	19.5	4.8	5	4		3-5	24
K_2O						0.4				3-5	
Al_2O_3								7		12-33	
B_2O_3			15								2
Ta_2O_5/TiO_2								6.5			
Structure	Glass and Glass-Ceramic	Glass	Glass	Glass		Glass-Ceramic	Glass-Ceramic	Glass-Ceramic	Glass-Ceramic	Glass-Ceramic	

Kokubo and Yamamuro and colleagues at Kyoto University. The self-setting bioactive glass-ceramic cement does not have the disadvantages of PMMA, such as the effect of the monomer on blood pressure and the exotherm which kills bone, and has the advantage of bonding across the interface to transfer load and maintain healthy bone. Longer term tests under simulated physiological conditions of loading are still underway in order to determine whether bioactive cements will provide a viable alternative to PMMA.

In-Vitro and *In-Vivo* Tests

The field of bioceramics needs standardized mechanical tests for the bioceramic materials under simulated load conditions and in simulated body fluids. Standardized test models are needed world wide to make comparison between various types of bioceramics and on the effects of changes in composition, structure, phase rates, or surface conditions on mechanical behavior. At present there are no standard tests and it is very difficult to compare materials from laboratory to laboratory.

Likewise, standardized models for *in-vivo* tests are also needed. Standardization of short-term push-out tests and longer term simulated loading tests are needed. Without the existence of standardized test conditions the variations in test results between labs make it impossible determine the effects of age and disease states on the behavior of bioceramics.

Because of the absence of standardized tests it is impossible to compare interfacial bonding strengths of various bioactive ceramic materials as a function of time to establish their relative merits when compared with PMMA bone cement. Standardized tests are also needed to compare lifetime prediction diagrams for bioceramics. The methods exist for determining probabilities of failure under realistic implant loading conditions. However, the methods are seldom used and have never been standardized.

VI. Long Term Opportunities

Resurfacing of Joints

An ideal alternative to losing the large amounts of bone that are removed during total joint replacement, is to develop a means to resurface joints rather than replace them. However, such a conservative approach to joint repair requires substantially more understanding of the biological response of materials. What is particularly needed is an understanding of the potential for regeneration and repair of the articulating cartilage in the joint. At present it is assumed that such damaged joint surfaces cannot be repaired naturally and therefore must be replaced by inorganic non-living mating surfaces. This assumption needs to be replaced with an experimental research program to identify means of restoring articulating surfaces more naturally. This approach offers the best long term solution for patients in the 30-60 year age range. Patients greater than 60 years of age can often obtain the critical 15-20 years of potential lifetime of total joint replacement using existing techniques. However, younger patients who require prostheses are almost certainly doomed to second or third surgeries due to failure of the implants or of the

implant/bone interface with time. With increasing life times of humans, past 75 years, it is especially important to have an alternative to total joint prostheses for younger patients.

Kinetics of Interfacial Reactions

In order to have an optimal opportunity to improve interfacial fixation of devices in the short term or to achieve resurfaciing of joints in the long term, it is essential to have a raore complete scientific understanding of the physical, chemical and biochemical reactions that occur at implant/tissue interfaces. The mechanisms of interfacial reactions must be established at the molecular level. The rates of reactions must be deterrnined, rate constants evaluated and the effects of composition and solution concentration of interfacial fluids on these rates must be determined. The influence of composition of an implant on the physiological factors must be established. Of particular need is an understanding of the adsorption of metabolic constituents on the surface of the implants and the effect of those constituents on cellular behavior. Crystal defects in hydroxyapatite may well give rise to highly specialized bonding sites between the apatite formed at an implant interface and organic constituents. These must be identified and their effects on bonding rates determined. Heterogeneous nucleation kinetics of hydroxyl carbonate apatite forming *in situ* on implant surface need to be measured. The role of metastable states on implants' surfaces in influencing nucleation kinetics must be investigated.

Biological Understanding of Interfacial Reactions

The kinetics of inorganic reactions on the implant interface, determined by studies such as outlined above, must be related to the adsorption of biological factors on the implant interface. The role of inorganic elements in biomineralization requires substantially more understanding than presently exists. For example, the function of a protein template and the relationship between the protein template and the heterogeneous nucleation of inorganic phases and *vice-versa* is poorly understood. A fundamental question in bone metabolism is that of the function of trace quantities hydrated silicon. It was established many years ago that silicon is a necessary trace element for bone mineralization. In spite of several decades of investigation the function of silicon in mineralization is still uncertain and its potential role in the mechanical behavior of bone and bone repair has received little attention. The role of biological silicon in interfacial stability of orthopedic prostheses has not been investigated.

Likewise, there has been very little investigation of the interaction between organic constituents such as glycoaminoglycans (GAGs), phospholipids and mucopolysaccharides together with the nucleation and crystallization of inorganic phases, particularly hydroxylcarbonate apatite

Tissue and Cell Culture Modeling of Reaction Processes

More laboratory studies on the effects of bioactive substrates on the differentiation attachment and proliferation of cells are needed. Pioneering work by Dr. J. E. Davies and colleagues at the University of Toronto needs to be expanded in other research centers. Davies et al. have shown that there are quantitative differences in the cellular response to the surface of bioactive materials and inert materials. The specific nature of these differences on the cellular phenomena are still being investigated. Of particular concern is the function of the substrate on cell membrane activity and the attachment complexes on cells. Work from our laboratory by Seitz et al. showed that it is possible for cultured fibroblasts to be put into long term resting stages on bioactive surfaces in contrast to the rapid cell division which leads to confluence on inactive surfaces. The reasons for this difference are still unknown, even after 15 years. Professor Gross' studies in Berlin have shown that glass-ceramic substrates affect macrophanges depending upon the relative bioactivity of the substrates. However, the reasons for this and the implications are still being established.

In general, there needs to be greatly expanded work on cell membrane interactions and changes of attachment complexes when interfacial bonding zones form between implant materials and living tissues. The biochemical changes that take place within the first four days of implantation are generally not understood. Longer term effects after the bond has been formed are now reasonably well understood, particularly due to the work of Gross and colleagues. The studies by Davies et al. are attempting to establish some of the basis for this interpretation, as summarized in the conference proceedings edited by Davies.

Genetic Coding of Mineralization and Repair Processes

Ultimately it will be necessary to establish the genetic basis for the bonding of hydroxylapatite crystallites to collagen fibrils and the mechanisms that occur intracellularly and extracellularly in achieving this type of interfacial bond. Similarly the role of inorganic interfaces on cellular attachment and differentiation will be needed to control interfacial reactions fully. The human genome project that is currently being pursued world wide may eventually provide the basis for this understanding. The bioceramics field needs to be aware of this effort and attempt to incorporate their findings into our field as they become available.

Molecular Orbital Modeling

At present, semi-empirical molecular orbital calculations make it possible to model the interfacial inorganic reactions that occur at the surface of bioactive

glasses. Figure 1 shows the molecular structures and reaction path that has been calculated for the polycondensation reaction that occurs between neighboring silanol units on a bioactive glass surface. The calculational method used was based on complete neglect of differential overlap models (AM-1) developed by Professor Dewar and colleagues at the University of Texas at Austin. Molecular clusters of up to 40 atoms can be calculated with the AM-1 method. Efforts are underway, directed by Dr. Jon West and the author and colleagues at the University of Florida, to expand the calculational base to model inorganic surfaces and their interaction with organic constituents present at the material/tissue interface. Results to date show that the silanol condensation reaction, Figure 1, can provide a heterogeneous pathway for adsorption and nucleation of a hydroxyapatite crystal. Efforts to include organic metabolites in the reaction pathways are underway. These studies will require severa1 years of investigations but may provide the fundamental information to couple the experimental interfacial reaction kinetics with tissue and cell culture modeling and eventually genetic coding.

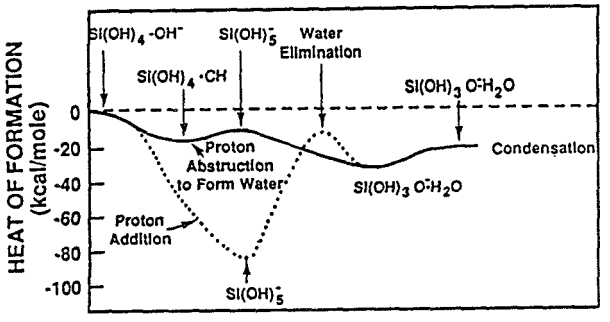

Figure I.: Reaction pathway for silica condensation from silicic acid or neighboring silanol groups.

VII. Summary

The long term goal of bioceramics research and development should be the molecular design of implant materials. They need to be tailored at a molecular level for control of biochemical interactions and optimized for a particular biomechanical behavior. The combination of biochemistry and biomechanics is especially difficult to achieve in a single material. Consequently it will probably be necessary to have advanced composite structures where the surface of the composite is optimized for the biochernistry and the interior of the structure is optimized for biomechanics. By using the anisotropy of composites it should be possible to tailor composite structures for high toughness and low modulus. It should also be possible to achieve composite structures that are compatible biochemically as well as mechanically with bone and other tissues that they are designed to replace.

The short term approach to achieve this long term goal appears to be the use of bioactive glass in the form of powders of fibers in composite structures with tough polymers such as polyethylene, as developed by Professor Bonfield's group. An alternative short term approach for a loadbearing tissue repair is to use bioactive glass in a particulate form to augment autogeneous bone. The combination of particulate glass and living bone chips results in a new bony structure which is created by the host. This approach has the enormous advantage of the newly created structure having the necessary blood supply and repair processes to achieve a revitalization of the tissue that was previously damaged or removed. Consequently, augmentation of bone avoids rejection problems. It creates self-repair capability and the built in response to stress that is characteristic of loadbearing tissues in humans. Studies underway in our laboratories have shown substantial enhancement of repair of bone structures by using the 50-50 mixture of bioactive glass particulate with autogeneous bone. This suggests that use of bioceramics to aid the body in creation of its own repair structures may be the most viable form of repair.

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Crystallization of Liquids and Glasses

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The scientific and technological importance of advanced materials are summarized. The governing theories of glass transition, crystal nucleation and crystal growth are combined with the overall theory of transformation kinetics to clarify the phenomenon of glass formation from the liquid state. Finally, examples of novel glasses as well as glass-ceramics obtained from the controlled crystallization of certain liquids are given.

I. Introduction

The contemporary, technology intensive, age with its high technology industries and services demands the use of novel materials with improved properties. For instance, in the opinion of the presidents of one hundred Japanese industries the following were the most innovative new technologies in the last two decades: VLSI, Biotechnology, Optical Fibers, Robotics, Special Ceramics, Interferon, Office Automation, New Materiais, Super-Computers and Space Technology[1]. It is obvious that most of them are directly related to advanced material~.

The study and development of useful materials demands highly interdisciplinary efforts from physicists, chemists, materials scientists and engineers. Materials Science emphasizes the relationships between the *structure* and *propertie::* of materials, providing a link between the fundamental sciences and applications, while Materials Engineering focus the study of the relationships between the *processing* techniques and the *applications. A* schematic view of the scope of the various segments of science and materials engineering is presented in Figure 1.

Materials can be classified in several ways; i.e., by:

i. ***The general bohavior:*** metals, ceramics, polymers and composites;
ii. ***Chemical nature:*** covalent, ionic, metallic, van der Waals, hydrogen, mixed bonding;
iii. ***Some property, e.g.:*** insulator, semi-conductor, conductor, superconductor, or;
iv. ***Structure:*** single crystal, polycrystal, vitreous, etc.

This article deals with the controlled crystallization of liquids or glasses of any type as a technique to obtain novel materials.

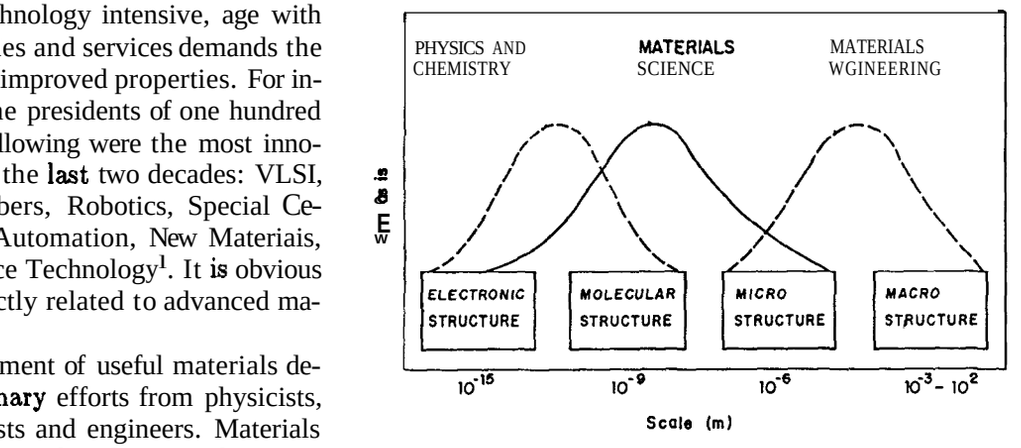

Figure 1: Scope of the basic sciences and materials engineering[2].

II. Types and applications of materials obtained via crystallization

The most obvious crystallization process is that frequently employed by chemists for the synthesis of purer or new compounds, i.e. the precipitation of powder particles from super-saturated solutions.

The geologists rely on the *post-mortem* study of crystallization to understand the formation of minerals and solidified magmas.

Many solid-state physicists depend on crystal growth from seeded melts to obtain a plethora of single-crystal specimens as well as commercially important materials such as silicon and lithium niobate.

Ceramicists and materials scientists dedicate a lot of time to the synthesis of novel ceramics and glasses employing the sol-gel technology. In this case the avoidance (or lack) of crystal nucleation and growth in the gel, during the sintering step, can lead to a glass.

Finally, the catalyzed crystallization of glass objects

can lead to a wide range of pore-free *glass-ceramics*, with unusual microstructures and properties, such as transparency, machinability and excellent dielectric, chernical, mechanical and thermal – shock behaviour. Many commercial glass-ceramic products are available for domestic uses, e.g. vision-TM, rangethops, feed-throughs, electronic substrates, artificial bones and teeth, radomes, etc.

III. The glass transition

Glasses are amorphous substances which undergo the glass transition. The most striking feature of the glass transition is the abrupt change in the properties of a liquid, such as the thermal expansion coefficient (a) and heat capacity (c_p), as it is cooled through the range of temperature where its viscosity approaches 10^{12} Pa.s. In that range the characteristic time for structural relaxation is of the order of a few minutes, so the effects of structural reorganization are easily detected by human observers.

Figure 2 shows the change in volume, V, of a glass forming liquid during cooling through the transition region.

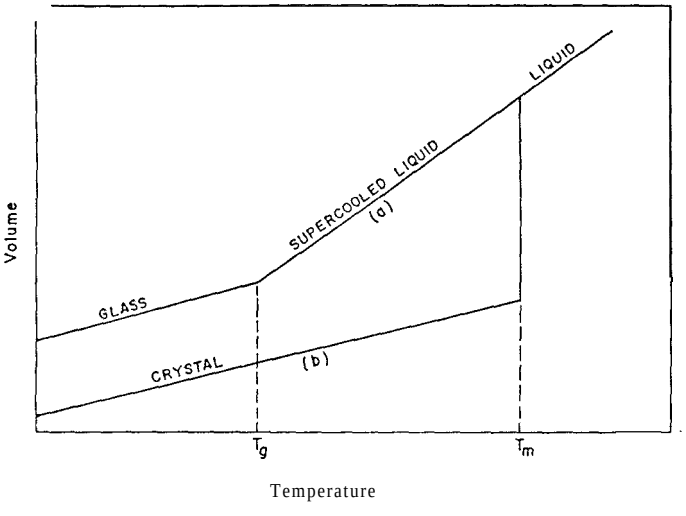

Figure 2: Schematic representation of glass transition (a) and crystallization of a liquid (b).

If the liquid is cooled slowly (path b) it may crystallize at the melting point, T_m. If the cooling rate is fast enough to avoid crystal nucleation and growth, a supercooled liquid would be produced (path a). As the temperature drops, the time required to establish the equilibrium configuration of the liquid increases, and eventually the structural change cannot keep pace with the rate of cooling. At that point a transition temperature, T_g, is reached below which the atoms are frozen into fixed positions (only thermal vibrations remain) and a glass is formed.

Thus, glass formation from the liquid state is feasible if path (a) is followed. On the other hand, all glasses heated to a temperature between T_g and T_m tend to crystallize to achieve thermodynamical equilibrium. If crystallization occurs from a large number of sites in the bulk, useful, fine grained, glass-ceramics can be produced. When crystallization occurs in an uncontrolled way (devitrification) from a few surface impurity sites, damage and cracking of the specimen may take place. In the following sections the relevant theories and experimental observations leading to controlled crystallization in the volume of glasses or supercooled liquids will be described.

IV. Crystal nucleation

When a liquid is cooled below its melting point, crystal nucleation can occur homogeneously (in the volume), by heterophase fluctuations. The Classical Nucleation Theory (CNT) was derived in the late 50s by Turnbull and Fischer[3]. The homogeneous nucleation rate I in condensed systems is given by

$$I = n_v \nu (n_s^*/n^*)(W^*/3\pi kT)^{1/2} \times \exp[-(\Delta G_D + W^*)/kT], \quad (1)$$

where:

n_v = the number of *molecules* or *formula units* of nucleating phase per unit volume of parent phase (typically $10^{28}10^{29}m^{-3}$);
ν = vibration frequency ($10^{13}s^{-1}$);
n_s^* = number of molecules on the surface of a critical nucleus;
n* = number of molecules in the critica1 nucleus;
W* = Thermodynamic barrier for nucleation;
ΔG_D = Activation energy for transport across the nucleus/matrix interface;
k = Boltzmann's constant;

The quantity $(n_s^*/n^*)(W^*/3\pi kT)^{1/2}$ is within one or two powers of ten for all nucleation problems of interest. Therefore, eq. (1) may be written with sufficient accuracy as

$$I = n_v \nu \exp[-(\Delta G_D + W^*)/kT], \quad (2)$$

where the pre-exponential factor $A \simeq (n_v \nu)$ is typically $10^{41} - 10^{42}\ m^{-3}s^{-1}$.

Assuming that the molecular re-arrangement for the nucleation process can be described by an effective diffusion coefficient, D, we have

$$D = \nu\lambda^2 \exp(-\Delta G_D/kT), \quad (3)$$

where λ is the jump distance, of the order of atomic dimensions. D can be related to the viscosity (η) by means of the Stokes-Einstein equation:

$$D = kT/3\pi\lambda\eta. \quad (4)$$

Combining eqs. (2), (3) and (4) we have

$$I = (n, kT/3\pi\lambda^3\eta)\exp(-W^*/kT). \quad (5)$$

For spherical nuclei

$$W^* = 16\pi\sigma^3 V_m^2/3\Delta G^2,$$

where V_m is the molar volume of the crystallizing phase, AG the thermodynamic driving force and a the surface energy. Therefore, eq. (5) can be rewritten in the form

$$\ln(I\eta/T) = (n, k/3\pi\lambda^3) - (16\pi\sigma^3 V_m^2/3k\Delta G^2 T) \quad (6)$$

Hence, a plot of $\ln(I\eta/T)$ versus $1/\Delta G^2 T$ should yield a straight line, with σ and the pre-exponential factor given by the slope and intercept, respectively.

To test the classical theory, accurate data for the thermodynamic driving force for the glass to crystal transformation (ΔG) are required. AG for a single component system, at temperature T below the melting point T_m, is given by

$$\Delta G = -\Delta H_{fM}(T_m - T)/T_m - \int_T^{T_m} \Delta C_p dT + T \int_T^{T_m} (\Delta C_p/T) dT, \quad (7)$$

where ΔH_{fM} is the heat of fusion per mole and $\Delta C_p (< 0)$ is the differencc in specific heats between the crystalline and liquid phases at constant pressure at temperature T.

Claasical Nucleation Theory has been used extensively by materials scientists for prediction of nucleation rates. However, the steady-state crystal nucleation rates (I) calculated with CNT are many orders of magnitude smaller than the experimental values for inorganic glasses[4,5].

Recently, Manrich and Zanotto[6] recalculated the crystal nucleation rates in six silicate glasses: $Li_2O.2SiO_2(LS_2)$, $Li_2O.SiO_2(LS)$, $CaO.SiO_2(CS)$, $BaO.SiO_2(BS_2)$, $Na_2O.2CaO.3SiO_2(N_1C_2S_3)$ and $Na_2O.CaO.3SiO_2(N_2C_1S_3)$. The nucleation parameters u, as well as the maximum experimental (I_{ex}) and predicted (I_{th}) nucleation rates, obtained from the mathematical fittings, are listed in Table I. The differences between (I_{th}) and (I_{ex}) are as large as 55 orders of magnitude!

Two main assumptions of CNT could be responsible for its failure to accurately predict experimental nucleation rates:

i) The activation energy for atomic jumps at the nucleus/matrix interface, the kinetic part of the classical expression, is normally associated with that of ordinary diffusion, and is eliminated in favor of the shear viscosity through the use of the Stokes-Einstein equation. However, this procedure has not been justified. Recently, a more rigorous approach, which makes use of the induction times for nucleation instead of viscosity, was suggested and tested[7]. Neither the magnitude nor the temperature dependence of the nucleation rates were well described by theory when the latter procedure was used. A good fit could be obtained only in the temperature range above the temperature of the maximum nucleation rate. Therefore, discrepancies between theory and experiment were found with both approaches implying that other problems exist with CNT;

ii) The capillarity approximation is the assumption that the free energy of a nucleus can be written as the sum of a bulk and surface free energy and that the surface tension (surface energy/area) is that of a flat interface and is independent of nucleus size. However, use of a constant liquid-crystal surface tension produces large discrepancies between measured and predicted I. James[4] observed that CNT could be made to agree with experimental data by employing a temperature dependent interfacial surface tension whose parameters were fixed by fit to experimental data. Although this procedure has been used by others for different types of materials, the use of a temperature dependent surface tension has been criticized by Oxtoby[8].

If the critica1 nucleus is small, then its surface free energy could be quite sensitive to its radius. Tolman[9] and others[10] have developed theories to account for this size dependence and applied it to liquid droplet nucleation from the vapor. Thus Manrich and Zanotto[6] have fitted experimental date to a modified form of CNT employing a radius dependent surface tension. The agreement between theory and experiment was better than that achieved with CNT, but still several orders of magnitude disagreement was found.

To summarize, CNT or its modifications are useful for qualitative understanding of the nucleation phenomenon. However, they are not capable of quantitatively predicting nucleation rates.

Table I

Nucleation parameters and rates using CNT[6]

System	σ (e)	$\log(I_{th})$
	(Jm^{-2}) ($m^{-3}\,s^{-1}$)	($m^{-3}\,s^{-1}$)
LS	0.21 11.45	-36.70
LS_2	0.21 9.63	-25.51
CS	0.28 6.22	-14.36
BS_2	0.14 12.17	-19.78
$N_1\,C_2\,S_3$	0.18 11.75	-43.41
$N_2\,C_1\,S_3$	0.31 13.63	-41.78

V. Standard Models of Crystal Growth

It is now generally accepted that the nature of the crystal-liquid interface has a decisive influence in the kinetics and morphology of crystallization. Theoretical treatments of crystal growth have therefore directed close attention to the nature of the interface and its relation to predicted behavior. It is useful to review briefly the standard models for crystal growth from the melt.

Three standard models[11] used to describe crystal growth and their respective predictions of kinetic behavior are:

a) *Normal growth:* Here the interface is pictured as rough on an atomic scale, with a sizable fraction of the interface sites being step sites where growth takes place. Assuming that this fraction does not change appreciably with temperature, the growth rate, u, is expressed by

$$u = \nu\lambda[1 - \exp(-\Delta H_{\mathrm{fM}}\Delta T/RTT_m)]. \quad (8)$$

Here ν is the frequency of atom jumps at the interface, λ is the distance advanced by the interface in a unit kinetic process (usually taken as a molecular diameter), ΔH_{fM} the molar heat of fusion, ΔT the undercooling, and T_m the melting point.

b) *Screw dislocation growth:* This model views the interface as smooth but imperfect on an atomic scale, with growth taking place at step sites provided by screw dislocations intersecting the interface. The growth rate is given by:

$$u = f\nu\lambda[1 - \exp(-\Delta H_{\mathrm{fM}}\Delta T/RTT_m)], \quad (9)$$

where f is the fraction of preferred growth sites (at the dislocation ledges) on the interface, given approximately by:

$$f \simeq \frac{\Delta T}{2\pi T_m}. \quad (10)$$

c) *Surface nucleation growth:* According to this model, the interface is smooth on an atomic scale and also perfect (free of intersecting screw dislocation). Growth takes place by the formation and growth of two-dimensional nuclei on the interface. The growth rate is expressed by

$$u = C\nu\exp(-B/T\Delta T), \quad (11)$$

where C and B depend on the time required for the formation of the nucleus relative to that for its propagation across the interface. When the nucleus propagates across the interface in a time short compared with the time between nucleation events (small crystal case),

$$C \simeq \lambda N_s A_0, \quad (12)$$

and

$$B = \frac{\pi\lambda V_M T_m \sigma_E^2}{k\Delta H_{fM}}, \quad (13)$$

where N_s is the number of atoms per unit area at the interface, A_0 the cross-sectional area of the interface, V_M the molar volume, σ_E the edge surface energy of the nucleus.

For the more generally applicable case where the lateral propagation rate of the surface nucleus must be considered (large crystal case),

$$C \simeq \frac{(\pi/3)^{1/3}}{\Gamma(4/3)} N_s^{1/3} a^{5/3} \times [1 - \exp(-\Delta H_{fM}\Delta T/RTT_m)]^{2/3}, \quad (14)$$

$$B = \frac{\pi\lambda V_M T_m \sigma_E^2}{3k\Delta H_{fM}}, \quad (15)$$

where Γ is the gamma function.

In his now-classic treatment of interface roughness, Jackson[12] used a single-layer Bragg-Williams model to describe the change in free energy of an initially plane interface on adding molecules at random to the interface. This free energy change, ΔF_s, was expressed:

$$\frac{\Delta F_s}{NkT_m} = -\frac{\Delta H_{fM}\Delta T}{RTT_m}X + f'X(1-X) + \frac{T}{T_m}[X\ln X + (1-X)\ln(1-X)] \quad (16)$$

Here N is the number of sites on the interface; X is the fraction of sites which are occupied and

$$f' = (\Delta S_{fM}/R)\xi, \quad (17)$$

where ΔS_{fM} is the molar entropy of fusion, and ξ is the number of nearest-neighbor sites in a layer parallel to the surface divided by the total number of nearest-neighbor sites. The factor ξ is largest for the most closely-packed planes of the crystal, for which it is $\simeq 0.5$.

For $f' < 2$, the minimum free energy configuration corresponds to half the available sites being filled ($X = 1/2$) and represents an atomically rough surface. In contrast, for $f' > 2$, the lowest free energy configuration corresponds to a few surface sites filled and a few molecules missing from the completed layer and represents an atomically smooth interface. Hence, for materials with $\Delta S_{fM} < 2R$, the most closely-packed interface planes should be small. For materials with $\Delta S_{fM} > 4R$, the most closely-packed surfaces should be smooth, the less-closely-packed faces should be rough, and the growth rate anisotropy should be large.

The above described theories describe reasonably well the experimentally measured growth rates at low undercoolings in glass forming liquids[11].

VI. Overall crystallization

The overall crystallization of a liquid occurs by the combination of nucleation and growth. The kinetics

of such processes is usually described by a theory derived in the period 1937-1939 by Kolmogorov[13], Johnson and Mehl[14] and Avrami[15-17], best known as the Kolmogorov-Avrami or Johnson-Mehl-Avrarni (JMA) theory. Since that time this theory has been intensively used by materials scientists to study the various mechanisms of phase transformations in metals. More recently, the JMA theory has been employed by polymer and glass scientists. Examples of technological importance include the study of stability of glass metals, curing of odontological plasters, devitrification time of radwast glasses, glass-ceramics and kinetics calculations of glass formation[18].

Avrami[15-17] has assumed that: (i) nucleation is random, i.e. the probability of forming a nucleus in unit time is the same for all infinitesimal volume elements of the assembly; (ii) nucleation occurs from a certain number of embryos ($\bar{N}$) which are gradually exhausted. The number of embryos decreases in two ways; by growing to critica1 sizes (becoming critica1 nuclei) with rate v per embryo and by absorption by the growing phase; (iii) the growth rate (u) is constant, until the growing regions impinge on each other and growth ceases at the common interface although it continues normally elsewhere.

Under these ccnditions Avrami[15,17] has shown that the transformed fraction volume, a', is given by

$$a' = 1 - \exp\left[\frac{-6g\bar{N}u^3}{v^3} \times \left(\exp(-vt) - 1 + vt - \frac{(vt)^3}{2} + \frac{(vt)^3}{6}\right)\right], \quad (18)$$

where g is a shape factor, equal to $4\pi/3$ for spherical grains, and t is the time period.

There are two limiting forms of this equation, corresponding to very small or very large values of vt. Small values imply that the nucleation rate, $\mathbf{I} = \bar{N}v\exp(-vt)$, is constant. Expanding $\exp(-vt)$ in eq. (1) and dropping fifth and higher order terms gives

$$\alpha' = 1 - \exp(-gu^3 I_0 t^4/4), \quad (19)$$

where $I_0 = \bar{N}v$.

This is the special case treated by Johnson and Meh1[2] and is valic for N very large when the number of embryos is not exhausted until the end of the transformation (homogeneous nucleation). Large values of vt, in contrast, means that all nucleation centers are exhausted at an early stage in the reaction. The limiting value of eq. (18) is then

$$\alpha' = 1 - \exp(-g\bar{N}u^3t^3). \quad (20)$$

Eq. (20) applies for small $\bar{N}$, when there is a rapid exhaustion of embryos at the beginning of the reaction (instantaneous heterogeneous nucleation). Avrami has proposed that for a three-dimensional nucleation and growth process, the following general relation should be used

$$a' = 1 - \exp(-Kt^m), \quad (21)$$

where $3 \leq m \leq 4$. This expression covers all cases where I is some decreasing function of time, up to the limit when I is constant. Eq. (21) also covers the case of heterogeneous nucleation from a constant number of sites, which are activated at a constant rate until becoming depleted at some intermediate stage of the transformation. In the more general case, where I and u are time dependent

$$\alpha' = 1 - exp\left(-\frac{4\pi}{3}\int_0^t I(\tau) \times \left[\int_\tau^t u(t')dt'\right]^3 d\tau\right), \quad (22)$$

where τ is the time of birth of particles of the new phase. Table II shows values of m for different transformation mechanisms. Thus, if spherical particles grow in the interna1 volume of the sample then m should vary from 1.5 to 4. If growth proceeds from the externa1 surfaces towards the center (collunar shape) then m will be different.

The above treatment, whilst including the effects of impingement neglects the effect of the free surfaces. This problem was recently treated by Weinberg[19].

Eq. (21) is usually written as:

$$\ln \ln(1-\alpha')^{-1} = \ln K + m \ln t. \quad (23)$$

This expression is intensively employed by materials scientists to infer the mechanisms of several classes of phase transformations from the values of m, that is the slope of $\ln \ln(1-\alpha')^{-1}$ versus $\ln t$ plots. The linearity of such plots is taken as an indication of the validity of the JMA equation. It should be emphasized, however, the ln − ln plots are insensitive to variations of a' and t and that the value of the intercept K is seldom compared to the theoretical value. This is mainly due to the great

Table II

Avrami parameters, m, for several mechanisms

(Spherical Growth)

	Interface Controlled Growth	Diffusion Controlled Growth
Constant I	4	2.5
Decreasing I.	3-4	1.5-2.5
Constant number of sites	3	1.5

difficulty in measuring the high nucleation and growth rates in metallic and ceramic (low viscosity) systems.

VII. Application to glass crystallization

The JMA theory can be shown to be exact within the framework of its assumptions. Hence, any violation must be a result of applying it to situations where its assumptions are violated, which may be the case in many crystallization situations.

In an extensive number of studies the JMA theory has been employed to analyze experimental data for crystallinity versus time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis was usually given to values of m obtained from the slopes of experimental ln $\ln(1-\alpha')^{-1}$ versus ln t plots. In[20-24] for instance, m ranged from 1 for surface nucleation to 3 for interna1 nucleation. In no case has the intercept been compared with the theoretical value.

Recently, Zanotto and Galhardi[25] carried out a series of experiments to test the validity of the Johnson-Mehl-Avrami theory.

The isothermal crystallization of a nearly stoichiometric $Na_2O.2CaO.3SiO_2$ glass was studied at 627°C and 629°C by optical microscopy, density measurements and X-ray diffraction. Both nucleation and growth rates were measured by single and double stage heat treatments up to very high volume fractions transformed and the experimental data for crystallinity were compared with the calculated values at the two temperatures. The early crystallization stages were well described by theory for the limiting case of homogeneous nucleation and interface controlled growth. For higher degrees of crystallinity, both growth and overall crystallization rate decreased due to compositional changes of the glassy matrix and the experimental kinetics could be described by theory if diffusion controlled growth was assumed. It was also demonstrated that the sole use of numerical fittings to analyse phase transformation kinetics, as very often reported in the literature, can give misleading interpretations. It was concluded that if proper precautions are taken the general theory predicts the glass-crystal transformation well.

VIII. Glass formation

Turnbull[26] noted that there are at least some glass formers in every category of material based on bond type (covalent, ionic, metallic, van der Waals, and hydrogen). The cooling rate, density of nuclei and various material properties were suggested as significant factors which affect the tendency of different liquids to form glasses.

This approach leads naturally to posing the question not whether a material will form an amorphous solid when cooled in bulk form from the liquid state, but rather how fast must a given liquid be cooled in order that detectable crystallization be avoided. In turn, the estimation of a necessary cooling rate reduces to two questions: (1) how small a volume fraction of crystals embedded in a glassy matrix can be detected and identified; and (2) how can the volume fraction of crystals be related to the kinetic constants describing the nucleation and growth processes, and how can these kinetic constants in turn be related to readily-measurable parameters?

In answering the first of these questions, Uhlmann[18,27] assumed crystals which are distributed randomly through the bulk of the liquid, and a volume fraction of 10^{-6} as a just-detectable concentration of crystals. In answering the second question, Uhlmann adopted[18,27] the formal theory of transformation kinetics described in this section.

In this paper I shall be concerned with single-component materials or congruently-melting compounds, and will assume that the rate of crystal growth and the nucleation frequency are constant with time. For such a case, the volume fraction, a', crystalized in a time t, may for small a' be expressed by a simplified form of Eq. (19):

$$\alpha' \simeq \frac{\pi}{3} I_0 u^3 t^4. \qquad (24)$$

In identifying I_0 as the steady-state rate of homogeneous nucleation, I shall neglect heterogeneous nucleation events-such as at externa1 surfaces – and will be concerned with minimum cooling rates for glass formation. Clearly, a glass cannot be formed if observable amounts of crystals form in the interiors of samples. I shall also neglect the effect of transients during which the steady-state concentrations of subcritical embryos are built up by a series of bimolecular reactions. Neglect of transients ín the present analysís is justified whenever the time required to establish the steady-state nucleation rate is small relative to the total transformation time.

The cooling rate required to avoid a given volume fraction crystallized may be estimated from eq. (24) by the construction of so-called T-T-T (time-temperature-transformation) curves, an example of which is shown in figure 3 for two different volume fractions crystallized. In constructing these curves, a particular fraction crystallized is selected, the time required for that volume fraction to form at a given temperature is calculated and the calculations is repeated for other temperatures (and possibly other fractions crystallized).

The nose in a T-T-T curve, corresponding to the least time for the given volume fraction to crystallize, results from a competition between the driving force for crystallization, which increases with decreasing temperature, and the atomic mobility, which decreases with decreasing temperature. The transformation times t_1, are relatively long in the vicinity of the melting point as well as at low temperatures; and for purposes of the present paper, I shall approximate the cooling rate re-

quired to avoid a given fraction crystallized by the relation

$$\left(\frac{dT}{dt}\right)_c \quad \frac{\Delta T_N}{\tau_N}, \tag{25}$$

where $\Delta T_N = T_{r_3} - T_N$; T_N is the temperature at the nose of the T-T-T curve; τ_N is equal to the time at the nose of the T-T-T curve, and T_m is the melting point.

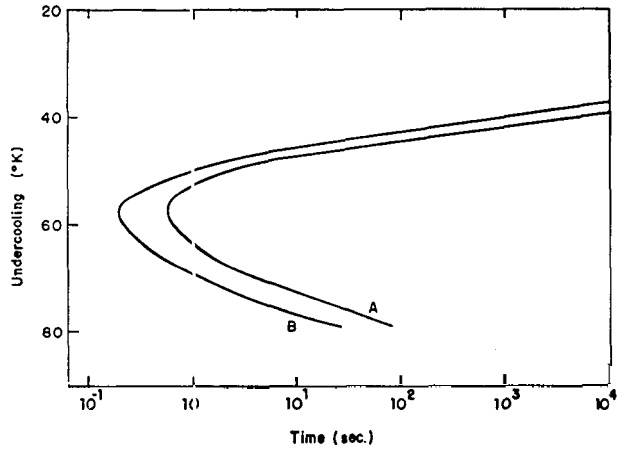

Figure 3: Time-temperature transformation curves for salol: (A) $a' = 10^{-6}$; (B) $a' = 10^{-8}$.

From the form of eq. (24), as well as from the curves shown in figure 3 which were calculated therefrom, it is apparent that the cooling rate required for glass formation is rather insensitive to the assumed volume fraction crystallized, since the time at any temperature on the T-T-T curve variss only as the one-fourth power of a'.

An alternativ: estimate of the glass-forming characteristics of materials may be obtained by considering the thickness of sample which can be obtained as an amorphous solid. Again using the criterion of a volume fraction crystallized less than 10^{-6}, and neglecting problems associated with heat transfer at the external surfaces of the sample, the thickness, y_c, of sample which can be formed without detectable crystallization should be of the order of[27]

$$y_c \approx (D\tau_N)^{1/2}, \tag{26}$$

where D is the thermal diffusivity of the sample.

To estimate the critica1 conditions to form a glass of a given material, one can in principle to employ the measured values of the kinetic factors to calculate the T-T-T curves. In practice, however, information on the temperature dependence of the nucleation frequency is seldom available; and in only a portion of the cases of interest there are adequate data available on the variation of the growtli rate with temperature.

IX. Concluding remarks

The kinetic approach of glass formation allows one to conclude that *all* materials are capable of forming arnorphous solids when cooled in bulk form from the liquid state. The question to be answered is how fast must a given liquid be cooled in order that crystallization be avoided. Thus novel materials such as metallic *alloys*, with unusual properties, have been successfully obtained by very fast quenching[28]. On the other hand, if crystal nucleation is controlled to occur uniformely in the bulk of certain glasses, a variety of advanced glass-ceramics can be and, indeed, are being commercially produced[29].

Deeper insights on the crystallization process, such as precise predictions of TTT curves, and consequently of critica1 cooling rates for glass formation, based solely on materials properties, will depend critically on new developments concerning the nucleation theory. One interesting attemp on that issue was recently advanced by Meyer with his Adiabatic Nucleation Theory[30].

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