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CRYSTAL STRUCTURES FORMATION IN GLASS FROM VIEW OF HRTEM

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The high-resolution transmission electron microscopy HRTEM study of the atomic scale mechanism of crystal structure organization within the amorphous polymeric structure of the model multicomponent glass TiO_2–MgO–Al_2O_3–SiO_2– in the glass transformation temperature range has been undertaken. In the glass transition (T_g) temperature range, glass transforms from the solid of rigid amorphous structure into viscoelastic state of weakened chemical bonds. This is an example of nuclei formation and crystal growth in the polymeric amorphous structure of low atomic scale homogeneity due to middle range ordering. It has been demonstrated that in this case crystal structure formation proceeds by successive displacement and local ordering of atoms in the amorphous structure, like disorder-order transformation in crystalline solid bodies. As the consequence in the crystallization by parent structure reorganization mechanism, traditional model of glass crystallization as well as kinetic models of reactions in solid bodies according Avrami or others, are worthy to be revised.

Keywords: *crystallization, glass, nucleation, solids, structural self-organization*

Introduction

In many thermochemical reactions theories the nucleation is accepted as an important parameter limiting the reaction kinetics. This refers in particular to reactions connected with the formation in the precursor structure of a new compound and its crystallization, including the crystallization of multi-component glasses. Properly programmed nucleation of solidified glass is a main technical operation in production of a modern material and nano-crystalline glass ceramics.

As it is known, the present day chemical kinetics is derived from the theory of molecular collisions and the assumption that the reaction rate is determined by the number of collisions of the free active molecules of the reagents. According to the law of mass operation it is proportional to the molar concentrations of the reagents. This kinetics refers directly to the reversible, stoichiometric chemical reactions, occurring in homogeneous systems, such as the mixture of ideal gases, composed of free atoms or particles. The influence of temperature on the rate of such reactions is defined by Arrhenius equation, which introduces the concept of activation energy of the process (E (kJ mol^{-1})) [1, 2].

The reaction medium represented by the structure of a solid body, differs widely from the model gaseous medium of chemical reactions for which the classic chemical kinetics with its functional dependences has been elaborated. In solids atoms of components are firmly localized and they occupy definite positions in the structure. They acquire a limited degree of freedom. The possibilities for displacement of the reacting elements atoms, with respect to both the rate and usually the direction are limited. Only those components which at the given temperature and pressure possess the appropriate mobility may participate in the internal solid state reactions. To attain this, they must have sufficient freedom of displacements, which is expressed by their diffusion coefficient according to the known Nernst–Einstein equation: $D_i=RTB_i$ where D_i is diffusion coefficient of element i, and B_i its mobility.

Diffusion coefficients of the various components of the given solid increase with temperature to various degrees. For this reasons, some of them reach the displacement freedom earlier, which allows them to take part in the chemical reactions and to form new compounds while others, at the same temperature, behave as a neutral matrix within which, the given reaction takes place [3].

The specific character of the structure of a solid body as the medium of the reaction, limiting the mobility of the reagents, causes that the mechanism of the reactions occurring in it becomes especially complex in comparison with reactions occurring in homogeneous gaseous systems and in most liquid systems. For this reason for a reaction in the solid phase there have been elaborated special theoretical models of various reaction mechanisms and the corresponding

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equations for the reaction rate describing the dependence of the reaction degree α on the time *t*. From the values of the parameters of the proposed equations conclusions are drawn about the mechanism of the given reaction (Johnson–Mehl–Avrami–Yerofeyev–Kolmogorov methods). They are commonly applied in the glass crystallization study [4, 5].

The parameters of these kinetic equations point to one-, two- or three-directional growth of the nuclei or the direction of diffusion from the surroundings to the interphase of the growing crystals or along the interphase as these define the reaction kinetics [2]. Worthy of note is the fact that these are concepts referring to phenomena on atomic scale, about which it is concluded on the basis of macroscopic measurements of the increase of mass or volume of the product with time. This causes doubts whether these relations are in agreement with the real mechanism of reactions in solid bodies, which are usually complex and proceed in several stages. Extension of the knowledge of the actual mechanism of thermal reactions by defining the structural changes and the atomic interactions has become possible using the modern methods of phase analysis, electron microscopy and the spectroscopic methods. To understand them the crystal-chemical interpretation, comprising among others the analysis of the strength of interatomic bonds in the structure, is helpful.

Such an approach has been applied by the author and his co-workers in the investigations of complex reactions of the thermal decomposition of bodies of polymeric structure, such as silicates, phosphates and borates, which in turn enabled to explain the mechanism of the multistage processes occurring in these bodies [2, 6–8]. At present, this approach is used in the investigations of the thermal stability of the glasses and their crystallization.

Using the crystallochemical factors in the investigations of the structure mechanism of thermal reactions has its tradition. Among others, Cyganski [9] and Ptaszynski [10] used the magnitude of the radius of the central cation of ligands as an indicator of thermal stability of complex compounds; Gorski and Gontarz [11], basing on the value of electronegativity of bonds and the resulting magnitude of acid-base interactions between the components, explained the thermal decomposition of inorganic compounds and the succession of the formation of intermediate compounds in multi-stage decompositions.

In many papers from time to time, there can be found examples of using Pauling’s electronegativity, Cartledge’s ionic potential or the force of the cation field to explain the observed phenomena connected with thermo-chemical processes.

Considering the important role ascribed to nucleation in the thermochemistry of solid bodies, attempt has been made to demonstrate the actual mechanism of formation of nuclei of a new phase in a solid body on the example of crystallization of multi-component glasses. The transition of the amorphous structure of glass into crystalline structure belongs to processes of structural self-organization, which recently have great interest in the technology of materials. Here have been used the possibilities offered in this respect by high resolution electron microscopy (HRTEM) to explain the observed phenomena and characterizing the bonds between the components and the resulting local chemical affinity were used.

Crystallization of glasses in the temperature range close to the glassy state transformation (T_g) was examined. This transformation is specific for amorphous bodies and is connected with transition of the structure of a rigid solid body into visco-elastic state with the primary structure retained to a great extent, which however with increasing temperature under the influence of thermal vibrations undergoes gradual destruction. It is manifested by the reduction of viscosity and simultaneous increase of the mobility of the components. This offers the possibility to observe the influence of the factors, mentioned increasing mobility of the compounds on the crystallization.

Nucleation at the glass transformation range is currently applied in the manufacturing of nano-crystalline, transparent glass-ceramics, among others kitchenware and plates on the electric ovens.

Experimental

Glass elaborated by Pinckney and Beall [12, 13] the nano-crystalline glass ceramics are well described by the crystallization process and it is why it was selected as a model glass for heterogeneous crystallization investigation. This glass allowing to obtain tough nanocrystalline glass – ceramics; it has the following composition: 47.1SiO_2, 22.0Al_2O_3, 16.9MgO, 1.7ZnO and 12.3TiO_2 mass%. Crystallization of the glass was studied using pieces of glasses heat treated at different temperatures for 4 h.

Crystal phase formation was investigated by the differential scanning calorimetry (DSC) and differential thermal analysis (DTA) at the heating rate 10 K min^{-1}, with temperature measurement accuracy 1 K. The phase composition of crystallized glass was investigated using X-ray diffraction (XRD), and scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) as well as transmission electron microscopy (TEM). The observations were carried out at the Institute of Metallurgy and Materials Science of the Polish Academy of Science in Cracow. The early stages of crystallization were investigated using high resolution transmission electron microscopy (HRTEM) in order to determine the character and size of nuclei. HRTEM observations were carried out at Silesian Universtity in Katowice.

Results

The DTA measurements (Fig. 1) indicate that dense, bulk crystallization starts at the temperature 820°C what is marked by the beginning of the exothermic effect of crystallization, and reaches the maximum at 869°C; the second stage of crystallization takes place at 935°C and the third at 1204°C. XRD investigations have revealed that first crystals are formed at 725°C, just at the beginning of glass transformation (T_g 750°C) there are lines of the (Mg,Al)-titanate and high quartz s. s. appear.

In glass structure derived materials there is a formation of silica rich crystal phase with the structure of high temperature modification of quartz stuffed with considerable amounts of Mg^{2+}, P^{5+}, Ti^{4+}, Al^{3+}. The total content of these admixtures varies and it may be considerable, reaching up to 40 mass% of the composition of the substance. It is named high quartz solid solution (high quartz s.s.).

The higher the heating temperature of the glass, the stronger is the characteristic line of high-quartz (3.44 Å), and at 850°C, it is the main crystal phase. At about 950°C there appear lines of clino-enstatite. Above 1000°C, on the expense of high quartz, indialite and/or cordierite crystallizes. These stages of glass crystallization have separate peaks on the DTA curve of glass (Fig. 1).

Observation of the transition of the amorphous into crystalline structure of the glass was made possible by HRTEM study at 10^6 magnification. There could be observed the formation of areas measuring up to 3–5 nm with ordered arrangement of atoms in the disordered structure of glass (Figs 2a and b). The degree of the organization of the newly formed crystal structures is various. There can be distinguished the lattice planes with the distance of about 0.5 nm, corresponding to [020] plane of $MgTi_2O_5$ phase. The phenomenon of immiscibility and drop-like glass in glass separation as the glass crystallization initiator, suggested in [12–14] was not observed. Early stage of silicates crystallization as crystal lattice formation into the amorphous surrounding is visible as well (Fig. 2b).

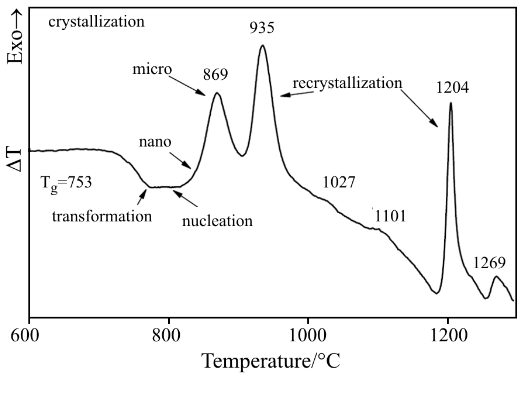

Fig. 1 DTA curve of glass

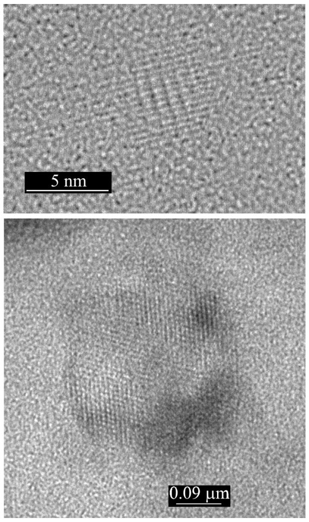

Fig. 2 Amorphous structure organization and crystal lattice of a – Mg,Al- titanate and b – high quartz s.s. formation showed at HRTEM

The growth of the crystals occurs through incorporation of the atoms of the components from the surrounding glassy matrix. Interface boundary between crystallites and glass is diffuse, about 0.5 nm wide. Taking into account similarity of the chemical composition of crystallite and glass this is a coherent interface. The formation of dendrite aggregates about 10–100 nm in size at 725°C has been observed as well. Moreover irregular areas of crystalline structure, indicating the beginning of the formation of another crystalline phases could be observed around them. Above 750°C they are much better developed and reach dimensions up to 100 nm (Fig. 3). They are large enough to determine their chemical composition by EDX investigations.

There have been observed various stages of the growth of fine crystallites of the size of 3–5 nm and

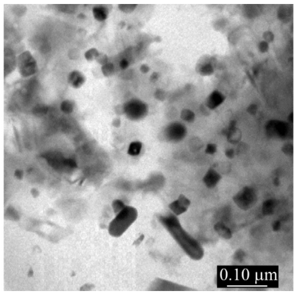

Fig. 3 Crystallites formed after 4 h heat treatment of glass at 850°C, (Bright field TEM image at 300 kV)

Table 1 Chemical composition of crystallites formed at 850°C after 4 h heat treatment

Oxides/mass%	High Qss	$MgTiO_3$	$(TiO_2–SiO_2)$s.s.
SiO_2	98.53	–	49.37
TiO_2	0.78	42.27	40.28
Al_2O_3	–	–	9.91
MgO	0.39	51.55	0.44
ZnO	0.29	6.17	–

formation of columnar crystals from them. According to classical nucleation theory (CNT) criteria, they can be treated as nuclei which exceeded the critical size and are able to grow further.

EDX investigations have shown that the newly formed crystallites have differentiated chemical composition (Table 1). Among them, there are many crystallites with the composition and structure corresponding to magnesium titanate $MgTi_2O_5$ or to solid solutions from the series $MgTi_2O_5–Al_2Ti_2O_2$. Besides them there are observed crystallites containing TiO_2 and SiO_2 of varying proportions of both components, representing the stable solutions $TiO_2–SiO_2$. Rutile crystals with Si and Al admixtures were also observed. This reveals the ability of rutile TiO_2 to form solid solutions with various oxides. As regards their number, among the crystallites the main component is SiO_2 while Al, Mg, Ti, P are present as admixtures. This is the phase of high-temperature quartz, stabilized by admixtures. It is often formed during crystallization of silicate glasses, due to the ability of high-temperature quartz (solid above 575°C) to accept considerable amounts of admixtures and formation of stuffed structure. TiO_2 and the crystal phases, containing considerable amounts of it, demonstrate great one-directional growth rate forming elongated needle-like crystals, distinct from the other crystallites.

Experimental results suggest that crystallization of glass starts with the formation of crystals composed of chemical components relatively weakly bounded in the structure and easy to be free and mobile. It means, that the temperature of beginning of crystallization, and order of the crystal phases formation as well as its crystallization rate is determined by the strength of the chemical bonds in the structure of glass. Structure of oxide glasses consists of network former cations joined together by oxygen anions-oxygen bridges and cations-modifiers connected with the spatial network. Bridging oxygen behaves as Lewis's base and acid-base interactions between bridge forming elements takes place.

Due to this strength of oxygen bridges and ionicity/covalency degree of Me–O bonds along the bridge determines in a considerable degree properties of glass. Accordingly, crystal-chemical analysis of oxygen bridges strength has been done. This procedure was elaborated earlier to explain the specificity of phospho-silicate glass crystallization [6–8, 15].

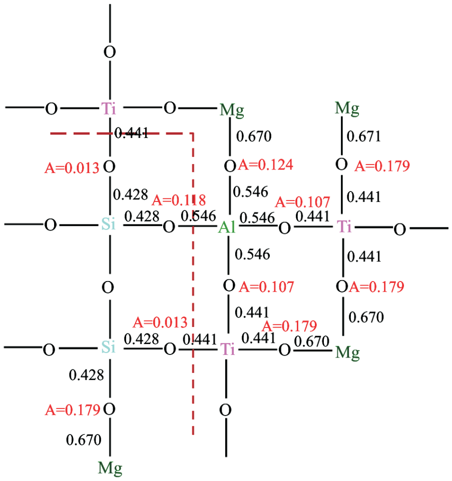

Fig. 4 Local chemical interactions in $TiO_2–MgO–Al_2O_3–SiO_2$ compositional system glass, showing the ionicity of chemical bonds (i_G) and strength of oxygen bridges (A)

In the present study values of the ionicity of cation-oxygen bonds, by Görlich (i_G) have been used as a measure of both strength and local acid-base interactions along the oxygen bridge [16]. Difference of the ionicity of cation-oxygen bonds in the bridge has been used here as measure of local chemical affinity of the joining components (A):$A=i_b–i_a$, where i_b is ionicity more basic and i_a more acidic component of the bridge ($i_b>i_a$). Higher the A value higher the chemical components affinity, stronger the acid base interaction and at the same stronger the bridge.

Ionicity of bonds and strength of oxygen bridges (A) in the structure of studied glass are presented schematically (Fig. 4). Lowest A values has the bridges Si–O–Ti (0.013), Al–O–Ti (0.107), Si–O–Al (0.124), and they should be broken as the first. It means the separation of glass structure into titanate and silica domains, that is confirmed by the titanate and high quartz crystallites formation.

In the applied method there are used simple parameters characterizing the bonds between the structure components which show, although only approximately, the interactions of chemical nature, such as the acid-base interactions and the related chemical affinity on local scale. In the case of polymeric structure of the glass, this is the interaction between components joined by oxygen (or anion) bridge.

At present the molecular dynamic modeling (MDM) of the structure of solid bodies is widely applied. It makes use of the classical Born–Mayer criteria as well as of the quantum interatomic forces. The complicated dependences, illustrating numerous, various interactions between the atoms, enable to determine their positions in the structure and the statistic image of this structure. However, the resulting consequences of chemical interactions character have not so far become an object of interest of MDM studies. The simplified approach used in this work undertakes this direction.

Discussion

Presented results demonstrate that near T_g, when the parent structure of glass is still preserved or changes only in a rather small degree, the nucleation can proceed by rearrangement and successive displacement and local ordering of atoms in the amorphous structure of glass. This crystallization mechanism is similar to disorder–order transformations in crystalline solid bodies. Glass in glass separation is not the obligatory for the beginning of crystallization.

HRTEM images (Fig. 2) proved that the first detectable new phase areas, of a few nanometers size, have determined the crystal lattice from the very beginning and the habit dictated by the crystal structure geometry. Their size 3–5 nm is close to the size, given in literature, of local domains or clusters connected with the middle range ordering of glass structure. They form as a result of chemical interactions between glass components. The size of the domains is estimated to 1–2 nm. It means that the middle range order domains, existing in the parent glass structure, can be precursors for the nuclei able to grow.

Mobility of components determines the course of crystallites formation below and little above the T_g. As a result, their chemical composition does not exactly correspond to the theoretical one due to the presence of components retained from the parent glass, as it has been demonstrated by the conducted EDX investigations. The increase in the mobility of the components, progressing with further increase of temperature, enables ordering of the structure and the chemical composition of the developed crystal forms becomes close to the theoretical one.

As a consequence crystallization with the mechanism of the disorder–order transformation of the parent structure enables to inherit the features of the previous glass structure, among others, its chemical components and, occasionally, also the order of their distribution. Nucleation of the examined glasses in the applied experimental conditions leads to the formation of crystallites of various composition, such as Mg,Al-titanates, high quartz s.s., SiO_2TiO_2 s.s. They correspond to fragments of the broken network in the glass structure. This is a confirmation of the crystallization mechanism proposed in this study.

It can be supposed that the inheritance of features of the parent glass structure by the newly forming crystal structure is the result of the mode of its formation by means of small diffusive rearrangements of the components to a degree limited by large viscosity at the temperature of transformation ($10^{13.5}$ dPa s). Consequently, firstly there should be formed phases, close to the primary structure and to the chemical composition of the parent glass structure as it has been established. Usually, they are metastable phases. With increasing temperature and mobility of the chemical components they become rearranged into phases close to the equilibrium state, determined by the position of the glass composition on the respective phase equilibria diagram. High quartz s.s. formation at the beginning and corierite at the end of crystallization is the example.

The analysis of the strength of the cation bonds by the oxygen bridges with the silicate network, measured by their ionicity and local chemical affinity, has shown that in the polycomponent glass, like that examined in this study, the Ti bonds with the silicate network are among the easiest to break, which accounts for the crystallization of Mg,Al-titanates, SiO_2TiO_2 s.s. and high quartz s.s. as the first crystal phases, formed by the rearrangement of the primary structure of the glass.

Crystallization of glass in the solidified form requires its heating to the structure transformation temperature or above it. This means that it becomes necessary to break an appropriate amount of the chemical bonds to make some components of the glass sufficiently mobile in a degree enabling their reorientation and reassembling required to form areas of ordered crystal structure. Therefore in spite of supercooling as an indispensable condition of crystallization of a liquid by nucleation and growth, a solidified medium crystallizing by internal structure rebuilding needs overheating to destruct the primary structure. The primary structure destructure should be considered as a factor limiting the crystallization kinetics of solids. Its energy probably represents a considerable part of the activation energy of the crystallization of solids.

The similarity of the composition and the structure of the newly formed crystals and parent glass, causes that the boundary between them is diffuse and broad (Fig. 2) and interface crystal-glass is coherent This should diminish also significance of surface tension and interface energy barrier as crystals formation and growth limiting factor. Its width in relation to the dimensions of the crystal structure at the initial stage of crystallization is relatively large and it decreases with the crystal growth. It corresponds well to the near-boundary diffusion layer of structure building components, typical for crystal growth process.

Conclusions

As the consequence of the observations which have been carried out in the crystallization by parent structure reorganization mechanism, traditional model of glass crystallization as well as kinetic models of reactions in solid bodies according to Avrami or others, are worthy to be revised.

However, traditional glass crystallization model based on CNT concept seems to be valid for glass in the state of homogenous liquid of relatively low viscosity as it is at liquidus temperature.

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