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IDEAS CONCERNING THE NON-CRYSTALLINE MATERIALS OBTAINMENT BY MELT UNDERCOOLING

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A short selective review of concepts and ideas concerning the conditions in which the melts may be undercooled in vitreous state is presented. The important role of the cooling rate in the broadening of the glass forming domains, encouraging the apparition of the new ultra high cooling rate techniques, is underlined. Correlation between the undercooling in the vitreous state tendency and basicity (pB in %) is demonstrated. The new evidenced fact that the classic glass formers are located in the central field of the basicity scales, i.e. approximately between 40 and 60 % of pB, is discussed. The speed of the heath dissipation V_{hd}, as a very general glass forming condition, is defined. The fulfilling of this condition allows obtaining every liquid or melt in vitreous state. The two new possibilities of melts undercooling tendency estimation are easily utilisable the necessary data being accessible.

1. Introduction

To obtain non-crystalline solids energy must be injected during the material processing. Many genesis routes may be used depending on the energy nature [1, 2, and 3]. These possibilities are suggested by the genesis routes triangle presented in figure 1, where S = solids, L = liquids, G = gases, V and V* are different resulting vitreous structures. For example, using thermal route, the solid is melted and the obtained L is undercooled to non-crystalline solid V.
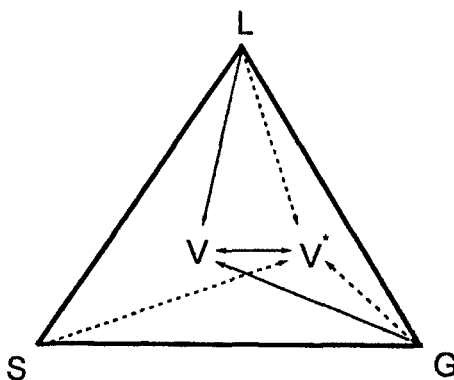

Fig. 1. Genesis routes triangle.

For thousand of years the main energy used for glass producing is the thermal one. After obtaining a melt it must be cooled up to the room temperature avoiding the crystallization to conserve the structural disorder. Because the nucleation and the crystallization processes devolve in time the cooling rate is one of the most important factors.

In the usual industrial technological conditions a reasonable slow cooling rate is necessary to allow the normal processing of glass products. For some glasses, like chalcogenide, metallic and others, interesting and important from scientific and application points of view, new technologies were elaborated.

In this work an attempt to update the ideas concerning the undercooling of melts in glassy state is presented.

2. A short review of the concepts concerning the possibilities of the melts undercooling tendency estimation

Efforts were made during the time to theoretically estimate the melt undercooling in vitreous state tendency. Many research workers approached this problem by following, mainly, two ways: 1) the consideration of the melt structure and of the nature of the chemical bonds and 2) the study of the kinetics of the crystallization process.

The first way resulted in the elaboration of rules, stepwise enriched with the progress of the glass chemistry. As examples, the Zachariasen rules are well known and also the use in this aim of the cation field strength introduced by Dietzel. Other attempts in this sense together with the use of the accumulated knowledge in the field of chemical bonds and of melt structure are presented in [1, 2, and 4]. Three categories of oxides are defined: glass formers, intermediates and modifiers. It was proved that these rules must be adjusted when new scientific and experimental data are accumulated. Thus, many compositionally new glasses and those obtained by the use of some ultra rapid cooling techniques made necessary a re-definition of the above mentioned three categories. For example, in chalcogenide glasses the role of modifiers seems to be played by the halogen atoms, which break the chalcogen bridges. In that concerns the formers this concept is less clear defined and consequently less used.

On the crystallization kinetics line the efforts were concentrated to express as correctly as possible the probability of nuclei apparition and the crystallization development. One of the early obtained results is a glass forming condition expressed by means of the so-called kinetic barriers for nucleation $\Delta G'$ and for crystallization $\Delta G''$, related to the viscosity influence increase, during the melt temperature decrease, on activation energies [1, 5]. For the case when the nucleation rate is of the order of 1 nucleus·cm^{-3}·s^{-1} and the crystal growth rate is less than 10^{-5} atomic dimensions per second, one obtain that the undercooling of a melt in vitreous state is possible when:

$$\Delta G' \approx \Delta G'' \geq 20 \cdot R \cdot T_m \tag{1}$$

where R is the gas constant and T_m is the melting temperature. That means that only the melts with a complex enough structure and with strong, active chemical bonds may be undercooled in vitreous state. Obviously the relationship (1) has been conceived mainly for usual industrial glass melting conditions. Taking into account the melt structural complexity and the chemical bonds energy the condition (1) is applicable to chalcogenide glasses too. However, many new glasses cannot be obtained in such conditions.

Stevels and collaborators [6] defined the notion of critical cooling rate CCR as the minimal cooling rate at which a melt with a given composition still can be obtained in vitreous state. Such experimentally accumulated information may be used to identify the compositions that can be processed in the usual industrial conditions without the risk of crystallization. However, getting such experimental data is laborious.

Uhlmann [1, 7, and 8] had the idea to establish the minimum crystal volume, detectable in glass by the usual techniques, which may make doubtful the quality of the given material as a glass. This volume fraction has been estimated at 10^{-6}. Uhlmann proposed a relation for the volume fraction of crystal calculation taking into account the nucleation frequency and the crystallization rate. Finally it may be drawn the so-called T-T-T curves, representing the temperature dependence of the time interval necessary for a given degree of melt-crystal transformation took place.

Using this kind of curves it may be approximated the cooling rate necessary for avoiding the formation of the previously established crystal volume fraction and even the thickness of the sample obtainable in vitreous state. A precious information is obtained in this way, as results from the table 1 [7, 8], that concentrates a part of the few data acquired in this field. It is evident the traditional glass forming character of SiO_2 and GeO_2 and the diminution of this property towards metal.

The knowledge concerning the melts nucleation and crystallization are considerable enriched in the time passed after the elaboration of the above ideas.

Table 1. Information obtained by means of T-T-T curves.

The substance	CCR ($K \cdot s^{-1}$)	The thickness of the sample obtainable in vitreous state
SiO_2	2.10^{-4}	400 cm
GeO_2	7.10^{-2}	~7 cm
Salol	50	0,07 cm
H_2O	10^7	~1 μm
Ag	10^{10}	1000 Å

It must be noted the importance of transient phenomena in the nucleation process and the role of non-steady state time lag in nucleation, outlined especially by Gutzow and collaborators [4]. A simple relationship was deduced for critical cooling rate (denoted in this case as q_c) calculation in the case of a catalyzed nucleation:

$$\log q_c \cong 17 - \frac{U(T_m)}{RT_m} \qquad (2)$$

where $U(T_m)$ is the activation energy at the melting temperature. Taken into account the correlation between this activation energy and the molar enthalpies of evaporation and of sublimation one obtain:

$$\log q_c \cong C - \frac{\Delta H_{subl}}{RT_m} \qquad (3)$$

where C is a constant. If a quite reasonable value of 1 $K \cdot s^{-1}$ is considered for q_c then results the condition:

$$\frac{\Delta H_{subl}}{RT_m} \geq C \qquad (4)$$

that may be used to conventionally separate the glass formers or "vitroids" from "crystalloids" [4]. The correlation possibility with melt structure and with chemical bonds is maintained.

The practical use of these ideas, of a high theoretical interest, encounters difficulties especially in the acquisition of the necessary for calculation data.

3. The use of basicity for the undercooling tendency estimation

As it is known, for solids the Lewis's theory of basicity seems to be the most adequate. In oxide glasses, oxygen is the basic partner donating the electrons needed for the bond. A simple image of such a bond offered by Lewis in 1916, cited and used by Pauling too [9], supported the idea that the shared electron pair is in general attracted more strongly by one than by other of two unlike atoms, according to the respective electronegativity values. The established equilibrium position of the electron cloud has important consequences, among them: a kind of mean electronegativity value, some partial charges on the partner atoms, a certain amount of ionic character of the bond etc. It is evident that the electron donating power of the oxygen atom and the acceptor ability of the partner atom must change too, the significance being a change in the basicity value.

The consequences may be seen also in certain modification of the electron levels (molecular orbitals), reflected by the electron transitions, by the polarizability values, by the refractive index and finally by all properties of glasses and all other oxidic materials. it is not surprising that many such influences have been proposed or used, with more or less success, as tools to measure the basicity.

The pB concept was published for the first time in a Romanian textbook of glass technology in 1984 [2] and then in English in 1985 [10]. Accepting the fact that oxygen is the basic part in oxides the amount of the ionic character (I_c), as defined by Pauling [9] was chosen to measure the electron donating power denoted, in this aim, pB. The immediate advantage was the possibility to calculate this magnitude by means of the known Pauling's relation, using the electronegativity (X_A and X_B) values:

$$I_c = 1 - e^{-0.25(X_A - X_B)^2} \qquad (5)$$

To consider also the co-ordination number CN and to use the ionisation potential of the cation

in the given oxide or glass instead of electronegativity a new relationship was elaborated for the amount of the ionic character, i. e. for pB, calculation.

$$\log pB = 1.9(CN)^{0.02} - 0.023\frac{P_i}{CN}$$ (6)

The P_i values are easily accessible from tables based on calculated or experimentally determined data. The P_i value (in eV) used in (6) accounts for the oxidation state (OS) of the cation too, which has an important influence on the amount of the ionic character. For oxides having the same OS and CN the amounts of the ionic character calculated by means of electronegativity(5) or with (6) are identical [10].

The formula (6) gives pB values in percents, the pB = 100 % being the value of a free O^{2-} ion, that is, an ideal, not achievable, limit of electron donating power. The expressing of basicity in percent has the advantage to make easier the comparisons and correlation. The acronym pB prompts, in principle, the analogy with pH and pO^{2-} and also the expressing in %.

For complex glasses and oxidic materials the pB value is obtained from:

$$pB_g = \sum_i pB_i \cdot c_i$$ (7)

c_i being the weight fraction of the oxide i and pB_i the respective basicity.

By means of the explicitly or implicitly included magnitudes, the basicity scale pB takes into consideration the properties of the atom (electronegativity, ionization potential), of the ion (oxidation state) and also the local chemical structure (coordination number CN) [2, 10-12]. For this reasons pB correlates in a direct and simple manner with all properties of glasses. The correlation between pB and the undercooling in the vitreous state tendency is illustrated by the data in the table 2.

The glass former, in the classical sense, oxides have pB values up to approximately 60 %, the intermediates between 60 and 70 % and modifiers over 70 %. It is interesting to note that the most different industrial glasses have pB values in the range of glass formers, up to 63 %. Because the pB scale was elaborated only for oxidic materials the basicity values of chalcogenides were obtained using the relationship (5) for the amount of ionic character calculation function of electronegativity.

Table 2. Basicity (pB) values for some compounds and glasses.

Oxides	pB (%)	Industrial glasses	pB (%)
P_2O_5 - former	38	BaO - modifier (CN =8)	89,5
B_2O_3 - former (CN = 3)	44.8	Schott C_1 solder glass	50.0
SiO_2 - former	49.4	Simax (Pyrex, Duran)	52.2
As_2S_3 - former	6.0	Solder glass for Kovar	54.1
GeS_2 - former	11.6	Schott C_{15} solder glass	57.1
Al_2O_3 - interm. (CN = 4)	61.6	Glass for high tension insulators	58.9
Al_2O_3 - interm. (CN = 6)	72.4	Window glass	60.0
Na_2O - modifier (CN =6)	89.0	E fiber glass	60.9
K_2O - modifier (CN =9)	94.2	Philips, for TV screen glass	62.8
CaO - modifier (CN=7)	88.4	Sovirel S 000,01 solder glass for Fe	63.0

As it is known and seen in the table 1, the amount of the ionic character of chalcogenides is small, that is, the basicity is low. Considering the pB values the examined chalcogenides are glass formers. This statement is valuable for many other chalcogenide compositions.

The increase of the amount of basicity over 60 % indicates the diminution of the glass forming tendency in the usual industrial conditions. However, the vitreous state may be obtained but only using rapid or ultra rapid cooling techniques.

The available CCR data [8] allow checking the correlation with pB. In the figure 2 were represented in semilogarithmic coordinates the CCR values calculated for the case of a homogeneous nucleation and for the case of a heterogeneous nucleation and contact angles of 100° and of 60°, versus basicity. The drawn curve evidences for the first time the existence and the nature of this correlation.

Although the available data are few it is showed the inedited fact that the crystallization tendency is minimal, respectively the undercooling in vitreous state tendency is maximal in the central zone of the basicity scale. The CCR increase by the basicity increase over about 60 % is known and easy explainable but the CCR increase when the basicity decreases, i.e. when the amount of the covalent character of the chemical bonds increase is unexpected.
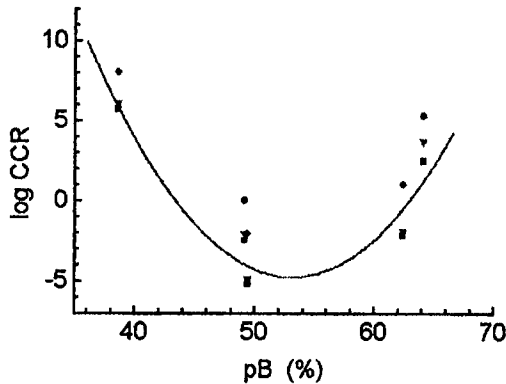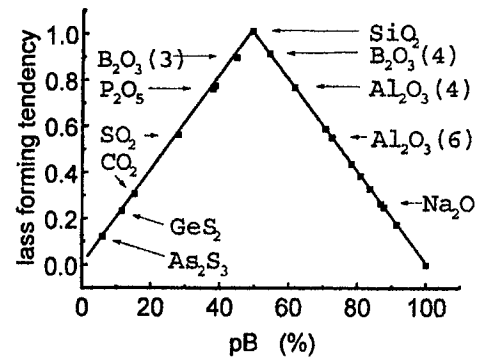

Fig. 2. The CCR dependence on pB.

Fig. 3. Glass forming tendency and pB.

To discuss these new aspects figure 3 was drawn based on the idea that SiO_2 is the best glass former in usual industrial conditions, at a pB value of about 50 %. In principle, figure 3 offers a more suggestive image, comprising also B_2O_3, P_2O_5, SO_2, CO_2, GeS_2 and As_2S_3 as examples. To obtain glasses from more basic compositions, with less complex ionic structures the rate of melts cooling must be correspondingly increased. As was shown above, at pB values between about 60 % and 40 % the glass-forming tendency is high and the respective materials may be quite easily undercooled.

The new revealed effect of the increase of the amount of the chemical bonds covalent character upon the undercooling in the vitreous state tendency deserves a deeper examination in the future. For the moment one may advance the hypothesis that the oxide glass forming tendency diminution towards smaller pB values is probably determined by a certain structure simplification continued, at lower basicities, by the formation of some small, isolated molecules, less active towards exterior. As a result the volatility increases in the same direction up to gases like SO_2 and CO_2. The diminution of the polymerization ability and the increase of volatility seems to be the reasons of the change in the basicity influence on glass forming tendency.

The position of chalcogenides in figure 3 was determined by the practical impossibility to obtain such glasses in the traditional industrial conditions because they important tendency to react with the atmospheric oxygen. In vacuum or in special protective atmosphere they show the glass former property indicated by the low pB values.

4. A new, very general, condition for melt undercooling

The cooling rate of a melt to obtain glass signifies the possibility to dissipate a given heat quantity in a short enough time to preclude crystallization. This process evidently depends on the heat quantity, respectively on the mass of the melt to cool and on the conditions in which the thermal transfer to the environment is realized. In the table 3 some data are presented for two very different situations in which glasses are obtained by undercooling [2, 14].

Table 3. Data for heath dissipation rate V_{hd}. Calculation.

The parameter	Industrial oxidic glasses	Metallic glasses
Cooling rate (C_r) degrees·s^{-1}	10^{-2}	10^5
Undercooled mass, (m) grams	10^6	10^{-1}
Heat capacity (c) $J\cdot degrees^{-1}\cdot g^{-1}$	0.33 - 1.04	0.12 - 1.13
Heat dissipation rate (V_{hd}) $kJ\cdot s^{-1}$	3.3 - 10.4	1.2 - 11.3

If in the classical expression of heat transfer the temperature difference is replaced with the cooling rate, i.e. with the temperature difference realized in a second, the transferred heat quantity in the

time unit (V_{hd}) may be calculated:

$$V_{hd} = C_r m c \qquad (8)$$

Using the data in table 3, from the last row results the condition:

$$V_{hd} \geq 10^0 \quad (kJ \cdot s^{-1}) \qquad (9)$$

For obtaining glass from any melt heat quantities of the order of units of kJ or greater must be eliminated in each second. Having no terms related to composition, structure, temperature, this condition has a very general character. Only the absence of an adequate technique for rapid heat dissipation may preclude the obtainment of a given melt in glassy state.

On the basis of the figure in the right side of the inequality (9) it may be established a new classification criterion of melts and glasses, taking into account the manner the heat dissipation necessary for undercooling may be realized. For example the present industrial oxidic glasses and also many chalcogenides might be characterized by a V_{hd} smaller than $10^0 kJ \cdot s^{-1}$. Some melts based on heavy element oxides, orthosilicates and metallic alloys might form an intermediate category with V_{hd} of the order of 10^0 $kJ \cdot s^{-1}$. Pure metals might form a category having a greater V_{hd}, value that, eventually, may not yet be realized.

The classification of melts in such categories might indicate in a direct manner in what conditions and with what processing methods become possible their obtainment in a non-crystalline state by undercooling.

5. Conclusions

A brief review of ideas concerning the melts undercooling was done.

In spite of the few available data it was shown the interesting CCR correlation with basicity.

The correlation between the undercooling into vitreous state tendency and melt basicity is outlined. For the first time was evidenced the fact that only the melts with basicities between 40 % and 60 % may be obtained in vitreous state in the present industrial conditions. The diminishing of the glass-forming tendency with the basicity increase above 60 % pB is quite easily explainable by the decrease of the structural melt complexity. When the basicity decreases under about 40 % a new, interesting feature appears, which has to be deeply examined in the future. It seems to be related to the prevalence of covalent bonds resulting in smaller, isolated structures with an increasing tendency to volatilize.

A new very general condition for melts undercooling was deduced, expressed as the rate of heat dissipation V_{hd}. If this condition is fulfilled every melt irrespective of his composition and structure can be obtained in vitreous state. The only restriction is related to the availability of a method able to realize the needed V_{hd}. A possibility of melts classification on the basis of their V_{hd} is suggested.

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