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THERMAL ANALYSIS OF GLASSES FOR PROECOLOGICAL APPLICATIONS

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Abstract

Thermal behaviour and biochemical activity of potassium-silicate-phosphate glasses modified by addition of Ca, Mg, acting as ecological fertilisers of controlled release rate of the nutrients for plants were studied.

It has been found that the biochemical activity of silicate-phosphate glasses depends on the nature and the number of components forming the glassy framework and is related to the thermal stability of glass demonstrated by the formation of new compounds during the process of crystallisation. It is proved that these seemingly different properties are determined by the same parameters which are the strengths bonds of glass network-formers and modifiers as well as their chemical affinity.

Keywords: bioactive glass, glass crystallisation, glass dissolution, silicate-phosphate glasses

Introduction

Manufacturing ecologically-friendly materials intended to be used for environmental protection is now perspective trend in the industry. The synthetic materials of appropriately formed properties may be helpful in the recovery and maintenance of the biogeochemical environmental equilibrium disturbed by human activity. A special type of materials are the bioactive materials, capable of participation in biological processes of living organisms [1]. Such materials are, among others, mineral fertilisers in the glassy form.

Glassy fertilisers can contain a complete set of macro- and microelements needed from the growth of plants. Due to the proper chemical composition and glassy form these compounds are to a minimal degree dissolved and carried away by the atmosphere water, which is a great disadvantage of the traditional fertilisers as well as the enveloped fertilisers. This property prevents the washing out of nutrients from the soil, thus glassy fertilisers do not contaminate the groundwaters which makes them ecologically safe. On the other hand, these materials release the macro- and microelements under the influence root systems in amounts needed at the particular stage of growth of plants, without the risk of overdosage. The receiving of the useful components proceeds through the weathering process of glass and the rate of this process may be controlled by a proper selection

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of the chemical composition of glass, which determines its biochemical activity. Glassy fertilisers allow to feed the cultures supplying the mineral components in natural way, which has been a problem so far, especially for ecological market gardening. Introduced into the soil they retain their activity for many months or even seasons, supplying continuously the nutrients and elements in the amounts required by the plants.

The usefulness and effectiveness of glassy fertilisers developed at the Department of Glass and Enamels of the University of Mining and Metallurgy [2] have been verified in pot cultivation and field cultivation [3, 4].

Thermal analysis of bioactive potassium-silicate-phosphate glasses modified by addition of Mg and Ca, acting as ecological fertilisers of controlled release rate of the nutrients for plants is the subject of the present study.

Experimental

Glasses of the K_2O–MgO–CaO–P_2O_5–SiO_2 – microelements (Mn, Cu, B, Mo, Zn, Fe) system were synthesised by the melting (1450°C) a mixture of apatite or phosphorite, serpentinite, potassium carbonate and oxides which introduce the appropriate microelements. The obtained batch was fritted in water and next refined to the required grain size.

The amorphous state of glasses and the structural changes during their heating were followed by XRD and thermal methods. To study the thermal stability of glasses, differential thermal analysis measurements were made with a Perkin-Elmer DTA-7 system operating in heat flux DSC mode. The samples of glass (30 mg) placed in platinum crucibles and dry nitrogen atmosphere were heated at a rate of 10°C min^{-1}.

The biological activity of glasses was estimated on the bases of their solubility in 2 mass% citric acid solution, which is an indicator of assimilativeness of fertiliser components by plants. The solubility of chemical components of glasses was measured using inductively-coupled plasma atomic emission spectrography method (ICP-AES).

Changes occurring on the surface of glasses generated by biological solutions were studied by scanning electron microscopy (SEM) and energy-disperse X-ray (EDS) methods.

Results

Thermal activity of glassy fertilisers

From thermal investigations (Fig. 1) it follows that during heating glasses of the K_2O–MgO–CaO–P_2O_5–SiO_2 – microelements system exhibit typical transformations: glass transition effect and crystallisation. The effect of chemical composition on the thermal properties (such as T_g, T_{cryst} and $\Delta T=T_{cryst}-T_g$) derived from the DSC experiments for glasses are shown in Table 1.

It has been seen that thermal activity of glasses expressed as ability of glasses for crystallisation and measured by values of the thermal stability parameter (ΔT) depends on the nature and the number of components forming the glassy network. From

Table 1 Thermal characteristics of silicate-phosphate glasses modified by addition of MgO and CaO

Nr	Content of macroelements/mass%					T_g/°C	T_{cryst}/°C	$\Delta T = T_{cryst} - T_g$/°C	Crystallizing phases
	P_2O_5	K_2O	CaO	MgO	SiO_2				
1	10.0	10	13	22	37	682	822	140	forsterite, Ca,Mg-phosphates
2	10.0	10	13	28	33	684	842	158	forsterite, Ca,Mg-phosphates
3	10.0	10	13	32	30	690	850	160	forsterite, Ca,Mg-phosphates
4	10.0	10	13	37	25	677	841	164	forsterite
5	10.0	10	13	40	22	692	856	164	forsterite
6	10.0	10	13	22	37	685	838	153	forsterite, Ca-phosphates
7	8.0	10	15	22	37	694	863	169	forsterite, diopside
8	5.0	10	18	22	37	701	919	218	forsterite, monticellite
9	2.0	10	21	22	37	721	971	250	forsterite, monticellite
10	0.3	10	23	22	37	714	922	208	acermanite, monticellite

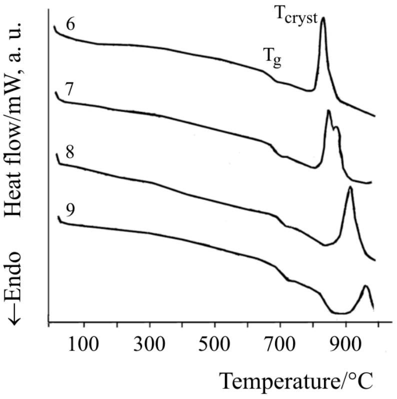

Fig. 1 DSC curves of chosen glasses from the K_2O–MgO–CaO–P_2O_5–SiO_2 system; 6, 7, 8, 9 – numbers of glasses (Table 1)

the earlier investigations [5] it follows that the thermal activity of glasses acting as fertilisers of controlled release rate of nutrients increases with increasing the content of P_2O_5 and K_2O. It is manifested in the decreasing values both of the temperature of the crystallisation and the thermal stability parameter of glasses. A different tendency can be observed in the case of the increasing content of CaO and MgO, at the constant content of K_2O in the structure of glassy fertilisers (Table 1). Generally, introduction of increasing amounts of MgO above 22 mass% and CaO above 13 mass% into the structure of potassium-silicate-phosphate glasses causes an increase in the temperature of crystallisation and an increase in the thermal stability parameter, which indicate smaller tendency of the glass for devitrification.

The thermal activity of these glasses depends however on the mutual proportions between the components forming their structure. In glasses from the system SiO_2–P_2O_5–MgO–CaO–K_2O-microelements, in which the ratios of the contents of the particular components are: $CaO/P_2O_5 \sim 1.3$; $MgO/P_2O_5 < 3.2$; $MgO/SiO_2 < 1.0$ with increasing content of MgO in the structure their thermal stability (ΔT) increases. Crystallization proceeds in two stages and its products are forsterite (Mg_2SiO_4) and calcium-magnesium phosphates (Table 1). In glasses with increased content of magnesium ($MgO/P_2O_5 > 3.2$; $MgO/SiO_2 > 1.0$) there can be observed little differentiated stability of the glassy form and preference for one stage crystallization of forsterite.

Glasses from the system SiO_2–P_2O_5–MgO–CaO–K_2O-microelements, in which the ratios of the contents of the particular components are as follows: $CaO/P_2O_5 < 1.3$, $CaO/SiO_2 < 0.6$, with increasing content of CaO in the structure are characterized by increasing thermal stability, and the products of crystallization taking place at higher temperatures are, besides forsterite, the calcium-magnesium silicates of monticellite ($CaMgSiO_4$) and diopside ($CaMg(SiO_3)_2$) type (Table 1). When the ratio of the content of $CaO/SiO_2 > 0.6$, a distinct increase in the glass ability for crystallization can be observed, and its product is monticellite, which crystallizes already at the temperature 870°C, the subsequent phase being akermanite ($Ca_2MgSi_2O_7$).

Biochemical activity of glassy fertilisers

It has been found [5] that the dissolution of the particular components of glassy fertilisers in biological solutions depends on their chemical composition and increases with increasing the content of P_2O_5 and K_2O in the structure. From the presented study it follows that biochemical activity of these glasses depends, similarly as their thermal activity, on the ratio of the content of the particular elements in the glass structure. Increased content of MgO and CaO in the composition of silicate-phosphate glasses reduces the chemical activity of glasses in which $CaO/P_2O_5>1.3$; $MgO/SiO_2<1.0$ and $CaO/SiO_2<0.6$ (glasses 1, 2, 3, 6, 7, 8, 9 in Fig. 2). A change in the mutual quantitative relations between CaO, MgO, SiO_2, P_2O_5 in the structure of the glasses ($CaO/P_2O_5<1.3$; $MgO/SiO_2>1.0$; $CaO/SiO_2>0.6$) causes a rapid increase of their solubility.

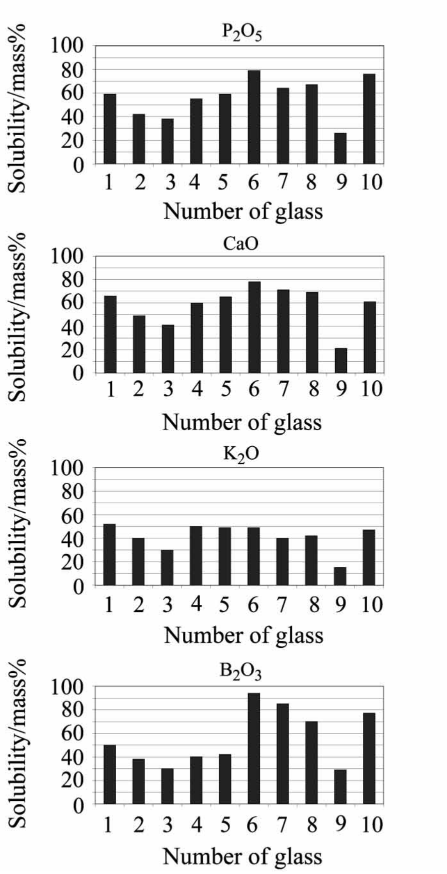

Fig. 2 Solubility of the chemical components of glassy fertilizers in citric acid solution

It follows from the earlier study that biochemical activity of glassy fertilisers is based on their incongruent dissolution [6]. It comprises gradual destruction of internal structure of glasses under the influence of the hydrogen ions present in citric acid solution and washing out of the glass components. The first stage of dissolution on the glass surface a layer of silica is formed, retaining in its composition potassium, magnesium, calcium and phosphorus. The components present in this layer become gradually washed out. Phosphorus and magnesium are the first become removed completely and the near-the-surface layer is made up of hydrated calcium or potassium silicates. Both these elements are washed out gradually, leaving on the glass surface a spongy silica gel. The interaction of glassy fertilisers under biological soil environment is also based on their incongruent dissolution (Figs 3, 4).

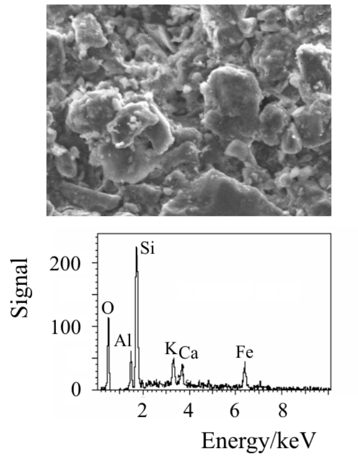

Fig. 3 SEM and EDS data of surface of glassy fertilizers after soil solution etching (6 weeks, 25°C, composition of soil solution: [NO_3] 31.4; [P] 75.4; [K] 259.9; [Mg] 181.8; [Ca] 4862.2 mg dm^{-3})

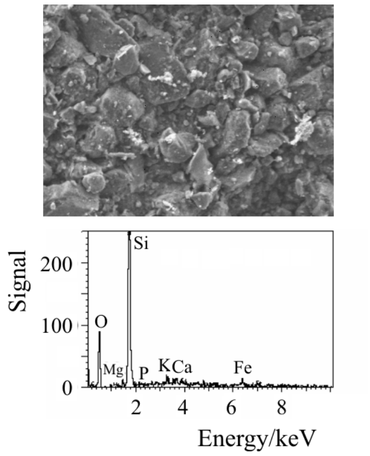

Fig. 4 SEM and EDS data of surface of glassy fertilizers after soil solution etching (6 weeks, 25°C, composition of soil solution: [NO_3] 22.3; [P] 52.3; [K] 98.2; [Mg] 123.0; [Ca] 961.3 mg dm^{-3})

Conclusions

The biochemical activity of silicate-phosphate glasses, modified by an addition of calcium and magnesium, changes with the change of their chemical composition, similarly as their thermal stability and ability to crystallize. The smaller ability of the fertilizing glasses for crystallization the smaller their ability to release the nutrients present the glassy framework. On the other hand, the ability to crystallize, the progress of crystallization and the type of newly formed crystal phases depend on the mutual proportions between the components forming the glass structure.

In many cases crystallization of these glasses has a two-stage character and its progress at the low temperature stage is substantially influenced by crystallochemical factors, i.e. the strength of bonds between oxygen and the cation modifiers and the bond inside the glass framework [7]. In the crystallization process there participates that part of the components of the glass structure whose bonds can be broken most easily. Within the framework of the silicate-phosphate glasses there are present the [SiO_4] and [PO_4] tetrahedra combined by means of the cation modifiers Ca^{2+}, Mg^{2+}, K^+. As the P–O bonds are more covalent in comparison with Si–O bonds, there occurs the tendency for breaking the oxygen bridges in the framework and its depolymerization. As a consequence the first to crystallize are silicates with simple structure. Some of [PO_4] groups released from the broken framework form calcium and magnesium phosphates, which become crystallized next. Change in the content of the particular components in the glass structure, e.g. increase of magnesium content, causes the decreasing of temperature and a one-stage course of their crystallization. This correlates with distinctly increased chemical activity of the glasses as it is an indication of the weakness of the glass framework. It causes simultaneously the increase in the content of K and Ca in the non-recrystallized glass, which distinctly increases its stability. Depending on the type of the glass it can crystallize at higher temperature and then calcium and magnesium phosphates are formed.

Increased content of calcium in the structure of glasses under discussion decreases at first their ability to crystallize. At the same time it reduces their chemical activity in solutions. Subsequent increase of content of calcium leads to crystallization of calcium and magnesium silicates with increasing degree of polymerisation of [SiO_4] tetrahedra.

It is showed that such seemingly different properties as the chemical activity and the thermal activity of glasses are determined by the same parameters which are the strengths bonds of glass network-formers and modifiers as well as their chemical affinity.

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References

1 I. Wacławska, L. Stoch and J. Ostrowska, Ceramics, 57 (1998) 221.
2 L. Stoch, Z. Stoch and I. Wacławska, Silicate glass fertilizer, P-324092

3 J. Ostrowska, A. Lis-Krzyścin and I. Wacławska, Chemistry for Agriculture, 2 (2001) 67.
4 A. Lis-Krzyścin, J. Ostrowska and I. Wacławska, Chemistry for Agriculture, 3 (2002) 313.
5 I. Wacławska and L. Stoch, J. Therm. Anal. Cal., 65 (2001) 141.
6 L. Stoch, I. Wacławska and A. Lis-Krzyścin, Chemistry for Agriculture, 2 (2001) 74.
7 L. Stoch, I. Wacławska and M. Ciecińska, J. Therm. Anal. Cal., 65 (2001) 341.