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Thermal analysis characterization of the reactions of metaphosphate glasses used as binders for oxides [1]

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Abstract

Differential thermal analysis has been used to characterize reactions involved in the consolidation of oxides (NiO, ZnO, Al_2O_3, TiO_2) with metaphosphate glasses. The exothermic phenomena of the reactions with sodium metaphosphate glass are discussed in terms of the electrostatic field strength (z/a^2) and the oxoacidity. The results were then extrapolated to ternary metaphosphate glasses of the Na_2O–CaO–P_2O_5 and Na_2O–MnO–P_2O_5 systems.

INTRODUCTION

In the field of ceramics and glass ceramics, condensed phosphates present interesting properties. Formulated condensed phosphates are used in the preparation of ceramic–metal composites [1], biomaterials [2] and sealing systems [3].

Phosphate binders are widely used in the elaboration of alumina-based refractories. Many studies of the thermal evolution of these binders [4,5] have shown that intermediate metaphosphates are formed and participate in the reactions with alumina. The ability of condensed phosphates to form very reactive amorphous phases can induce a sintering mechanism in the presence of a liquid phase.

The reactivity of metaphosphates is usually discussed in terms of oxoacidity, based on electrochemical measurements in molten media [6,7]. However, this approach does not really explain the phenomena occurring at the grain boundaries. Moreover, phase diagrams cannot predict the temperatures of reactions and the nature of the intermediate compounds.

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TABLE 1

Characteristic temperatures (°C) of metaphosphate glasses: T_g, glass transition temperature; T_d, devitrification temperature; T_m, melting point

Glass formulation	T_g	T_d	Crystalline species after T_d	T_m
$Na_2O-P_2O_5$	280	360	$Na_3P_3O_9$ [10]	625
$0.9Na_2O-2.1CaO-3P_2O_5$	360	485	$NaCa(PO_3)_3$ [9]	740
$1.1Na_2O-1.9MnO-3P_2O_5$	360	470	$NaMn(PO_3)_3$ [11]	800

Very few methods, except for thermal analysis, permit the study of these complex media, to which thermodynamic principles are difficult to apply under non-equilibrium conditions. Therefore we have conducted a thermal analysis study of the reactivity between metaphosphate glasses and several oxides (ZnO, NiO, Al_2O_3, TiO_2). This paper first deals with the reactions of sodium metaphosphate glass with oxides in order to model the more complex behaviour of the ternary metaphosphate glass/oxide systems used in the above-mentioned applications [1–3].

EXPERIMENTAL

The formulations of the metaphosphate glasses used in this work are $Na_2O-P_2O_5$ (sodium metaphosphate, Merck), $0.9Na_2O-2.1CaO-3P_2O_5$ and $1.1Na_2O-1.9MnO-3P_2O_5$.

The precursors of the latter two glasses were prepared by a coacervation method [8]. The glasses were obtained by a thermal treatment according to the experimental procedure described elsewhere [9]. Table 1 lists the characteristics of the glasses used in this work.

Mixtures of the oxides with the metaphosphate glasses were prepared in atomic ratio $M_xO_y/P_2O_5 = 0.5$ (M = Zn, Ni, Al, Ti); α-Al_2O_3 and the anatase form of TiO_2 were used.

Differential thermal analysis was carried out with a heating rate of 5°C min^{-1}. Carbon crucibles and an argon atmosphere were used in all experiments.

The thermograms were recorded up to the melting temperature of the glasses in order to avoid P_2O_5 evaporation or metaphosphate reduction by carbon.

REACTIONS OF SODIUM METAPHOSPHATE GLASS WITH OXIDES

Figure 1 shows the thermograms obtained with mixtures of sodium metaphosphate glass and oxides. The glass transition of $NaPO_3$ is observed at 280°C, followed by an intense exothermic peak due to its devitrification into cyclic sodium trimetaphosphate $Na_3P_3O_9$ [10].

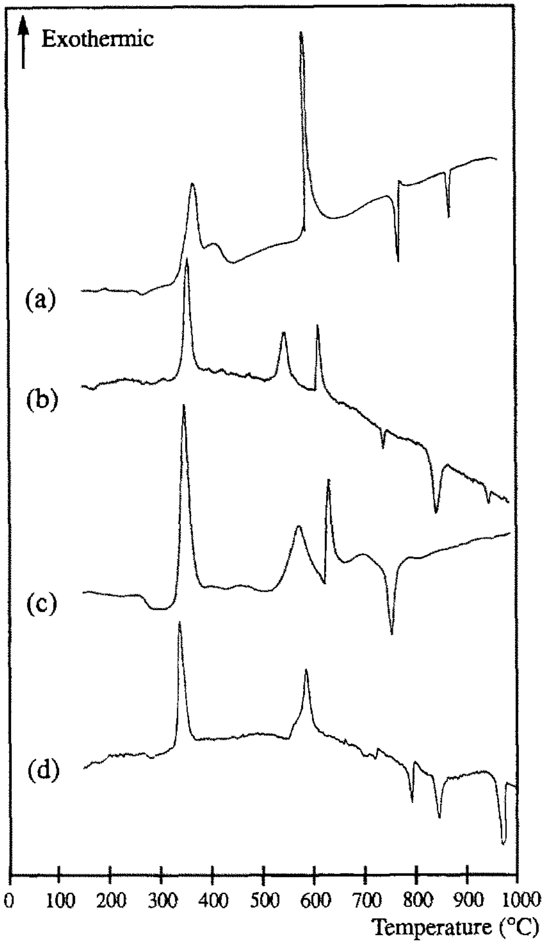

Fig. 1. DTA thermograms of mixtures of $NaPO_3$ glass with ZnO (curve (a)), NiO (curve (b)), Al_2O_3 (curve (c)), TiO_2 (curve (d)).

The exothermic phenomena which occur between 400 and 650°C are not observed on the thermogram of sodium metaphosphate glass alone. Therefore these phenomena can be attributed to reactions of oxides with sodium metaphosphate.

In all the experiments, two exothermic phenomena were detected. The first exothermic peaks are observed at 400, 545, 540 and 550°C for ZnO, NiO, Al_2O_3 and TiO_2 respectively. The temperatures of the second peaks are 600, 620, 625 and 575°C for ZnO, NiO, Al_2O_3 and TiO_2.

The mechanism of the reaction of devitrified sodium metaphosphate glass with the oxides can be considered in a first approximation to proceed via the chemical reaction of two crystalline species. Thus a layer of reaction products grows at the interface. To explain the variation of reaction temperatures observed on the thermograms, three parameters have been

TABLE 2

Values of electrostatic field strength (z/a^2), the Duffy–Ingram factor G_i and the oxoacidity factor pO

Oxide	z/a^2	G_i (Duffy–Ingram)	pO
Na_2O	0.18	0.87	
CaO	0.36	1.01	
MnO	0.41	1.69	
ZnO	0.45	1.82	0.54
NiO	0.49	2.09	0.47
Al_2O_3	0.83	1.69	0.67
TiO_2	0.93	1.69	1.18

considered for the interaction of oxides with metaphosphates: the energetic factor (intensity of electrostatic field and rate of diffusions); the steric and spatial factors (ion arrangement); and the solvent effect (oxoacidity).

When mixtures of powders are heated together, the ions in the crystal lattice must overcome the lattice forces due to the increased energy in order to replace each other in their respective positions. Consequently, the first exothermic phenomena is due to the beginning of such diffusions.

The temperature of reaction at the beginning of the first phenomenon can be correlated to the attractive coulombic forces between cations and anions. This is expressed by the z/a^2 ratio (z is the cation charge and a the M–O bond length). Table 2 gives the z/a^2 ratios of the different oxides used in this study. These values lead to a classification of the reactivity of the oxides with sodium metaphosphate, according to their temperature of reaction: $Na_2O \gg ZnO > NiO > Al_2O_3 > TiO_2$.

The formation of amorphous species at the grain boundaries lowers the rates of diffusion; therefore the second exothermic phenomenon occurs close to the melting point of the $NaPO_3$ glass. The presence of liquid phase induces oxoacidity reactions of the oxides with molten sodium metaphosphate. The oxoacidity of the oxides calculated according to the Duffy–Ingram theory, which considers the polarizability of the ions [12], is reported in Table 2. The oxoacidity factor, pO, is calculated from the relation $pO = \Sigma z_i n_i / 2G_i$, where z_i is the anion charge, n_i the ionic fraction of the $NaPO_3$/oxide mixture and G_i the Duffy–Ingram factor.

We can propose the following classification, in decreasing basicity: $NiO > ZnO > Al_2O_2 \gg TiO_2$.

Therefore, the electrostatic field strength influences the description of the solid state reactions between $Na_3P_3O_9$ and the oxides (first exothermic peak), whereas the oxoacidity factor is only influential at the melting of the glass, or at the melting of a eutectic composition resulting from the first reaction (second exothermic peak).

This thermal analysis approach permits us to characterize a mechanism in several steps with formation of intermediate species. The nature of the

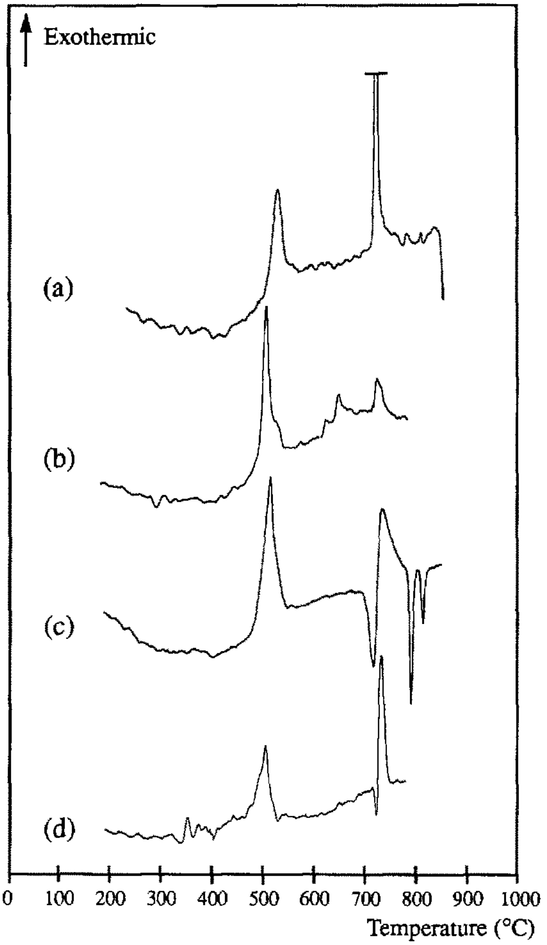

Fig. 2. DTA thermograms of mixtures of $0.9Na_2O$–$2.1CaO$–$3P_2O_5$ glass with NiO (curve (a)), ZnO (curve (b)), Al_2O_3 (curve (c)), TiO_2 (curve (d)).

final product of the reaction between metaphosphates and oxides will depend on the diffusion rates after the formation of intermediate species during the first reaction. A thermal treatment at 650°C for 60 h yields double sodium metal pyrophosphates as the major product for mixtures of $NaPO_3$ with NiO and ZnO, whereas double sodium metal orthophosphates are formed with Al_2O_3 and TiO_2 [13].

REACTIONS OF TERNARY METAPHOSPHATE GLASSES WITH OXIDES

The thermograms of the mixtures of $0.9Na_2O$–$2.1CaO$–$3P_2O_5$ glass with the oxides are shown in Fig. 2. The characteristic features of these thermograms are exothermic phenomena at 630 and 710°C for the mixtures with ZnO and NiO respectively, a second exothermic peak being present at

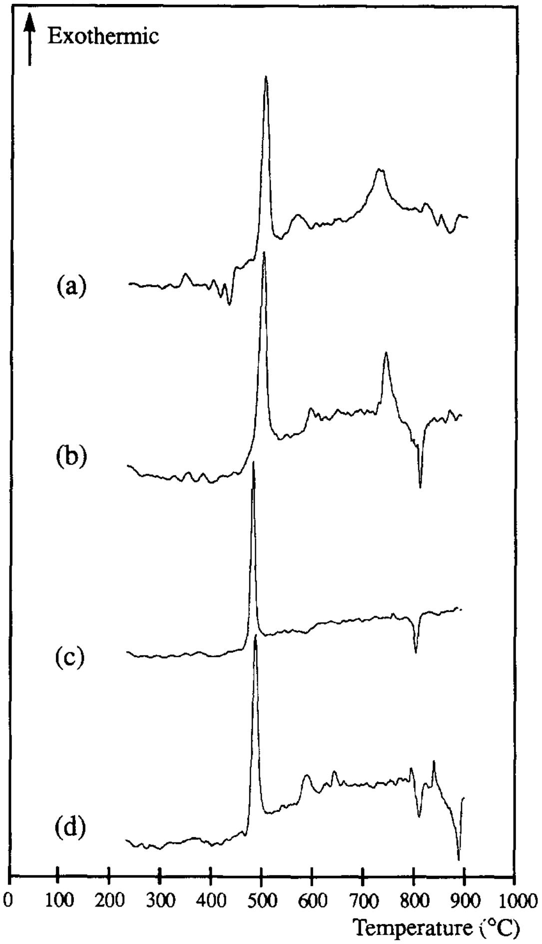

Fig. 3. DTA thermograms of mixtures of $1.1Na_2O-1.9MnO-3P_2O_5$ glass with NiO (curve (a)), ZnO (curve (b)), Al_2O_3 (curve (c)), TiO_2 (curve (d)).

approx. 725°C with ZnO. Thermograms of the mixtures with Al_2O_3 and TiO_2 show an intense exothermic phenomenon at 740 and 725°C respectively, preceded by an endothermic phenomenon at 710°C, caused by the melting of the glass.

Figure 3 shows the thermograms obtained with mixtures of $1.1Na_2O-1.9MnO-3P_2O_5$ glass with the oxides. Weak exothermic phenomena are detected between 540 and 605°C. They are due to the reaction of oxides with sodium metaphosphate. The presence of a small amount of sodium metaphosphate in the ternary glass results from its preparation by a coacervation method [11]. Strong exothermic peaks are observed at 660 and 720°C for the mixtures with ZnO and NiO. In the cases of mixtures with Al_2O_3 and TiO_2, only endothermic peaks are detected at the melting of the glass (800°C). Nevertheless, the weak intensity of these peaks may be due to a superposition of endothermic and exothermic phenomena, as was observed on the thermograms of the mixtures of Na_2O–CaO–P_2O_5 glass with Al_2O_3 and TiO_2.

As a general feature, the exothermic phenomena observed on all the thermograms of the mixtures of $0.9Na_2O$–2.1CaO–$3P_2O_5$ and $1.1Na_2O$–1.9MnO–$3P_2O_5$ glasses with the oxides occur either between the crystallization and the melting of the glass (reactions with ZnO and NiO) or after the melting point of the glass (reactions with Al_2O_3 and TiO_2).

These observations can be interpreted, as above with sodium metaphosphate, by considering the electrostatic field strength z/a^2. ZnO and NiO have small z/a^2 values compared with Al_2O_3 and TiO_2 (see Table 2). Therefore ZnO and NiO can react at a lower temperature than Al_2O_3 and TiO_2 because of their easier diffusion in the metaphosphate network.

The electrostatic field is reinforced in the $0.9Na_2O$–2.1CaO–$3P_2O_5$ and $1.1Na_2O$–1.9MnO–$3P_2O_5$ glasses, compared with $NaPO_3$, owing to the presence of calcium or manganese cations. Thus solid state reactions of oxides with the glass occur less easily than with sodium metaphosphate. This explains the presence of only one exothermic reaction peak on the thermograms of the mixtures of oxides with ternary glasses.

CONCLUSION

Even if grain boundary reactions are only one step of the sintering mechanism in the presence of a liquid phase, differential thermal analysis provides a global approach to these local reactions. A previous study of these non-equilibrium reactions in the sodium metaphosphate/oxide systems allowed us to determine some parameters influencing these reactions. The results were then extrapolated to the more complex ternary glasses.

Two mechanisms are required to explain metaphosphate glass/oxide reactions: solid state reactions are controlled by the electrostatic field strength of the cations and their diffusion rates; however, the fusion of eutectic compounds formed in earlier reactions involves oxoacidity reactions between metaphosphates and oxides. Thus the pO calculations corroborate the temperatures of reactions measured by differential thermal analysis.

In addition, the preferential formation of orthophosphates or pyrophosphates complicate the reaction mechanisms. The control of these intermediate compounds will influence the final sintering process.

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