

## INFLUENCE OF TEMPERATURE AND CHEMICAL COMPOSITION ON PHASE TRANSFORMATIONS OF SELECTED OXIDE MELTS

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The paper deals with structural changes of solid phase of selected oxide systems during their transition into liquid state. Analyses concerned poly-component systems forming basis of casting powders for CCM mould. Industrially used oxide system with prevailing contents of CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> components and with numerous accompanying admixtures was tested. Investigation was focused on temperatures, during which individual phases disappear and precipitate, as well as on influence of CaO content on phase composition at selected temperatures. The experiments were realised with use of original methodology consisting of shock cooling of the tested melt in liquid nitrogen. Thus obtained samples were further investigated by X-ray diffraction phase analyses at ambient temperatures. The obtained results provide additional data on physical-chemical properties of oxide systems, such as surface tension, viscosity, sintering intervals, etc., which can be used in technological practice for appropriate lubrication effect of casting powders in the mould.

*Key words:* slag, phase transformation, oxide melts

### INTRODUCTION

Majority of the commonly accepted concepts of inorganic melts was based on simplified concepts that assumed homogeneous melt, in which the individual physico-chemical properties (namely viscosity, surface and interfacial properties) changed continuously with changes of temperature and chemical composition [1-5]. Similar concepts are used also in majority of mathematical models simulating the mentioned behaviour [6-8].

More complex oxide systems can, under certain conditions (temperature, chemical composition), change from homogeneous to heterogeneous state with consequent changes of their phase composition in the heterogeneous state. Particularly the wide temperature area of formation of the melt of oxide systems, forming the basis for casting powders intended for a CCM mould, is problematic, due to their considerable complexity and heterogeneity. These processes are usually accompanied by the dissolution of the initial components of the poly-component mixture accompanied by a series of chemical reactions.

The issues of precipitation of nano-particles in ternary systems of the type MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> were investigated namely by Frans [9], phase changes in ternary glass systems were studied by Milanova [10], who in his work published designs of 3-D ternary phase diagrams. These authors have used experimental approach at the research of structural changes of materials. Different method for study of mineralogical composition is the method “ab-initio” based on mathematical model-

ling of structures, used for example by the team of authors Kana et al [11].

This work focuses exclusively on the experimental study of selected oxide systems because of their considerable complexity and poly-component nature that precludes effective mathematical modelling. Phase transformations have been studied in terms of changes in temperature of the melt and its chemical composition.

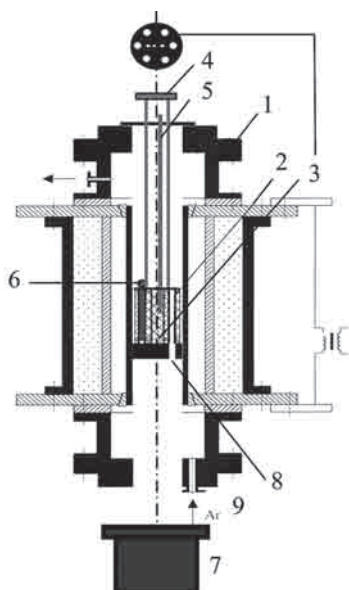
Knowledge of phase transformations serves also as an additional input for the study of anomalies of temperature dependences of viscosities, surface and interfacial properties of oxide systems, and it thus contributes to the overall understanding of the structural regularities of oxide melts.

### EXPERIMENT

At our working site we have developed our own methodology for study of phase transformations. In this context, the equipment (Fig. 1) was designed and manufactured, which enables very rapid cooling of the investigated system at certain stage of melting. The sample then preserves even at normal temperature the same phase composition as in the molten state. It is then possible to apply the X-ray diffraction phase spectral analysis, on the basis of which it is possible to obtain a notion of the phase composition of the melt, already at ambient temperature. In this way, the inaccuracies caused by phase shifts at X-ray diffraction analysis at high temperature are eliminated.

The basic structural unit of the equipment is the resistive Tamman's furnace, in the working space of which the swivel system is located with graphite crucibles containing the investigated melt. It is basically a turret sys-

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**Figure 1** Diagram of equipment designated for shock cooling of the melt

tem, the rotation of which makes the crucible with the melt fall into liquid nitrogen placed under the working space of the furnace, which causes almost immediate freezing of the melt and thus fixation of phases corresponding to the temperature before the fall of the sample. The temperature during the experiment was measured by thermocouple of the type B (Pt-Rh) and the working space of the furnace was filled with argon. The rate of temperature rise was chosen to be 5 °C / min.

The sample obtained by shock cooling was then mechanically homogenised and submitted to a X-ray diffraction phase analysis performed already at ambient temperature on refurbished, fully automated diffractometer URD-6 (Rich. Seifert-FPM, SRN) under the following conditions:

Radiation CoK $\alpha$ /Ni filter, voltage 40kV, current 35 mA, step mode with a step of 0,05° 2 $\theta$  with time of the step of 3s and with digital processing of the resulting data. A proprietary program RayfleX (RayfleX ScanX and RayfleX Analyze, version 2,289) was used both for measurement and for evaluation.

For qualitative assessment the database of diffraction data PDF-2, version 2001 (International Centre for Diffraction Data, Pennsylvania, USA) was furthermore used.

For semi-quantitative analysis the program RayfleX Autoquan version 2,6 was used.

For the presentation of the obtained results a characteristic oxide system was chosen serving as the basis for casting powders, hereinafter referred to for simplification as the system A. Its dominant components are Al<sub>2</sub>O<sub>3</sub>, CaO and SiO<sub>2</sub>. It contains also a number of accompanying admixtures and has relatively high carbon content (7,6 wt.% C). The exact chemical composition was obtained by the X-ray fluorescence spectrometry (Table 1). Carbon was before the experiment calcined at 850 °C for 12 h. Removal of carbon was necessary in

order ensure the non-wettability with the graphite parts of the equipment, as well as running of parallel experiments performed on this system. These, together with the knowledge of phase transformations provide more comprehensive information on the physico-chemical properties of oxide melts [2, 13-15]

**Table 1** Chemical composition of investigated system

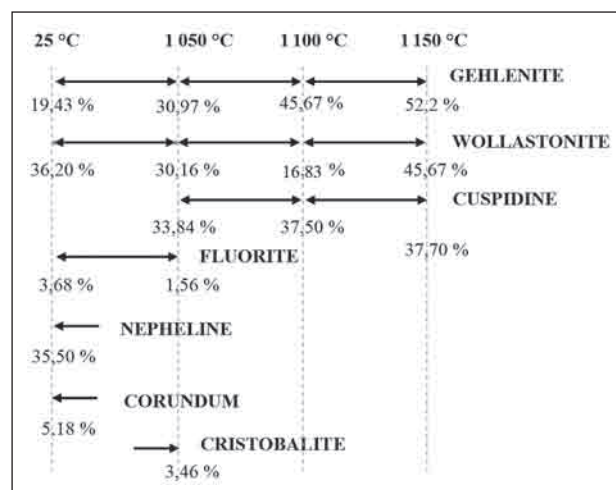
component	wt.%	component	wt.%
SiO <sub>2</sub>	36,0	MnO <sub>2</sub>	0,1
CaO	32,0	Na <sub>2</sub> O	4,9
MgO	1,3	K <sub>2</sub> O	0,4
Al <sub>2</sub> O <sub>3</sub>	12,1	P <sub>2</sub> O <sub>5</sub>	0,1
TiO <sub>2</sub>	0,5	F-	3,9
Fe <sub>2</sub> O <sub>3</sub>	0,64	C	7,6

Influence of CaO contents on phase transformations was investigated with use of additions of CaO of 3 wt. % and 6 wt. %.

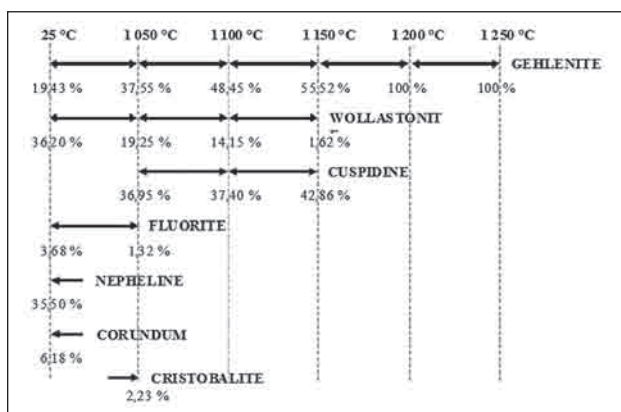
## RESULTS

The investigated sample was at the beginning of the experiment tested from the viewpoint of its phase composition at ambient temperature (25 °C). This was followed by an analysis of the melt at 1 050 °C, which represents the softening point of the oxide system, and then always at an increase of temperature by 50 °C up to 1 600 °C. At 1 300 °C all the systems were already amorphous and the outputs of the phase analyses therefore do not contain the temperatures above 1 250°C. The results of the analyses are presented in Figures 2, 3 and 4. The system was at higher temperatures already completely amorphous.

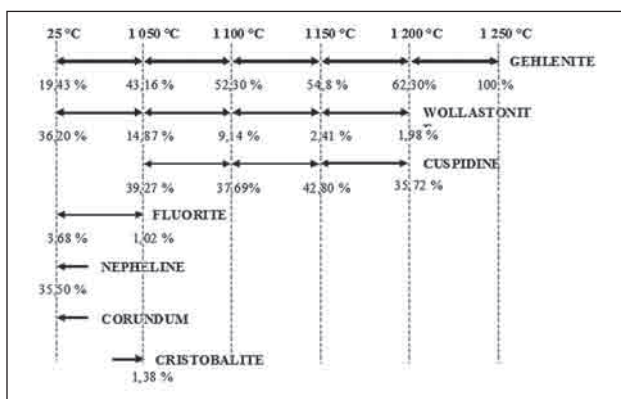
For clarity, the individual outputs are presented in the form of lines, which present the identified mineralogical phases at given temperatures, or at temperature intervals, in which they were detected (Figures 2-4). In this way it is possible to make an easy comparison of



**Figure 2** Dependence of phase composition on temperature of the initial system A



**Figure 3** Dependence of phase composition on temperature of the system A with addition of 3 wt.% of CaO



**Figure 4** Dependence of phase composition on temperature of the system A with addition of 6 wt.% of CaO

the presence of individual phases at different temperatures and with different chemical composition. The percentage proportion of the phases is related to the ratio to other phases and it does not include the amorphous share. Its representation was not analysed due to the small volume of the samples obtained and the possibility of subsequent error occurred at additions of internal standards.

## DISCUSSION AND CONCLUSIONS

The presented experiments confirmed the gradual extinction of individual phases in the initial system A in the temperature range from 1 100 °C to 1 300 °C, while at the temperature of 1 200 °C the sample was already completely amorphous and it preserves its character up to the temperature of 1 600 °C, when the experiment was terminated.

It is thus possible to reflect the area of melt formation and transformation from the solid state via plastic area to the liquid phase, and to define thus more precisely its lubrication function in the mould at various temperatures. Wollastonite, gehlenite and cuspidine, which were detected in the initial state of the sample were the longest present phases of all the phases, as they were detected during temperature loading even at the temperature of 1 150 °C. At the same time, during the

temperature loading individual phases not only disappear (fluorite and nepheline), but also new phase precipitate. This concerns the phases of cuspidine at the temperature of 1 050 °C and cristobalite, which afterwards disappear again.

Again, similarly as in the initial system, Wollastonite was detected in both systems with an increased contents of CaO by 3 and 6 wt.% in the broad temperature interval. Gehlenite behaved differently, as it disappeared only at higher temperatures. Similarly Nepheline and Corundum disappear again at the temperature of 1 050 °C with simultaneous precipitation of cristobalite in all the systems of the concentration series. The increasing content of CaO in the system A causes generally a shift of extinction of some phases to higher temperatures. This concerns namely the phases Wollastonite, Gehlenite and Cuspidine. The lower temperature limit of extinction and precipitation of individual phases remains, however, preserved and the region of transition of the system from solidus to liquidus is thus expanded.

From the previous experiments it is therefore possible to make the following conclusions:

- The original method of shock cooling of melts allowing investigation of their phase transformations at selected temperatures was successfully tested.
- In this way, the selected oxide system was investigated, which forms a basis for casting powders. Especially the temperature ranges of precipitations and extinction of individual phases were identified.
- A concentration series was formed by successive additions of CaO to the initial system A. In this way the influence of chemical composition on the changes of phase transformations was tested. It was found that increase of the of CaO content led to an enlargement of the area of softening of casting powders and to shifting of extinction of some phases shift to higher temperatures.

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**Note:** The responsible translator for English language is B. Škandera, Czech Republic