INVESTIGATION OF INFLUENCE OF STRUCTURAL CHANGES ON SURFACE PROPERTIES OF MELTS

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Abstract
Simplified concepts of inorganic melts and particularly majority of mathematical models generating selected physical-chemical properties of slag melts assume homogeneity of investigated melt.

Real systems may under certain conditions (temperature, chemical composition) pass from homogeneous to heterogeneous state with subsequent changes of phase composition in heterogeneous state. These changes may be in great extent projected into their numerous physical-chemical properties, among others for example into temperature dependencies of surface stress. Wide temperature interval of melt formation, which consists of melting and dissolution of initial components of heterogeneous mixture accompanied by many chemical reactions, remains especially problematic.

The presented work deals with investigation of surface properties of molten oxidic systems in connection with changes of internal structure of the melt and running chemical reactions. Individual experiments were realised on original equipment enabling shock cooling of investigated systems. The samples obtained in this manner with preserved internal structure, corresponding to the relevant temperature, were subjected to X-ray diffraction phase analyses already under normal conditions.

The system forming the basis of casting powders was chosen for the research itself. It was a quasi-ternary system with dominant components CaO – Al₂O₃ – SiO₂. This inorganic oxidic system contains moreover numerous accompanying admixtures. Prior to individual experiments it was annealed in order to remove carbon and moisture. After shock cooling of the system and after completion of experiments individual fixed phases were independent on modernised, fully automated diffractometer URD-6 (Rich. Seifert-FPM, Germany).

Keywords: slag, phase transformation, oxidic melts

1. INTRODUCTION

Usually mentioned structural concepts of inorganic melts assume their phase homogeneity. Models used for calculations of surface properties of slag systems also often fail due to considerable heterogeneity of real melt.

Real systems may under certain conditions (temperature, chemical composition) pass from homogeneous to heterogeneous state with subsequent changes of phase composition in heterogeneous state. These changes may in great extent be projected into their numerous physical-chemical properties, among others for example into temperature dependencies of surface tension [1-3].

Wide temperature interval of melt formation, which consists of melting and dissolution of initial components of heterogeneous mixture accompanied by many chemical reactions, remains especially problematic. For this reason the presented work deals below with experimental investigation and analysis of surface properties of slag systems as it wants to approach the mutual relationship of investigated parameters with chemical and structural changes on the basis of phases analyses [4, 5]. Its aim is also to find relations between the obtained outputs from phase analyses and surface properties of the melts.
1.1. Analysis of problems of phase thermodynamics

Diversion from an ideal assumption, or real existence of heterogeneous system, requires approximation of regularities of transition of concrete homogeneous system into heterogeneous system and, of regularities of transition of crystalline phase at solidification. Analogically it is possible to to assess the course of melting of these substances.

From the viewpoint of thermodynamics these processes may be characterised by changes of Gibbs' energy $\Delta G$, while stable equilibrium of the system corresponds to its smallest value and equilibrium of two phases is conditioned by equality of their molar Gibbs' energies. The following thermodynamic equation must be valid for phase transformations:

$$\Delta G = \Delta G_v + E_s + E_d$$

where $\Delta G_v$ represents change of chemical Gibbs' energy, $E_d$ deformation energy and $E_s$ surface energy. Assuming an ideal arrangement of the system, it means without structural anomalies, the value of $\Delta G$ is equal only to the change of chemical Gibbs's energy. In case that melt contain an area with different structure (such as grain boundaries or lattice imperfections) energy of the given phase, defined by surface and deformation energy, increases. Due to the fact that this process is in a given direction thermo-dynamically feasible subject to condition $\Delta G < 0$ and to the fact that values of deformation and surface energy are positive, phase transformations reduce the effect of chemical Gibbs’ energy.

Each phase represents a homogeneous system. Two different phases therefore must differ by some of their properties (density, thermal capacity, magnetisation, etc.), or two different phase of the same substance must differ at least by some derivation of chemical potential. Single-component system may be from the viewpoint of phase transformations classified on the basis of discontinuities of derivations of the Gibbs’ potential [4-6].

2. EXPERIMENT

2.1. Experimental methods

Research of phase transformations during melting was performed by so called shock cooling. Phase displacements occur at phase measurements at high temperatures with use of PAAR cells. These displacements must be corrected and measurement is thus always influenced by certain degree of inaccuracy.

This problem was dealt with by use of device, which was designed and constructed at our working site (Fig. 1), which enables very rapid cooling of investigated system at certain phase of melting. The sample thus preserves even at normal temperature the same phase composition as in its molten state.

The device consist of vertical resistance Tamman’s furnace, into working space of which a graphite cylinder is placed onto support plate. Graphite crucibles containing investigated samples are placed in the holes of this cylinder. The arms designated for cylinder rotation around its axis are anchored in its body, as well as thermocouple of the type B (Pt-PtRh). Cylinder support plate with a hole enables at certain angle of rotation fall of the crucible containing melt into liquid nitrogen. The working space of the Tamman’s furnace is during heating closed and it is filled with argon.
A rate of temperature increase of 5°C/min was chosen. At the chosen temperature the bottom part of furnace was opened and by turning the "revolver system" the crucible was lowered into a bath of liquid nitrogen, where internal structure was almost immediately fixed. This was followed by mechanical homogenisation of the sample and by X-ray diffraction phase analysis – already at normal temperature on modernised, fully automated diffractometer URD-6 (Rich. Seifert-FPM, SRN) under the following conditions:

Radiation CoKα/Ni filter, voltage 40kV, current 35 mA, single-step mode with a step of 0.05° 2Θ with a time per step of 3s and with digital processing of resulting data. Proprietary program RayleX (RayleX ScanX and RayleX Analyze, version 2.289) was used both for measurement and for evaluation.

For the purposes of quantification of amorphous fraction a weighted quantity of internal standard (~5 wt.% ZnO) was added into the sample. The samples was together with the standard homogenised by micro-grinding.

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

For semi-quantitative analysis the program RayleX Autoquan version 2.6 was used. It is in fact commercial, adapted version of the program BGMN (e.g. Taut, Kleeberg, Bergmann, 1998). Designation "Autoquan" relates to the program interface BGMN for work in the environment of Windows NT 4.

2.2. Experimental material

Numerous systems were subjected to analyses at our working site during our long-term research. For presentation we chose for transparency the system, which serves as a basis for casting powders for continuous casting machines (CCM) – marked below as “system A”. It is quasi-ternary system composed mostly of the components CaO, Al₂O₃ and SiO₂. It contains moreover many accompanying admixtures that are present in tenths and hundredths of percent. The exact chemical composition was obtained by X-ray fluorescent spectrometry of this system.
Tab. 1.: Chemical composition of investigated system A

<table>
<thead>
<tr>
<th>component</th>
<th>wt.%</th>
<th>component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.1</td>
<td>Na₂O</td>
<td>5.1</td>
</tr>
<tr>
<td>CaO</td>
<td>29</td>
<td>K₂O</td>
<td>0.4</td>
</tr>
<tr>
<td>MgO</td>
<td>1.7</td>
<td>P₂O₅</td>
<td>0.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.5</td>
<td>F⁻</td>
<td>4.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5</td>
<td>C_{tot}</td>
<td>7.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.64</td>
<td>C_{vol}</td>
<td>6</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.1</td>
<td>CO₂</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Initial X-ray diffraction phase analysis of the system A was performed in two steps. The system A represents predominantly oxidic composition designated for continuous casting of steel, ti contains therefore comparatively large amount of carbon (7.2 wt.% C). At this carbon content, however, it is impossible to guarantee water repellency of graphite support plate at subsequent determination of surface tension [4, 5], and that’s why carbon was removed by annealing at the temperature of 850°C for 12 hours. This temperature represents approximately the limiting boundary, at which already the first phase transformations occur. For this reason the original carbon system was subjected to phase analyses as first, and it was then followed by the sample after annealing (marked here below as “system B”), prepared for further investigation of surface properties.

3. RESULTS

Results of analysis of the initial system A and of the annealed system are given in Figures 1 and 2.

![Fig. 1: Initial X-ray–diffraction phase analysis of the system A containing carbon](image1)

![Fig. 2: X-ray–diffraction phase analysis of the system B with carbon removed by annealing](image2)

Phase composition of the original system B during thermal load is presented in Fig. 3 at 1100°C, and in Fig. 4 at the temperature of 1200°C. At the temperature of 1300°C all the phases were already extinct and the sample was then amorphous. The measurement was terminated at the temperature of 1600°C.
Fig. 3: Phase composition of the system B at the temperature of 1100°C

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2AS Gehlenite</td>
<td>23.50 ± 3.60 %</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.00 ± 0.00 %</td>
</tr>
<tr>
<td>Spinel</td>
<td>0.97 ± 1.17 %</td>
</tr>
<tr>
<td>Wollastonite 2M</td>
<td>34.70 ± 3.60 %</td>
</tr>
<tr>
<td>Cuspidin</td>
<td>40.80 ± 3.90 %</td>
</tr>
</tbody>
</table>

Fig. 4: Phase composition of the original system B at the temperature of 1200°C.

4. DISCUSSION AND CONCLUSIONS

The presented work introduces possibilities of phase composition of oxidic systems in molten state. In this connection an original device was developed at our working site, which thanks to by rapid freezing makes it possible to preserve internal structures of investigated materials, which are afterwards studied.

X-ray analyses of individual systems (composition – see tab. 1) were realised in a modernised manner with use of shock cooling. Phase changes in the investigated systems were confirmed already at annealing at the temperature of 850°C. The system shows after annealing overall deficiency of phases, only the phases of corundum, fluorite and wollastonite remain preserved. At the same time new phases of gehlenite and nepheline precipitate (Figs. 1, 2). It is therefore obvious that even such comparatively low temperatures below the liquidus phase have a decisive significance for its other properties. After melting of the system above the temperature of 1100°C some phases remain preserved and their further diminution occurs at the temperature of 1200°C, when only the phase of wollastonite is identified (Figs. 3, 4). Phase composition at the temperature of 1300°C is not presented, because the system was already completely amorphous.

Very interesting is also comparison of these findings with development of temperature dependence of surface tension of the system B (Fig. 5)

Fig. 5: Temperature dependence of surface tension of the system B.

The data presented in Fig. 5 were determined experimentally by sessile drop method, the principles of which were published already some time ago [8]. Area of the diagram is divided into two zones. In the zone I
progressive extinction (but simultaneously also precipitation) of individual phases occurs. This zone is characterised by an increase of the values of surface tension. Behaviour of the system in these temperature intervals is very difficult to interpret from the viewpoint of physics and chemistry. For this reason we have resigned in the relevant zones to mathematical modelling of surface properties of similar systems in previous publications [9]. Around the temperature of 1270°C the system is already amorphous (zone II) and surface tensions drops in almost linear manner with an increasing temperature, or with an increasing kinetic energy of particles.

It is therefore possible to summarise the obtained results in the following manner:

- method of research of phase properties of melts by shock cooling was successfully mastered
- changes of phase compositions were proven already below the liquidus temperatures
- a relationship between surface properties and its phase composition was established.

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