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Ultraviolet/visible reflection spectroscopy of molten and glassy silicates

$(CaO-Fe_2O_3-SiO_2)$

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1 Introduction

Molten alkaline earth silicates and phosphates are the basis of important metallurgy slag systems. Silicates are used in the glass industry. In the metallurgic extraction technique, slags have a key position for the production of pure steels. They absorb contaminations as sulphur and phosphorus and they transfer these components from the liquid metal phase to the liquid slag phase. An important point is the oxidation potential of a slag. It can be described via the content of Fe^{3+} . In the Fe-metallurgy, the oxygen transport in the slags proceeds in so-called refining process. Caused by the reaction of Fe^{3+} to Fe^{2+} , for example phosphorus (in the liquid Fe) is oxidised to phosphates (in the liquid slag) or silicium (in the liquid Fe) is oxidised to silicates (in the liquid slag) at the boundary layer liquid iron/slag phase.

Many researchers try to apply spectroscopic methods in order to describe properties of slags and glasses via a molecule chemical concept. The basicity theory developed by Duffy and Ingram [1] is based on donator properties of the bounded O^{2-} . This concept is often used for describing properties of slags (basicity, component activity,

redox properties, viscosity). The s-p-transition (nephelauxetic effect) of main group cations Pb^{2+} , Bi^{3+} or Tl^+ in glasses is measured optical-spectroscopically at room temperature. It has not been possible to establish completely and sufficiently exactly the connection between the optical basicity, slag properties and the content of oxide ions as electron donators in different glassily solidified borates, phosphates and silicates. The deviations are probably caused by a change of the chemical bond with a variable MeO_x -content that is not reflected by the simple correlation mentioned at the beginning.

However, extensive investigations have been accomplished and theoretical efforts have been taken in order to apply the concept of optical basicity to metallurgy slag systems and to extend it partially. The reason is that, caused by its simplicity, the concept seemed to be strongly impressive at first view. Mills [2,16], Young [3] applied it to numerous slag systems (oxide component activities, sulphur capacities, oxidation degree, viscosity etc.). Moretti, Ottonello et al. [4,5] extended the concept of optical basicity and combined it with thermochemical models (polymerization equilibria and redox properties) for liquid silicates. The result have been optical basicity parameters that describe well the tendencies but that are partially speculative and contradictory. The reasons for this have been rudimentarily described in [1]. Essentially, the O^{2-} electron donator properties depend on the chemical bond proportions (coordination number, bond distance, bond polarity) of the bound oxygen ion with respect to the cation. The optical basicity that is obtained via the correlation with the electronegativity can take into account this fact only partially. In glasses, the coordination behaviour of the O²⁻-ion at room temperature is well-known and consequently, it is possible to use this value. There, the coordination number is an important parameter for describing the chemical bond. In liquid systems, thermal dissociation equilibriums of coordinative bonds (complexes) dominate [6,7]. Caused by the strong thermal fluctuations, the bond distances become fuzzy and the measurements provide only average coordination numbers [8-14]. This fuzziness is expressed by the square root of the average bond distance (± 10 pm up to ± 20 pm for CaO, MgO, FeO or Na₂O in liquid silicates). The bond dissociation energy of complexes is inversely proportional to the bonding distance $r^5(Me^{n+}/O^{2-})$. A destroyed bonding Me^{n+}/O^{2-} is a consequence of this fact. VIS-spectroscopical measurements of the complex dissociation of the tetrahedral $Co^{2+}(O^{2-})_4$ -complexes in glassy and liquid silicates have been investigated. The dissociation equilibrium in silicates can be described as follows [24]:

 $\text{Co}^{2+}(\text{O}^{2-})_4$ (tetrahedral symmetry) $\leftrightarrow \text{Co}^{2+} \cdots \text{n O}^{2-}$ (diffuse distribution) (1)

 $Co^{2+} \cdots n O^{2-}$ means, that Co^{2+} is solved by statistically distributed oxide ions of the Si-O-network (liquid state). The average coordination number CN and the average bond distances are important values for describing molecular structures of liquid

slags. In order to obtain such a description, Waseda et al. [8-11] have carried out X-ray diffraction investigations at liquid silicates. The coordination numbers CN_{i-Q} are not constant. They differ strongly depending on the composition of the silicates. The situation is different in glassy and crystalline slags. In that case, the coordination numbers are rather constant and they are integers. Therefore, with an increase of the Na₂O content (N: mole fraction), the coordination number CN of the Na⁺-ion might strongly increase from 3.6 to 6.3 in liquid silicates. Such a variability is unknown in the chemistry of glassy and crystalline slags. The situation for CaO, MgO and FeO is similar. For Ca-O groups, the coordination number is $CN_{Ca-O}=6$ in the glassy state. In numerous solid silicates, a coordination number up to $CN_{Ca-O}=8$ has been determined for the Ca²⁺-ion. Whereas in liquid silicates (1600 $^{\circ}$ C), the coordination numbers are lower in the average. With an increase of N_{CaO} from $CN_{Ca-O}=5.4$ $(N_{CaO}=0.41)$ to $CN_{CaO}=6.6$ ($N_{CaO}=0.50$), they shift rather linearly [8-10]. A similar dependency has been detected for the coordination number of the Mg²⁺-ion in liquid MgO-SiO₂-slags [8-10] in the concentration interval N_{MaO} between 0.44 and 0.56: CN_{Mq-O} =4.3 and CN_{Mq-O} =5.1. The reason is the successive conversion of the polymeric Si-O network. For low Me_xO [Me=Li, Na, Mg, Ca, Fe(II)] molar fractions the coordination polyhedron is mainly built from ligands of so-called ..bridging oxyen" \equiv Si-O-Si \equiv (=BO). A smaller part of the ligands has the type "nonbridging oxygen" \equiv Si-O⁻ (=NBO). The relatively rigid Si-O-network does not allow the composition of a bigger coordination polyhedron (steric disability). Only at higher molar contents of Na₂O, MgO, FeO or CaO, flexible NBOs are built. This perspective has been validated in simulation calculations on molecule dynamics (MD) concerning this subject [19]. The Si-O-network is broken under a formation of "channels". In these cavity channels, the cations are situated with the function of network-modifier that are coordinated via NBOs and BOs. A segregation of the cations takes place. The network-modifier are distributed inside the so-called "iceberg". They stabilise the "iceberg structure". These ideas about the structure are supported by MB simulation calculations. The result of such calculations and the corresponding ideas about the structure are contained in the works [18,19].

In a work of Wagner [15], different ways for recording the basicity of liquid slags are described. The fundamental idea is that the electron donator property of the bound O^{2-} -ion is not the essential point. Whereas the tendency to emit an O^{2-} -ion in a reaction is basic for the oxide activities and the basicities. Principally, it is not possible to determine the thermodynamic O^{2-} -activity. But it can be defined indirectly via chemical reaction equilibriums of the bound O^{2-} -ion as reacting species. For example the chromate capacity:

$$2 \operatorname{Cr}^{3+} + {}^{3}/_{2} \operatorname{O}_{2}(g) + 5 \operatorname{O}^{2-} \quad \leftrightarrow 2 \operatorname{Cr}\operatorname{O}_{4}^{2-} . (2)$$

It turned out that the CrO_4^{2-} -anion is stable only at room temperature. In liquid slags, a chromate/ dichromate equilibrium of the following kind

$$2 \operatorname{CrO}_4^{2-} + \equiv \operatorname{Si-O-Si} \equiv \quad \leftrightarrow \operatorname{Cr}_2 \operatorname{O}_7^{2-} + 2 \equiv \operatorname{Si-O^-} . (3)$$

Even during quenching with a cooling speed above 200 °C/s down to room temperature, CrO_4^{2-} degenerates, whilst, in liquid slags, the $\text{Cr}_2\text{O}_7^{2-}$ -anion dominates. For the conception [15], this means that additional equilibriums have to be taken into account. Furthermore, $\text{Cr}_2\text{O}_7^{2-}$ is not stable in liquid slags, gaseous CrO_3 forms from the dichromate-anion [17]:

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} \longrightarrow \operatorname{Cr}\operatorname{O}_3(g) + \operatorname{Cr}\operatorname{O}_4^{2-}$$
. (4)

2 Experimental method

This work is about the reflectivity of CaO-Fe₂O₃-SiO₂- slag melts in the ultraviolet and visible spectral range under the reflection angle 0° . For these considerations, we have developed a spectroscopic reflection method (impulse-flash-technique).

In order to measure the reflectance in the range of the Fe³⁺/O²⁻ - charge-transfer - and d-d-transitions, we can use a flash lamp with a high efficiency as a light source and focus it on the liquid silicate surface. The transfer of the UV-light ray can be carried out through an optical fiber. For taking reflection spectra a light flash of high energy (0.6 J/flash, duration of an impulse approximately 10^{-6} s, efficiency of an impulse above 10^3 W/mm²) is fired. In the wavenumber range between ν =50000 and ν =14000 cm⁻¹ maximally 80 impulses per second (= scan rate) can be fired.

By use of this method, we can also record kinetic processes as e. g. crystallisation processes of an supercooled glassy matrix to a crystalline equilibrium phase at high temperatures (transition of a mirror reflection to a diffuse reflection).

We investigated the system CaO-Fe₂O₃-SiO₂ with Fe₂O₃-contents above 24 % (mass percent) in the temperature range 1400 $^{\circ}$ C to 1550 $^{\circ}$ C with an oxygen partial pressure of p(O₂)=0.21 bar.

For a comparison UV/VIS-reflection measurements of the systems $CaO-Fe_2O_3-P_2O_5$, CaO-MnO-SiO₂ and CaO-Fe₂O₃[liquid state, $p(O_2)=0.21$ bar] have been carried out. In order to investigate influencing factors, certain concentration lines have been chosen in the respective three-component-systems (concentrations are given in mass-%):

(I) CaO-Fe₂O₃-SiO₂ [Fe₂O₃]_x+[54.5CaO+45.5SiO₂]_{1-x} , x=0.25, 0.40, 0.6 :

influence of increasing Fe_2O_3 -contents (increasing oxidation degree caused by Fe^{3+});

(II) CaO-Fe₂O₃-SiO₂ [60CaO+40Fe₂O₃]_y+[60SiO₂+40Fe₂O₃]_{1-y}, y=0.28, 0.55, 0.60:

influence of the basicity related to increasing SiO_2 -contents with constant Fe_2O_3 -content;

(III) CaO-Fe₂O₃-P₂O₅ [77Fe₂O₃+23P₂O₅]_z+[43CaO+57P₂O₅]_{1-z}, z=0,39, 0.52, 0.69, 0.85 :

influence of the network-former SiO_2 and P_2O_5 ;

(IV) CaO-Fe₂O₃ 60 % Fe₂O comparison to a slag without network-former ;

(V) CaO-MnO-SiO₂ [75.5MnO+24.5SiO₂]_k+[42.5CaO+57.5SiO₂]_{1-k} , k=0.32, 0.47, 0.57 :

comparison to the two isoelectronic d^5 -cations Fe^{3+} and Mn^{2+} .

3 Results and Summary

The increased specular reflectivity of the liquid silicate surface in the ultraviolet spectral range is based on the very intensive electron transfer (charge transfer bands, CT) from the oxide ion (bound to the respective matrix) to the Fe³⁺-ion [7,17,22,23]. For Fe³⁺-O²⁻ - complexes (where the ion considered as an O²⁻-ion appears in a bound form), very strong absorptions develop in the UV-range that are caused by the photochemical process of the temporary metal cation reduction by a light quantum hc ν (h=Planck' constant, ν =wavenumber, c= vacuum light velocity) :

 $Fe^{3+}-O^{2-} + hc\nu(UV) \rightarrow Fe^{2+}-O^{-}.$ (5)

The base of the quantitative evaluation is the Fresnel equation for the specular reflection under a reflection angle of 0° .

The increased reflectivities in the visible spectral range evolve from d-d-transitions in the Fe³⁺-ion in Fe³⁺-O²⁻-complexes. They can be proven in this way. The reflection bands in the visible range are much less pronounced than the CT-bands in the UV range. In the fluxes, complexes with the coordination number 4, Fe³⁺(O²⁻)₄ have been proven. In glassy silicates, complexes with coordination number 6 dominate. While quenching a silicate at a temperature in the solidus range (up to 900 °C) the complexes with coordination number 6 form with minor order in the glassy matrix. This happens through a rapid temporal reaction. Afterwards, the crystallisation of the

silicates in equilibrium phases starts (diffuse reflection). The two-constants-theory by Kubelka and Munk is the most important prerequisite in the reflection spectroscopy of diffusely reflecting surfaces.

The reflection spectra have been analysed quantitatively and they have been related to the molecular structure of the liquid and glassily solidified systems.

4 Conclusion

In this work, we describe a quantitative correlation between the reflectivity in the UV range and the molar Fe^{3+} -content. The foundational investigations for in-situ recording the redox state of liquid silicates are part of this work. Preferably, these are measurements in the wavenumber range below 33000 cm⁻¹ as this range is not disturbed by the emitted natural VIS-radiation of the liquid silicate. The UV/VIS-reflection spectroscopic measurement technique described in this work is suitable for the investigation of liquid silicates and glasses with high absorption properties as they exist for the d-complexes (for example Fe^{3+} or Mn^{2+}). In the range of higher wavenumbers, the weaker d-d-transitions in the stable $Me^{n+}-O^{2-}$ -complexes can be recorded. The knowledge derivable from this refers to the studies of coordination numbers in d-complexes and reactions with d-complexes in liquid systems at high temperatures (up to 1600 °C). In quenched glassy silicates and aluminates, higher coordinated complexes exist. Applying the described UV/VIS-spectroscopic measurement technique, changes in the coordination number of d-complexes can be determined for different temperatures.

Furthermore, we can determine the precipitation kinetics of solid phases from liquid or glassily solidified silicates at high temperatures using the time-resolved reflection flash spectroscopy. By measuring the transition from the direct mirror reflection (range of high direct specular reflections) to the range of diffuse reflections (range of low directed diffuse reflections), the formation of heterogeneous constituents is detected.

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