Contribution to the Study of the Structure of the Melts of the System $FeO-SiO_2-Fe_2O_3$[†]

Pavol Vadasz* and Karel Tomasek

Technical University of Košice, Faculty of Metallurgy, Department of Ceramics, Letná 9, 042 00 Košice, Slovak Republic

The presented paper is oriented to the processing of the results obtained from the measurement of the physical and chemical properties of the synthetic melts of the system $FeO-SiO_2-Fe_2O_3$. On the basis of these results and knowledge obtained from the literature, we present an image of these melt structures. The structure of the system $FeO-SiO_2-Fe_2O_3$ may be characterized as an amorphous solidified melt. The basic structural component of such sets is the chemical compound fayalite ($2FeO\cdot SiO_2$), which is ionized in cation Fe^{2+} and anion complex SiO_4^{4-}. In the course of melting, the components are ionized, and formed are simple cations (e.g., Fe^{2+}, FeO^+, and Fe^{3+}), anion complexes (e.g., SiO_4^{4-}, FeO_2^-, $Fe_2O_5^{4-}$, $SiFeO_7^{7-}$, FeO_3^{3-}, etc.) and, clusters, the composition of which corresponds to the present chemical components (for example: wüstite, magnetite, fayalite). Tetrahedral SiO_4^{4-} is a principal structural unit of the silicate melts. When increasing its content in the system, polymerization occurs with the formation of more complex anions (e.g., $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_3O_9^{6-}$, $Si_2O_6^{4-}$, etc.). Knowledge about the non-negligible effect of iron upon the properties of these melts was obtained from analysis of the physical and chemical properties of the fayalite melt. Ferrous oxide behaves in these systems as the donor of the oxygen anions. The gradual transfer of the ferrite−oxygen complexes from tetrahedral to octahedral co-ordination depends on the reduction in the number of oxygen anions in the system. Existence of the individual ferrito−oxygen and silico−oxygen complexes is reflected in the physical properties of the fayalite melts.

Introduction

A decisive role in nonferrous metals pyrometallurgical production is played by fayalitic slags, which are formed when silica oxide is applied as the major slag forming additive. Such slags represent the so-called "acidic" slags, the composition of which may by characterized by the basic system $FeO-SiO_2-Fe_2O_3$.[1] Indisputable advantages (low melting temperature, ability to react with the ballast components of the charge under the formation of low-temperature melting eutectics, suitable physical and chemical properties, etc.) of such slag application in pyrometallurgical processes of metal production confirm their almost exclusive application in the production of nonferrous metals.

Experimental results from the measurement of the physical and chemical properties and knowledge obtained from the literature enable characterization of the melts with the high probability the structure of melts can be given under given conditions.

It is possible to observe the structure of the melts based on the physical and chemical property measurements—applying so-called indirect methods. Density, surface tension, viscosity, conductivity, and mole volume react sensitively to changes in the melt's internal structure.

Applied Experimental Methodologies

In the present paper are described the processed experimental results of measurements of the physical and chemical properties[2] of the synthetic system of melts: $FeO-SiO_2-Fe_2O_3$ [3−6] These are combined with literature information from which assumptions related to the structure of fayalitic melts are declared.

To measure the density, the method of maximum gas pressure in a bubble was applied, which has been described in detail previously.[3] Pure nitrogen was blown through a platinum capillary under the melt surface, and values of the maximum pressure in the bubble when released were measured using a manometer. Measurements were conducted with a multiplied depth of capillary submersion. The obtained results were processed, and derived were the values of density and mole volume of the melts under given conditions. The overall error of the measurement was ± 7 %, and the standard deviation of the measurement was ± 1 %. The bubble, when released, overcomes the hydrostatic pressure and the pressure acting against the new surface creation. To calculate the density, eq 1 was applied

$$P_{1\max}+P_{2\max}=\left(\rho\cdot gh_1+\frac{2\sigma}{r}\right)-\left(\rho\cdot g\cdot h_2+\frac{2\sigma}{r}\right) \tag{1}$$

For two depths of submerging and after adjustment, the resultant equation for the density calculation was obtained

$$\rho=\frac{\Delta P}{\Delta h\cdot g} \tag{2}$$

where ΔP is the difference of maximum pressures; g is the acceleration due to gravity; Δh is the difference of submersion depths or height of the melt; σ is the surface tension; and r is the capillary radius.

Surface tension was estimated in the silicate melts by applying the cylinder detachment method (4). A platinum ring was placed on the surface of the melt (reversed Pt crucible), and the force needed for tearing off the ring from the melt surface was measured. The surface tension was calculated from the equation

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* Corresponding author. E-mail: pavol.vadasz@tuke.sk.

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$$\sigma = \frac{m \cdot g}{4 \cdot \pi \cdot R_t} \cdot K \qquad (3)$$

where m is the weight of the balance corresponding to the tearing off force; g is the acceleration due to gravity; R_t is the mean radius of the ring at the temperature t; $R_t = R_{20}(1 + 2 \cdot \alpha_{Pt} \cdot \Delta t)$; and K is the correction factor expressing the effect of the melt torn off by the ring. R_{20} is the mean radius of the ring at the temperature 20 °C; α_{Pt} is the Pt thermal expansion coefficient, $\Delta t = t - 20$; and t is the temperature measurement.

The probable error of ten repeated measurements (standard deviation of the measurement) for the slag of the same composition was ± 1 %, but the overall error of the measurement was ± 7 %.

To measure the viscosity of melts of the system $FeO-SiO_2-Fe_2O_3$, the rotation method was applied in such an arrangement: when in a static Pt crucible, a cylindrical sensor made of platinum is rotated submerged under the surface of the oxide melts. The viscosimeter by Gebrüder Haake Rotovisko was used, and the viscosity is measured by resistance, by which the melt acts against the rotary movement. For the calculation, eq 4 was used

$$\eta = f\left(K\frac{M}{\omega}\right) \qquad (4)$$

where η is the dynamic viscosity; K is the constant of the instrument; M is the torsion momentum; and ω is the angle speed.

A detailed description of the applied methodology has been provided previously.[5] The experimental method was tested with liquids and melts of known viscosity, and the adjusted value of the constant K for the temperature of 1300 °C was determined. The resulting error of the viscosity measurement was ± 12 %, and the standard deviation of the measurements was ± 5 %.

Measurement of the conductivity of liquid oxide melts was conducted using the bridging method. The main part was the radio frequency RLC bridge B 601 by Wayne Kerr with the attached adapter Z 601. The bridge operates on the principle of the Wheatson Bridge. The sensors for resistance were Pt electrodes. A detailed description of the experimental apparatus and measurement methodology is provided in the work.[6] The relative error of the measurement was ± 2 %. Under the minimum deviation on the detector, the value of the total resistance was measured, from which the conductivity was calculated according to the equation

$$\chi = C/(R - R_0) \qquad (5)$$

where C is the constant of the measuring crucible; R is the experimentally obtained value of the resistance; and R_0 is the resistance of the electrodes and connected leads.

Melts were prepared from pure chemicals and of purity p.a.: Fe_2O_3 and SiO_2 were melted in iron crucibles placed in an electrical resistance furnace, and measurements were carried out at a temperature of 1300 °C in an atmosphere of air. More detailed conditions of experiments, preparation of melts, and chemical analysis are provided in the corresponding works.[3−6] The experimental measurements were time limited, for at the melts surface a "crust" was formed, i.e., a layer of the solid magnetite ($FeO \cdot Fe_2O_3$). The results of these works were processed for the needs of the melt's structural study.

Results and Their Analysis

The density of the melt $FeO-SiO_2-Fe_2O_3$ was measured by applying the method of maximum gas pressure (nitrogen) in the bubble at a temperature of 1300 °C in an atmosphere of air. Experimental results were processed and are provided in Figure 1 as the relation between density of melt and ratio FeO/SiO_2, with a constant content of Fe_2O_3 in the melt within the interval (3 to 7) mol %. The density lies within the interval (3.5 to 4.3) g $\cdot$cm^{-3}, and the ratio FeO/SiO_2 changed from 1.25 up to 2.75. It is obvious from the given relationship that an increase of the ferrite oxide content in the melt causes an increase of its density. In the interval of the melt's chemical composition, which is close to the composition of the chemical compound fayalite ($FeO/SiO_2 = 2$), there is a certain "retaining line". In this interval, the density of melts, under the given conditions, was (3.92 to 3.96) g$\cdot$cm^{-3}. When the content of FeO in the melt was further increased, its density gradually increased until, with the value of $FeO/SiO_2 = 2.72$, it reaches the value 4.28 g$\cdot$cm^{-3}. On the basis of the values of the density of the melt and its chemical composition, the molar volume of the melt was calculated (Figure 2). The effect of the ratio FeO/SiO_2 upon the molar volume of the melt shows a behavior similar to density but in the opposite direction; i.e., with the rise in the ferrite oxide content, the molar volume of the melt decreases. In the given relationship, there is an area limited by the values of the ratio FeO/SiO_2 within the interval 1.9 to 2.1, where the molar volume of the melt practically does not change with a change of its composition.

With regard to the low content of Fe_2O_3 in the melt [(3 to 7) mol %], the effect of ferrite oxide upon the density and molar volume of the observed melt was not evaluated. From these results, it is obvious that the increase of Fe_2O_3 content will be reflected in the rise in density of the melt, mainly when there is

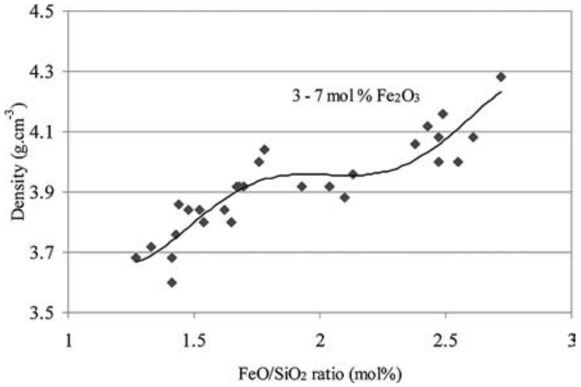

Figure 1. Relation between the density of the melt $FeO-SiO_2-Fe_2O_3$ at 1300 °C and the value of the ratio FeO/SiO_2 (in mol %).[3]

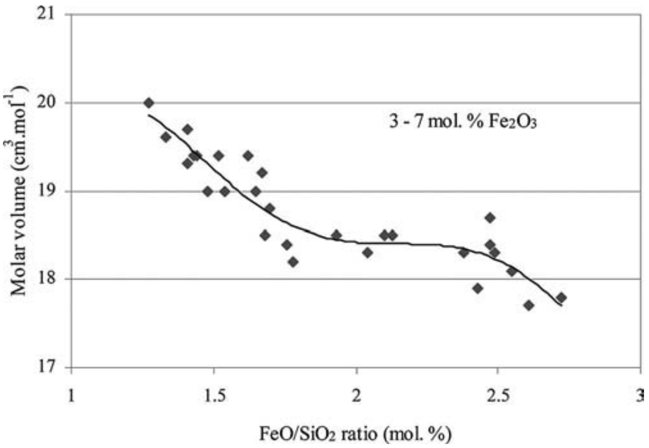

Figure 2. Relation between the mole volume in the melt $FeO-SiO_2-Fe_2O_3$ at 1300 °C and the ratio FeO/SiO_2 (in mol %).[3]

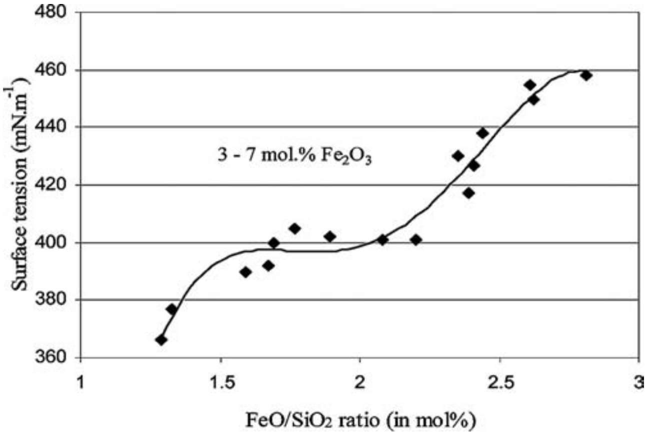

Figure 3. Relationship between surface tension in the melt $FeO-SiO_2-Fe_2O_3$ at 1300 °C and value of the ratio FeO/SiO_2 (in mol %).[4]

replacement of silica oxide in the system. The molar volume of the melt of the system $FeO-SiO_2-Fe_2O_3$ is similarly dependent upon the content of SiO_2 and Fe_2O_3.

The surface tension of the system $FeO-SiO_2-Fe_2O_3$ melts was measured by applying the tearing off method at a temperature of 1300 °C in an atmosphere of ambient air.[4] In Figure 3 are provided the processed experimental results from this work. Provided is the effect of the ratio FeO/SiO_2 upon the surface tension of the melt at a constant content of Fe_2O_3 [(3 to 7) mol %] in the melt. With a rise of the value of the ratio FeO/SiO_2, which corresponds to an increase of ferrite oxide in a melt, the surface tension of the melt also increases. However, this continuous rise in surface tension stops in the interval, where the ratio FeO/SiO_2 is 1.75 to 2.25. The surface tension does not practically change in this interval (σ = (401 to 403) $mN \cdot m^{-1}$). As was the case with density, when assessing the surface tension in this system, it was not possible to observe the effect of Fe_2O_3.

With the rise in ferrite oxide concentration and silica oxide, the surface tension of the melt drops, while the lowest values of the surface tension lay within the area of system saturation by magnetite or tridymite (SiO_2). The highest values of the surface tension are in the area of melt saturation in the system $FeO-SiO_2-Fe_2O_3$ by iron (wüstite + Fe-γ) (Figure 4). From the given results, it follows that the surface tension in the melt $FeO-SiO_2$ continuously rises with a rise of the value of the ratio FeO/SiO_2.

The viscosity of the melt of the system $FeO-SiO_2-Fe_2O_3$ was measured by applying the rotation methodology at a temperature of 1300 °C in an atmosphere of pure air (Figure 5). The highest value of the viscosity (1100 $mPa \cdot s$) was gained with the ratio $FeO/SiO_2 = 1.75$ and content of 37 mol % Fe_2O_3. The rise in the ratio FeO/SiO_2 causes a decrease of the viscosity of the melt an the range of fayalite existence—there is a minimum. When the ratio FeO/SiO_2 is 1.75, the effect of Fe_2O_3 upon the melt is most visible. The lowest viscosity values were observed in the saturation melt wüstite. An increase in the silica oxide content as well as that of ferrite oxide increased the viscosity of the melt.

To measure the conductivity of the slag melt, the "bridge method" was applied. The effect of Fe_2O_3 content upon the value of the conductivity of the melt under a constant ratio of FeO/SiO_2 is provided in Figure 6. It is obvious from the obtained results that ferrite oxide intensively increases the system conductivity at almost the same level as the ferrous oxide. The highest values of conductivity (1 430 $S \cdot m^{-1}$) were obtained with Fe_2O_3 contents [(48 to 53) mol %] and a ratio FeO/SiO_2 = 3.5. The experimental results confirm that the conductivity of the melts of the system $FeO-SiO_2-Fe_2O_3$ depends decisively on the FeO and Fe_2O_3 content of the system. These results confirm information from the literature about the presence of the ion and electron conductivity in such melts.[7−12,19]

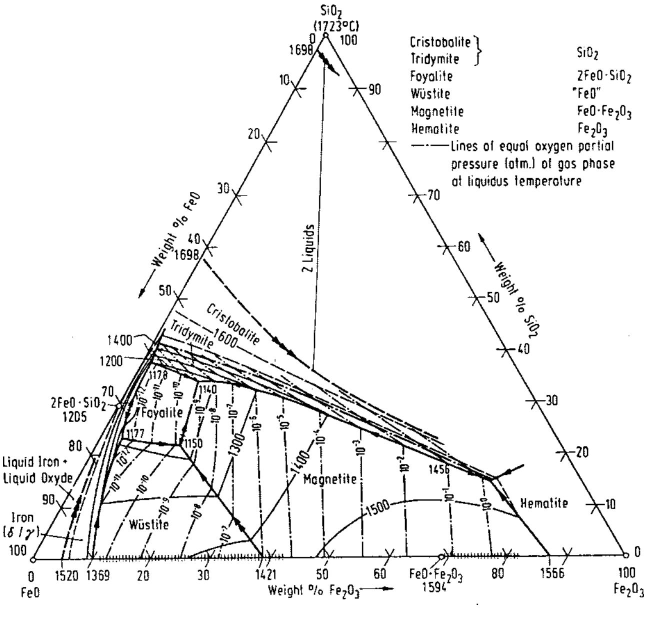

Figure 4. Phase diagram of the system $FeO-SiO_2-Fe_2O_3$.[1]

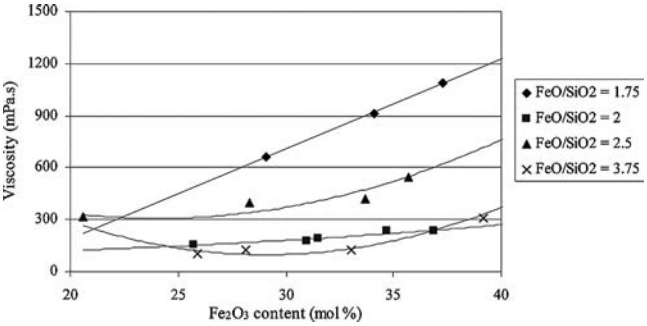

Figure 5. Effect of Fe_2O_3 content upon the viscosity of the melt of the system $FeO-SiO_2-Fe_2O_3$ at 1300 °C and various constant ratios FeO/SiO_2.[5]

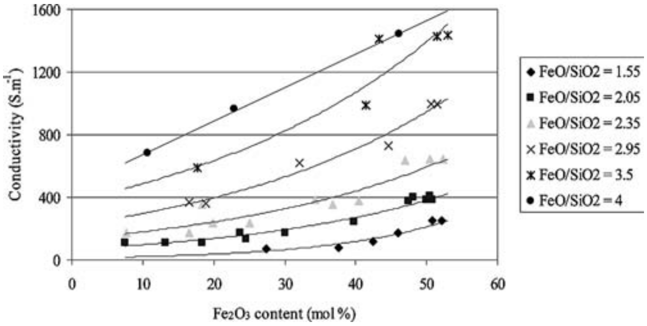

Figure 6. Effect of Fe_2O_3 content on the conductivity of melts $FeO-SiO_2-Fe_2O_3$ at 1300 °C and various ratios FeO/SiO_2.[6]

Comparison of the obtained values of density, surface tension, viscosity, and conductivity, corresponding to the melt of the composition of $2FeO \cdot SiO_2$, and values given in the literature[7,13,14] is given in Table 1. Experimental results were obtained from measurements in the systems with a variety of ferrite oxide content and applying a variety of experimental methods. We

Table 1. Comparison of the Selected Physical Properties of Fayalite at a Temperature of 1300 °C Obtained from the Literature[13,14] and from Experimental Measurements in References 3 to 6

	Physical properties (Fe_2O_3 content in mol %)			
fayalite	density ($g \cdot cm^{-3}$)	surface tension ($mN \cdot m^{-1}$)	viscosity ($mPa \cdot s$)	conductivity ($S \cdot m^{-1}$)
literature [13,14]	3.65 to 3.8	430	700 − 2 100	400
exptl results	3.92 to 3.96 [(3 to 7) mol % Fe_2O_3]	401 to 403 [(3 to 7) mol % Fe_2O_3]	174 to 194 (31 mol % Fe_2O_3)	175 (30 mol % Fe_2O_3)

assume that this was caused by the different methodology and conditions of measurements.

Physical properties of fayalite, obtained from the literature as well as from experimental measurements and provided in Table 1, represent a broad interval of compositions of slag melts. Significant compliance of data was obtained in the case of density and surface tension (Figures 1 and 3), where we succeeded to prevent significant oxidation of Fe^{2+} during the experiments. Values of density and surface tension show in the area of chemical composition corresponding to the fayalite retaining line that the viscosity has its lowest values.

Discussion

From point of structure we may include the systems $FeO-SiO_2-Fe_2O_3$, with regard to relatively high content of silica oxide, among so-called invert glass, i.e., amorphous (noncrystalline) solidified melts. Amorphous systems feature specific noncrystalline arrangement of atoms within short distances. For such arrangement, a local spatial heterogeneity is typical, i.e., arrangement of the atoms of various elements into more stable amorphous clusters formed of several atoms or several tens of atoms mutually bound through the bond, which is stronger than the bonds with other atoms existing in a less arranged amorphous matrix. Another significant phenomenon in such systems is the medium distance heterogeneity and from derived secondary anisotropy.[7,8,15−17,19]

In the course of melting the slag of the system $FeO-SiO_2-Fe_2O_3$, the ionizing of the components occurs and formed are simple ions (e.g., Fe^{2+}, FeO^+), more complex ion complexes (e.g., $SiO_4{}^{4-}$, $FeO_2{}^-$, $Fe_2O_5{}^{4-}$, $SiFeO_7{}^{7-}$, $FeO_3{}^{3-}$, etc.), and clusters, the composition of which corresponds to the present chemical components (e.g., wüstite, magnetite, fayalite). Tetrahedral $SiO_4{}^{4-}$ is, according to the authors, the principal structural unit of silicate melts, when SiO_2 in the melt is less than 30 mol %. In the case of higher contents, more complex anions are formed (e.g., $Si_2O_7{}^{6-}$, $Si_3O_9{}^{6-}$, etc.).[7,8,15−41]

Simplifying considerations on the structure of melts applied, geometrical ideas on building in the various modifying cations in the structure of the melts, and considerations about the strength of bonds, by which the individual ions are bound in the structure of the melts, we may attempt to describe the structure of fayalitic melts. Polymerization or dissociation can be expressed in the following equilibrium terms.

The main component of melts of the system $FeO-SiO_2-Fe_2O_3$ is the chemical compound fayalite ($2FeO \cdot SiO_2$), ionization of which may be described by the following equation

$$2FeO \cdot SiO_2 = SiO_4^{4-} + 2Fe^{2+} \tag{6}$$

When the content of ferrite oxide in the melt is increased (eqs 7 and 8), the structure of the melt changes, and the ions FeO^+ and $FeO_2{}^-$ are formed, which increase the density and surface tension of the melt. It is then possible to describe theoretically the structure of the melt by the following equations

$$2FeO \cdot SiO_2 + FeO = SiO_4^{4-} + FeO^+ + 2Fe^{2+} + e^- \tag{7}$$

$$2FeO \cdot SiO_2 + 2FeO = SiO_4^{4-} + FeO_2^- + 3Fe^{2+} + e^- \tag{8}$$

An increase of the ferrite oxide in the system shifts its composition into the range of wüstite existence. According to the authors of the work (7, 8, 15, 19, and , etc.), the structure of melted wüstite is formed of ions Fe^{2+} and a cluster of ions Fe^{3+} and O^{2-}, the structure of which is close to that of magnetite. The specialty of the magnetite crystal lattice is that not all crystallographic equivalent posts must be filled by cations; i.e., in such a lattice statistically distributed vacancies may be present. Ionization of magnetite may then be expressed by eq 9

$$FeO \cdot Fe_2O_3 = 2FeO_2^- + Fe^{2+} \tag{9}$$

In this case, Fe^{2+} ions are in octahedral positions, and Fe^{3+} ions occur in both octahedral and tetrahedral positions. The presence of surface active anions $SiO_4{}^{4-}$ in the structure of wüstite causes reduction in the density and surface tension of the system. The viscosity of the melts increases, and their conductivity reduces. The reduction of the ion conductivity of the melts is partially compensated by the electron conductivity of such melts. The decisive significance for the concentration of Fe^{3+} and Fe^{2+} ions in the fayalitic melts has the content of free ions of oxygen present in melts which in turn depends on the oxygen partial pressure in the system.[7,8,15,19,24]

To express the conductivity of ferrite oxides melts seems to be justified by the theory of polarons. On the basis of this theory, the free electrons and vacancies are localized on the microvolumes of melts (clusters), which change their structure and physical properties in connection with the electron or vacancy localization. According to the theory, the electron conductivity is caused by the possibility of the electrons skipping from a cation with a lower valency to a cation with a higher power.

When the fayalite melt is enriched by silica oxide (eqs 10 and 11), the density and surface tension significantly decrease, while the molar volume increases (Figures 1 to 3). Also the viscosity of system sharply rises, and the conductivity drops. Tetrahedral $SiO_4{}^{4-}$ anions in the structure undergo polymerization into spatial forms (rings), for example, according to equation

$$2(2FeO \cdot SiO_2) + SiO_2 = Si_3O_{10}^{8-} + 4Fe^{2+} \tag{10}$$

$$3(2FeO \cdot SiO_2) + 3SiO_2 = 2Si_3O_9^{6-} + 6Fe^{2+} \tag{11}$$

The effect of ferrite oxide upon the change of the melted fayalite structure may be theoretically expressed by the following equation

$$2FeO \cdot SiO_2 + Fe_2O_3 = SiO_4^{4-} + FeO_2^- + FeO^+ + 2Fe^{2+} \tag{12}$$

The presence of ferrite oxide in the system $FeO-SiO_2$ causes an increase in density as well as in the molar volume of the melts.[7,8,19,40,41] Due to the effect of octahedrally coordinated FeO^+ ions, the surface tension of the melts is reduced.[7,8,19,40,41] From the theory of the chemical bond, it follows that there must be one double bond with a higher percentage of covalency in the frame of the FeO^+ ions. They state in the literature that substances with covalent bonds feature lower surface tension, and also the mutual interaction of the particles in mixed bonds with a higher share of covalency is weaker. The viscosity of melts of the system $FeO-SiO_2-Fe_2O_3$ is significantly less than in the melt $FeO-SiO_2$. This fact is caused by the existence of FeO^+ ions, which disturb the polymerization of SiO_4^{4-} anions. The existence of polymerized or partially polymerized networks in melts increases their viscosity. Conductivity of the observed melts is based on the ion and electron conductivity of the components.[7−12,19,39−41] In Figures 5 and 6, the striking effect of iron oxides upon the conductivity and viscosity of the melts is clearly visible. The conductivity of melts in the system $FeO-SiO_2-Fe_2O_3$ continuously rises with an increasing value of the FeO/SiO_2 proportion as well as with an increase in Fe_2O_3 content. A change in the proportion of Fe^{2+}/Fe^{3+} ions as well as the total amount of iron ions in the system are reflected in the rise in conductivity of the melts. An increase in SiO_2 content significantly reduces the conductivity of the melts (Figure 5). From the above results, it is obvious that in the observed melts there is a drop in ion conductivity that is replaced by electron conductivity, caused by the presence of Fe^{2+} and Fe^{3+} ions in clusters (polarons) present in these systems. The existence of the bivalent and trivalent iron ions in the magnetite structure in equal crystallographic positions enables the jumping of electrons between both iron cations.[7,8,19,24]

There are most probably ion complexes between Fe^{3+} and O^{2-} ions in the fayalitic slag. Depending on the ratio FeO/Fe_2O_3, the melt will contain complexes corresponding to the individual components of the system ionization; for example ($FeO^+ + FeO_2^-$),[7,8,19,30,40,41] ($2FeO_2^- + Fe^{2+}$) magnetite,[7,8,19,30,40,41] or combined complexes, for example, $SiFeO_7^{7-}$.[7,8,29,30,41] The formation of such complexes may be described by the equation

$$2FeO\cdot SiO_2 + 2FeO + Fe_2O_3 = SiFeO_7^{7-} + 2FeO^+ + 3Fe^{2+} + e^- \quad (13)$$

The individual stages of polymerization or dissociation, which overlap with one another, can be described as follows. Existence of the individual ferrite−oxygen complexes will be reflected in the physical properties of the fayalitic melt.

Conclusion

In the present paper, we have attempted to summarize the results from the experimental study of the physical and chemical properties of the oxide melts of the system $FeO-SiO_2-Fe_2O_3$ and published knowledge on the structure of the oxide melts. It is obvious from the obtained results that the given melts form ion systems, which will be formed of anion complexes of the ions Si^{4+} and Fe^{3+} with oxygen (for example, FeO_2^- and SiO_4^{4-}) as well as simple cations Fe^{2+} and FeO^+. It is necessary to consider the existence of clusters in the melt, the composition of which will correspond to fayalite ($2FeO\cdot SiO_2$). In the field of chemical composition which corresponds to this chemical compound, the melt may behave as a “molecular liquid”.

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