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PHYSICAL PROPERTIES OF FeO-Fe₂O₃-SiO₂-CaO MELT SYSTEMS

WŁASNOŚCI FIZYCZNE ROZTWORÓW W UKŁADZIE FeO-Fe₂O₃-SiO₂-CaO

Ferritic slags are characteristic for steel production processes but mainly for processes of non-ferrous metals, e.g. copper or lead production. Iron partly oxidizes in the process of its refining or during concentration melting of concentrates in non-ferrous metals production and oxides of iron pass into the slag. CaO and SiO₂ are the main components of such slag systems but certain amount of iron may be in the form of FeO and Fe₂O₃. Slags, which due to their composition after solidification spontaneously decay, i.e. they undergo a volume change during re-crystallization of dicalcium silicate (2CaO.SiO₂) are used preferentially. In real slag systems these main components are accompanied with other oxides – MgO, MnO, Al₂O₃, P₂O₅ or ZnO.

Our work was aimed at observation of density, molar volume, surface tension and viscosity in the basic slag system consisting of FeO – Fe₂O₃ – CaO – SiO₂. We had obtained the knowledge during the study of physical properties of fayalitic (FeO – Fe₂O₃ – SiO₂) or calcium ferrite (FeO – Fe₂O₃ – CaO) slag at 1300°C. The density of melts was measured by maximum gas pressure in bubble method. The molar volume of the melt at a given temperature was calculated from experimental results of its density and chemical composition. It is evident that silica decreases the density of FeO – Fe₂O₃ – CaO – SiO₂ melt system and on the contrary it increases its molar volume. The surface tension was measured by ring method and maximum gas pressure in bubble method. Increasing content of silica in slag melt causes decreasing of its surface tension which proves the knowledge about surface activity in such melt systems. Viscosity of FeO – Fe₂O₃ – SiO₂ – CaO slags was measured by rotating method.

Addition of calcium oxide into FeO – Fe₂O₃ – SiO₂ melt showed a decrease of its viscosity while addition of silica into FeO – Fe₂O₃ – CaO melt caused an increase of its viscosity. Due to those facts we have also made an idea on the structure of such melt systems. From presented results of density, surface tension and viscosity measurements appears that silica in FeO – Fe₂O₃ – SiO₂ – CaO stabilizes Fe²⁺ ions and calcium oxide supports the existence of Fe³⁺ ions. Ions of three valent iron behave in that slag system as complexation able cations transiting from a prevailing octahedral into a prevailing tetrahedral coordination. We assume that the structure of FeO – Fe₂O₃ – SiO₂ – CaO melt system in an observed interval of chemical composition might be made of Fe²⁺ and Ca²⁺ cations or FeO²⁻, Fe₂O₅⁴⁻, FeO₄³⁻ and SiO₄⁴⁻ anions.

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Żuźle ferrytyczne są charakterystyczne w procesach otrzymywania stali oraz metali nieżelaznych np. Cu i Pb. Reakcje utleniania przebiegające w procesie topienia koncentratów przy otrzymywaniu metali nieżelaznych powodują powstawanie tlenku żelaza (II), który przechodzi do żuźla. Głównymi składnikami tych żużli są CaO i SiO₂, a żelazo występuje w nich w postaci FeO i Fe₂O₃. Żuźle, w których występuje efekt samorozpadu to jest objętościowa zmiana przy rekrytalizacji ortokrzemianu wapnia (2CaO·SiO₂) są najchętniej stosowane. W rzeczywistych składach żużli oprócz tych podstawowych związków występują także inne tlenki np. MgO, MnO, Al₂O₃, P₂O₅ lub ZnO.

Badania dotyczą określenia gęstości, objętości molowej, napięcia powierzchniowego oraz lepkości w żuźlu zasadowym w układzie FeO-Fe₂O₃-SiO₂-CaO. Wyniki te uzyskano przy badaniu fizycznych właściwości żużli fajalitowych (FeO-Fe₂O₃-SiO₂) oraz ferrytycznych (FeO-Fe₂O₃-CaO) w temperaturze 1300°C. Do mierzenia gęstości roztworów wykorzystano metodę maksymalnego ciśnienia w pęcherzykach gazowych. Na podstawie wyników eksperymentalnych pomiaru gęstości roztworu i jego składu chemicznego obliczono objętość molową w danej temperaturze. Stwierdzono, że krzemionka obniża gęstość roztworu FeO-Fe₂O₃-SiO₂-CaO, a tym samym zwiększa objętość molową.

Napięcie powierzchniowe mierzono metodami odrywającego pierścienia oraz maksymalnego ciśnienia w pęcherzykach gazowych. Podwyższenie zawartości SiO₂ w stopionym żuźlu obniża jego napięcie powierzchniowe, co potwierdza znany fakt o jej aktywności powierzchniowej w tych układach.

Lepkość żużli FeO-Fe₂O₃-SiO₂-CaO mierzono metodą obracającego się cylindra. Wprowadzenie tlenku wapnia do roztworu FeO-Fe₂O₃-SiO₂ spowodowało spadek lepkości, a dodatek SiO₂ do roztworu FeO-Fe₂O₃-CaO jej wzrost. Na podstawie tych badań przedstawiono pogląd o strukturze tych żużli.

Z prezentowanych wyników pomiarów gęstości, napięcia powierzchniowego i lepkości wynika, że dwutlenek krzemu w żuźlu FeO-Fe₂O₃-SiO₂-CaO stabilizuje jony Fe²⁺ i odwrotnie tlenek wapnia zwiększa możliwość występowania jonów Fe³⁺. Jony żelaza Fe³⁺ w żuźlu są czynnikiem kompleksującym i mogą przechodzić z tetraedrycznej do oktaedrycznej koordynacji lub odwrotnie. Zakładamy, że struktura roztworu o składzie FeO-Fe₂O₃-SiO₂-CaO w badanym zakresie składu chemicznego może się składać z kationów Fe²⁺, Ca²⁺ lub anionów FeO₄⁵⁻, Fe₂O₅⁴⁻, SiO₄⁴⁻ i SiFeO₇⁷⁻.

1. Introduction

Calcium ferrite slags represent a new type of slags that have recently been used in nonferrous metallurgy, mainly in copper, nickel and lead pyrometallurgy. These slag systems are characteristic in steelmaking where the basic CaO-SiO₂ system is enriched with iron oxides. When they are used in nonferrous metallurgy, e.g. at concentrate smelting, oxides of iron are bound into slag. Ferrous oxide, calcium oxide and silica make the main components of these slag systems but certain amount of iron is present also in the form of ferric oxide. In case of typical fayalitic slags utilization the limiting factor is magnetite creation in slag (p_{O_2} is from 10⁻⁷ to 10⁻¹¹ atm). Calcium ferrite slags are liquid in a wide range of oxygen partial pressure (p_{O_2} is from 10⁰ to 10⁻¹¹ atm). The field of SiO₂-CaO-FeO-Fe₂O₃ melt systems utilization is shown in Fig. 1 [1]. Advantageous is the use of such slag compositions which after their solidification self-desintegrate which means they undergo a bulk change in the course of recrystallization

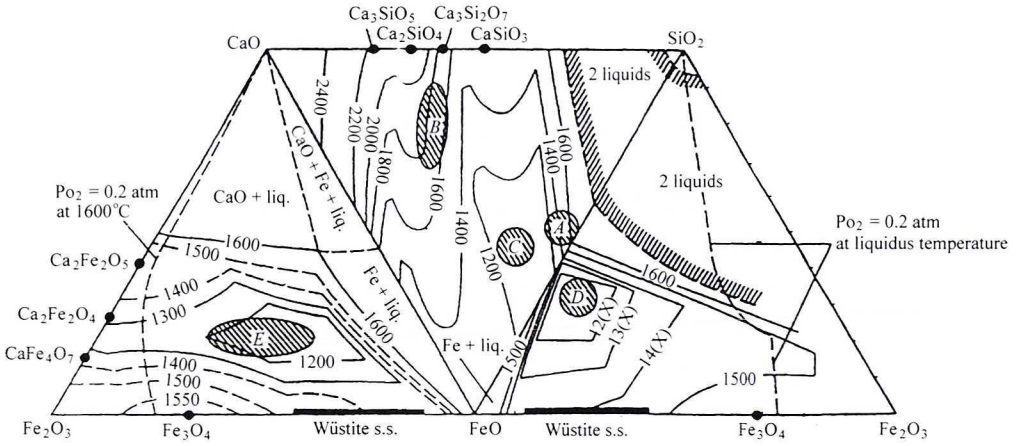


Fig. 1. The slag system FeO – Fe₂O₃ – SiO₂ – CaO, liquidus surface [1]

of dicalciumsilicate (2CaO.SiO₂). The objective of our work was the measurement of density, molar volume, surface tension and viscosity in FeO-Fe₂O₃-CaO-SiO₂ basic slag system. We have gained the knowledge studying physical properties of fayalitic (FeO-Fe₂O₃-SiO₂) or calcium ferrite (FeO-Fe₂O₃-CaO) slags at 1300°C. On the basis of our experimental results we tried to describe the structure of the studied slag melts.

2. Density, molar volume, surface tension and viscosity of slags

Fig. 2–5 presents the results of density, molar volume, surface tension and viscosity measurements in FeO – Fe₂O₃ – SiO₂ melt system at 1300°C [2–6]. The melt’s density

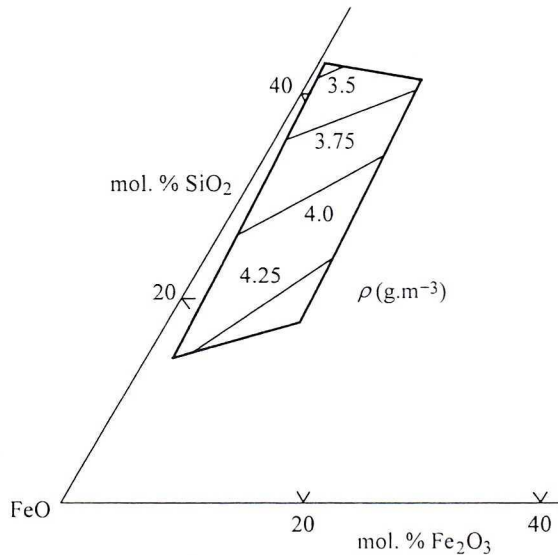


Fig. 2. Density isolines in the melt slag system FeO – Fe₂O₃ – SiO₂ at 1300°C [7, 16]

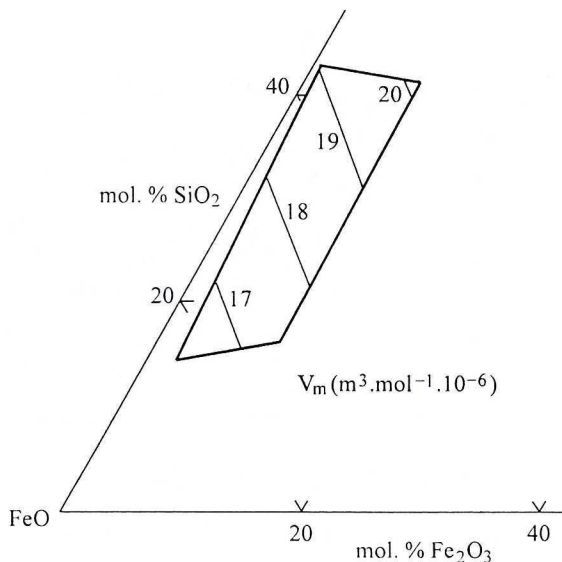


Fig. 3. Molar volume isolines in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ at 1300°C [7, 16]

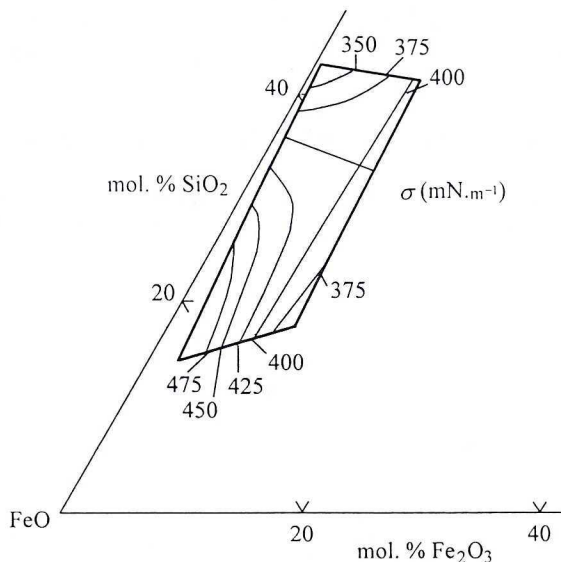


Fig. 4. Surface tension isolines in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ at 1300°C [7, 16]

was measured by maximum bubble pressure method, the surface tension by ring method and the viscosity by rotation method. Silica has a considerable effect on the decrease of the melt's density while on the contrary, ferric oxide increases the slag's density. The melt's molar volume at a given temperature was calculated from the data of the melt's density and its chemical composition. Silica as well as ferric oxide increase the molar volume of such molten system approximately in the same proportion. The surface tension isolines of such system have interesting courses. The

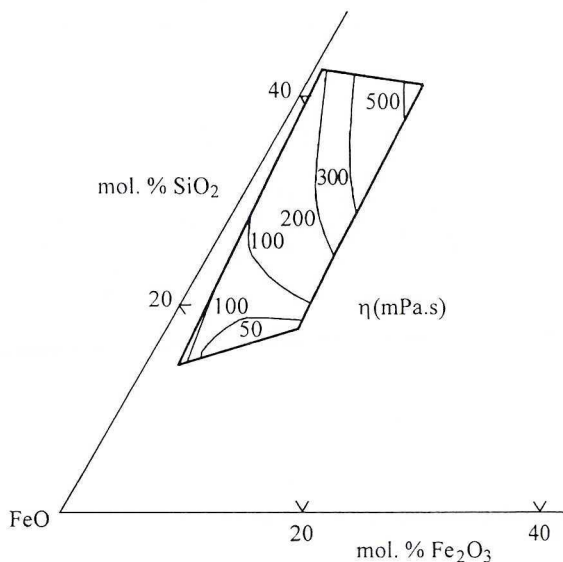


Fig. 5. Viscosity isolines in the melt slag system FeO – Fe₂O₃ – SiO₂ at 1300°C [7, 16]

value 410 mN.m⁻¹ approximately corresponds to the surface tension of fayalite given in literature [8]. The result of the addition of silicon and ferric oxide at 1300°C is that the surface tension of fayalitic melt decreases. Both silica and ferric oxide behave in this slag system as surface active components. Viscosity of FeO – Fe₂O₃ – SiO₂ slag system is affected in a considerable extent by contents of silica and ferric oxide. The increase of concentration of Si⁴⁺ and Fe³⁺ complexation cations causes the increase of the melt's viscosity under given conditions.

The effect of calcium oxide on the physical properties of FeO – Fe₂O₃ – SiO₂ slag system at 1300°C is shown in Fig. 6–10 [5, 6, 9–11]. The above mentioned results

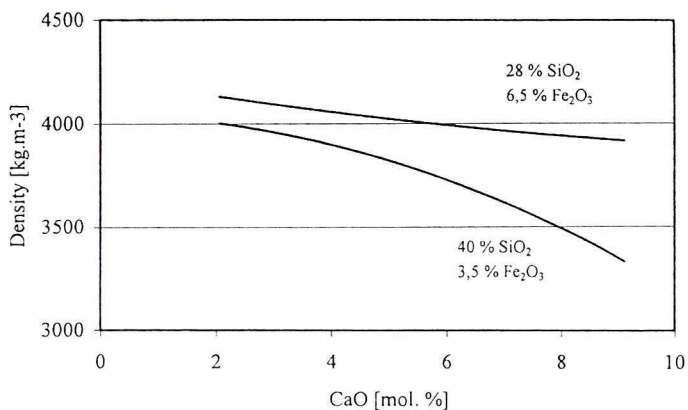


Fig. 6. Influence of CaO content on the density in the melt slag system FeO – Fe₂O₃ – SiO₂ at 1300°C [7, 16]

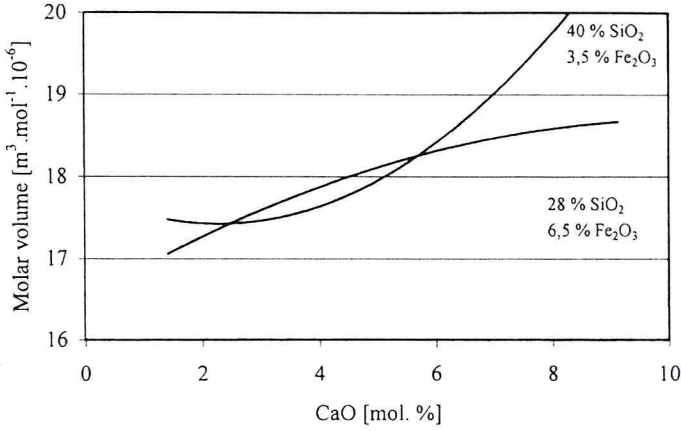


Fig. 7. Influence of CaO content on the molar volume in the melt slag system FeO - Fe₂O₃ - SiO₂ at 1300°C [10]

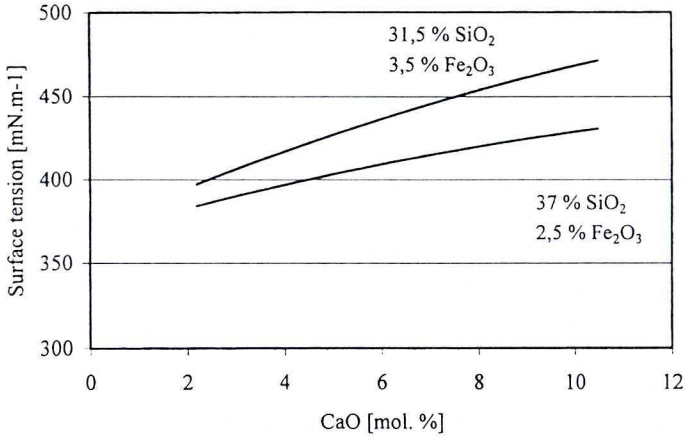


Fig. 8. Influence of CaO content on the surface tension in the melt slag system FeO - Fe₂O₃ - SiO₂ at 1300°C [5, 9]

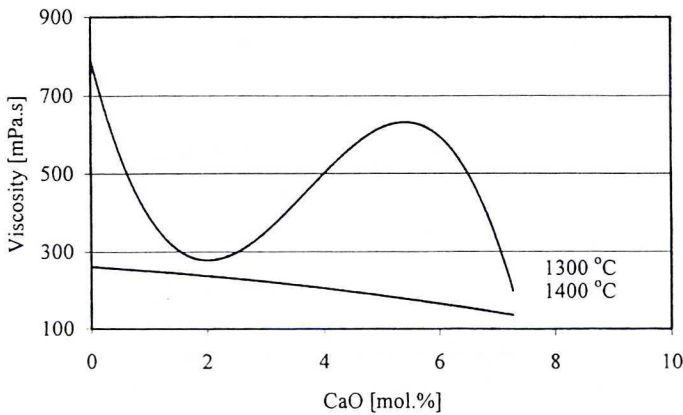


Fig. 9. Influence of CaO content on viscosity in the melt slag system FeO - Fe₂O₃ - SiO₂ at 1300 and 1400°C. Initial composition of slag 43.2 mol% SiO₂, 7.5 mol% Fe₂O₃ and 49.3 mol% FeO [6, 11]

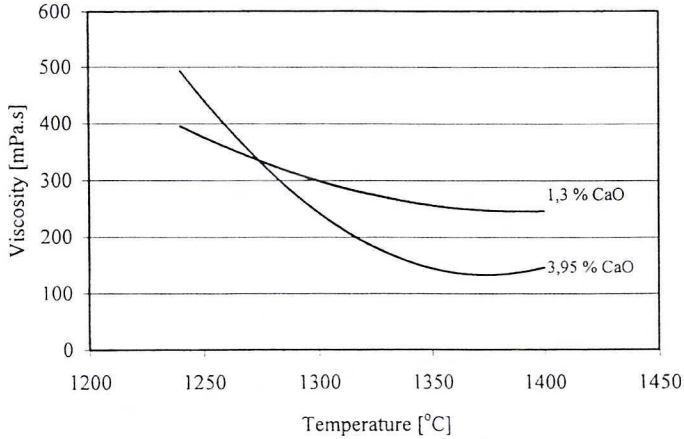


Fig. 10. Influence of temperature on the viscosity in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ at 1.3 and 3.95 mol% content of CaO. Initial composition of slag 43.2 mol% SiO_2 , 7.5 mol% Fe_2O_3 and 49.3 mol% FeO [6, 10]

imply that calcium oxide in fayalitic slag brings down its density and in turn increases its molar volume and surface tension of the melt. This may be caused by the fact that calcium oxide dissociates in the melt and is effective as a donor of oxygen ions which means that anionic complexes change their character and Ca^{2+} cations enter the structure and bring about an increase in surface tension of the melt. Viscosity of fayalitic melt decreases by addition of calcium oxide as a result of an impair of the melt's structure.

Another basic type of the melt system is created by $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaO}$ and the physical properties of this melt are given in Fig. 11–14 [7, 12–15]. Density and surface tension of these melts were measured by maximum bubble pressure method and viscosity by oscillatory method. The density of calcium ferrite slag depends to a con-

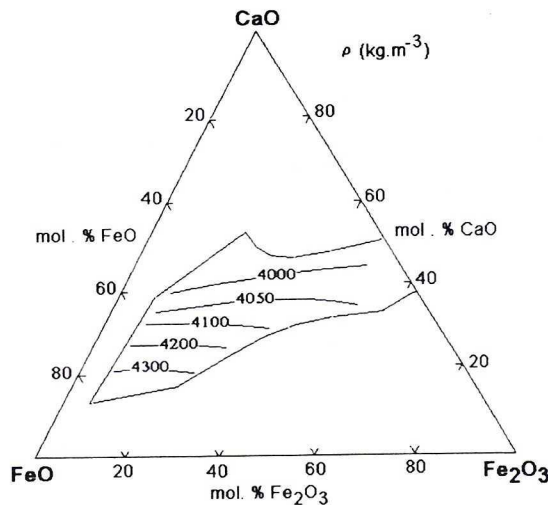


Fig. 11. Density isolines in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaO}$ at 1300°C [7, 12, 14]

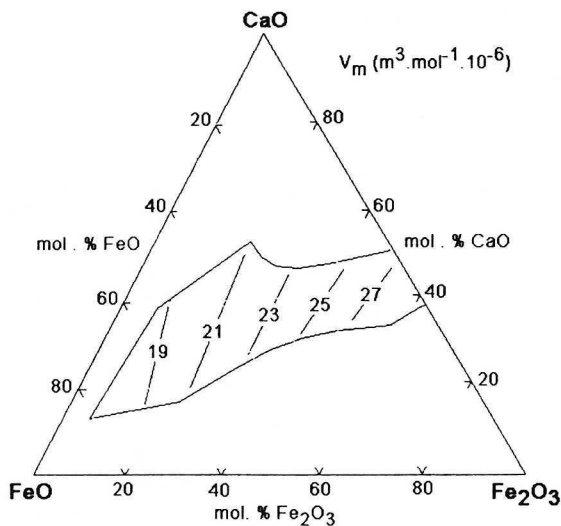


Fig. 12. Molar volume isolines in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C [7, 12, 14]

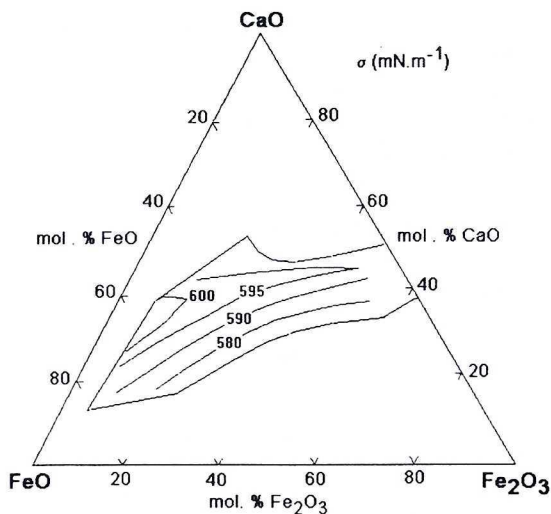


Fig. 13. Surface tension isolines in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C [7, 13, 14]

siderable extent on the content of calcium oxide in the melt which has been proved by the results of density measurements. With increasing concentration of calcium oxide decreases the melt's density while the affect of ferric oxide on the melt's density shows up only at high concentrations. On the contrary, the molar volume of such slag melt depends in a decisive measure on the content of ferric oxide. Surface tension in this melt shows maximum values in the region of saturation with iron and the surface tension isolines at 1300°C approximately keep up with the isotherm which defines the region of magnetite's presence in this system. Increasing content of calcium oxide up to the values corresponding to calciumferrite (Fe₂O₃ · CaO) causes a slight increase of surface tension

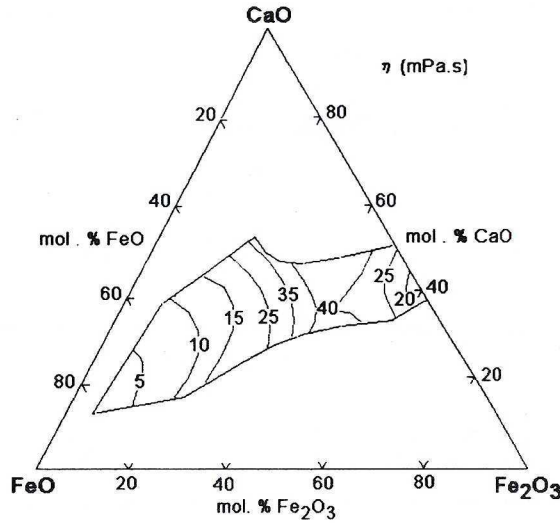


Fig. 14. Viscosity isolines in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C [14, 15]

in the melt. In case this concentration is exceeded the surface tension of the system decreases. Viscosity of calcium ferrite slag at 1300°C is from 3,0 mPa.s to 40,0 mPa.s and the maximum value of viscosity is in the region of FeO.Fe₂O₃.CaO. A change in the melt's composition causes a change in the arrangement of the structure which shows up in a decrease of viscosity of the molten system.

The effect of silicon dioxide on the change of the studied physical properties is given in Fig. 15–22 [17–19]. The density of calcium ferrite melt decreases with the addition of SiO₂ also in the case when it replaces calcium oxide in the system. The result of the increasing content of silicon dioxide is that the melt's molar volume increases but in case that silica replaces ferric oxide the increase is only slight and depends on the total

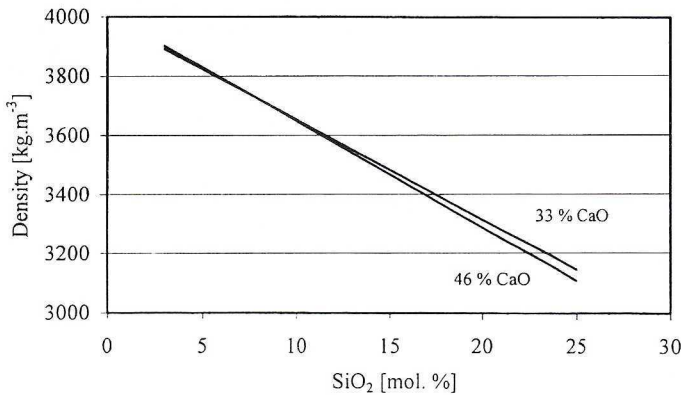


Fig. 15. Influence of SiO₂ content on the density in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C and p₀₂ = 0,21 atm and the content of CaO 33 and 46 mol%, (Fe₂O₃ + FeO)/Fe₂O₃ ratio = 1,05 – 1,08 [17, 18]

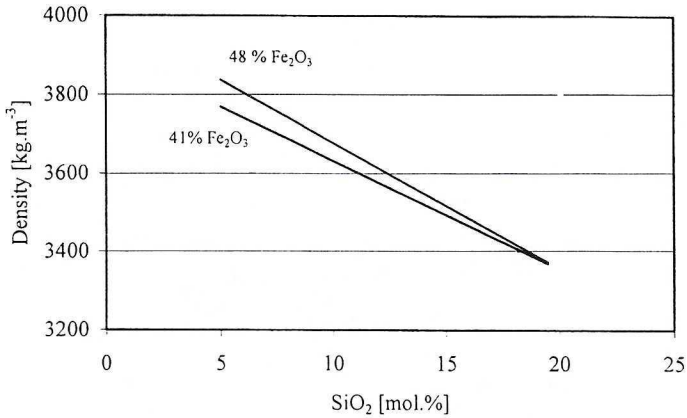


Fig. 16. Influence of SiO_2 content on the density in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaO}$ at 1300°C and $p_{\text{O}_2} = 0.21$ atm and the content of Fe_2O_3 41 and 48 mol%, $(\text{Fe}_2\text{O}_3 + \text{FeO})/\text{Fe}_2\text{O}_3$ ratio = 1.01 – 1.08 [17, 18]

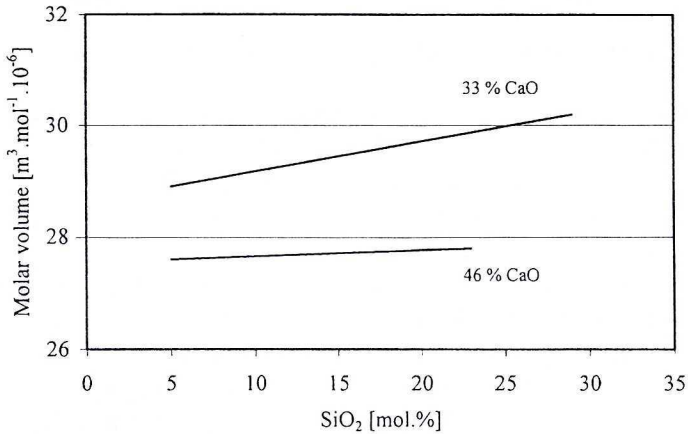


Fig. 17. Influence of SiO_2 content on the density in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaO}$ at 1300°C and $p_{\text{O}_2} = 0.21$ atm and the content of CaO 33 and 46 mol%, $(\text{Fe}_2\text{O}_3 + \text{FeO})/\text{Fe}_2\text{O}_3$ ratio = 1.05 – 1.08 [17, 18]

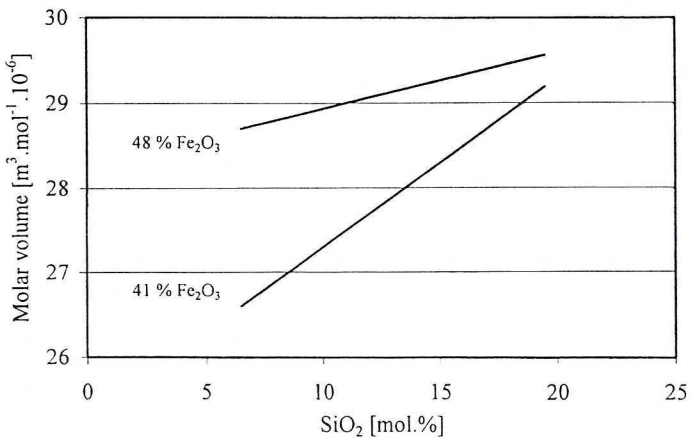


Fig. 18. Influence of SiO_2 content on the molar volume in the melt slag system $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaO}$ at 1300°C and $p_{\text{O}_2} = 0.21$ atm and content of Fe_2O_3 41 and 48 mol%, $(\text{Fe}_2\text{O}_3 + \text{FeO})/\text{Fe}_2\text{O}_3$ ratio = 1.01 – 1.08 [17, 18]

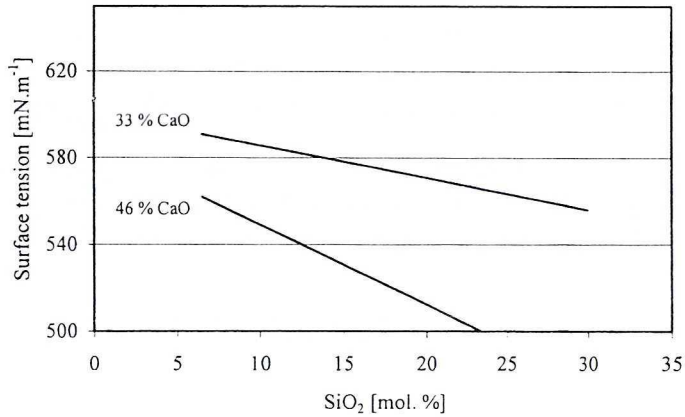


Fig. 19. Influence of SiO₂ content on the surface tension in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C and $p_{O_2} = 0,21$ atm and content of CaO 33 and 46 mol%, $(Fe_2O_3 + FeO)/Fe_2O_3$ ratio = 1,05 – 1,08 [18]

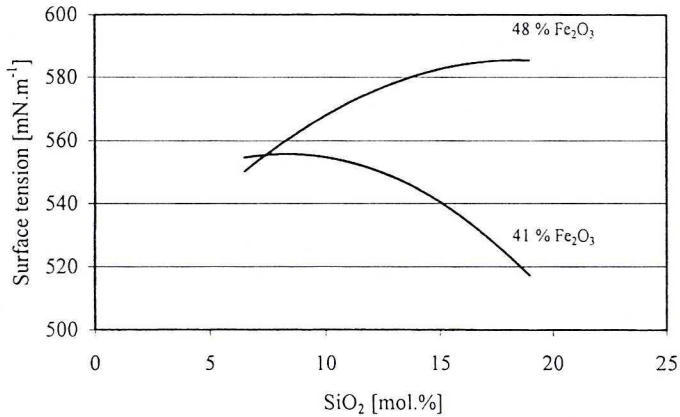


Fig. 20. Influence of SiO₂ content on the surface tension in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C and $p_{O_2} = 0,21$ atm and the content of Fe₂O₃ 41 and 48 mol%, $(Fe_2O_3 + FeO)/Fe_2O_3$ ratio = 1,01 – 1,08 [18]

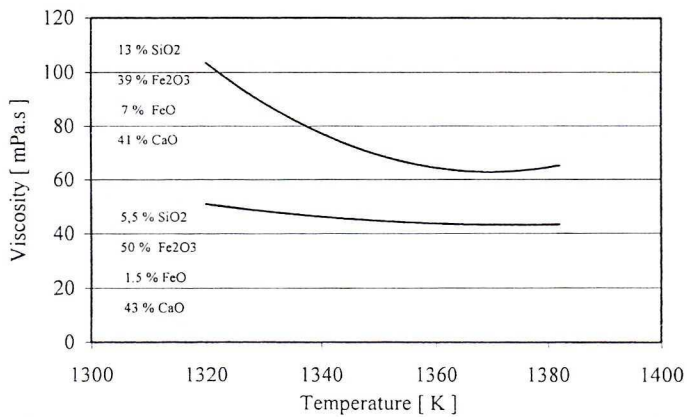


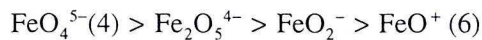
Fig. 21. Influence of temperature on the viscosity in the melt slag system FeO – Fe₂O₃ – CaO at 1300°C and p_{O_2} atm and content of SiO₂ 5.5 and 13 mol% [20]

content of calcium oxide in the system. Addition of silica into calcium ferrite slag causes the decrease of the surface tension and this fact corresponds to literary data [e.g 8, 20, 21] on silica surface activity in slag melts. Viscosity of calcium ferrite slags shows lower minimum by an order of magnitude than the fayalite slag. The increase of viscosity of FeO – Fe₂O₃ – CaO molten system by addition of silica is caused by the creation of oxy-silicon complexes which make the melt's structure complicated. Silica is probably present in the melt in the observed intervals of compositions as SiO₄⁴⁻ anion.

3. Conclusion

Presented results of measurements of the physical properties in FeO – Fe₂O₃ – SiO₂ (CaO) and FeO – Fe₂O₃ – CaO (SiO₂) slag molten systems at 1300°C support the idea that there are two diametrically different systems, e.g. the values of surface tension differ in about 40% and the values of viscosity are different even by two orders. The results of measurements of the melt's physical properties may be used as an indirect method to study the structure of such melts.

Our results support the idea that FeO – Fe₂O₃ – SiO₂ – (CaO) and FeO – Fe₂O₃ – CaO – (SiO₂) slag melts behave as ion solutions but also as molecular solutions in the region of chemical compounds existence. Fayalite (2FeO.SiO₂) whose physical properties characterize the melt behaves this way in FeO – Fe₂O₃ – SiO₂ system and in the case of FeO–Fe₂O₃–CaO system it is the compound of FeO.Fe₂O₃.CaO. We suppose that clusters might arise in the melt, which owing to their composition correspond to those compounds. Ions of three valent iron in FeO – Fe₂O₃ – CaO slag melt behave as complexation cations and they, in dependence on the concentration of oxygen ions in the melt continuously pass from tetrahedral to octahedral coordination or, on the contrary, according to the following scheme:



(figures in brackets are the coordination numbers of Fe³⁺ ions in oxygen complexes)

Detailed study of molar volumes and surface tension of FeO – Fe₂O₃ – CaO – SiO₂ slag melts at 1300°C enabled us to find out their probable structure [22]. Thus the melt may consist of Fe²⁺ and Ca²⁺ cations and SiO₄⁴⁻, FeO₄⁵⁻ and SiFeO₇⁷⁻ anion complexes.

Particular data on the values of the physical properties are significant also in practice for copper production, actually for the process of distribution of the products of smelting in individual phases as well as in evaluation of corrosion slag resistance of refractories.

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