Determination of thermophysical properties for molten slags by maximum bubble pressure method

Tobias DUBBERSTEIN, Hans-Peter HELLER and Piotr R. SCHELLER
Institute of Iron and Steel Technology IEST, Technical University Bergakademie Freiberg, 09599, Germany

Abstract: The knowledge and precise experimental determination of material properties such as density and surface tension for molten slags and fluxes is necessary in industrial steel making processes, e.g. correct simulations of metallurgy casting processes, mathematical modeling of emulsification between steel and slags and computer fluid dynamics. Thermophysical properties of slags are dependent upon temperature and their chemical compositions. Due to the introduction of new steel grades produced in metallurgical plants also new slag related systems were developed. For investigations on these slag systems and their behavior of absorption for nonmetallic inclusions from steel bath right thermophysical properties have to be determined for these systems. Furthermore mold powders are used in continuous casting processes whereby the material properties also affect the efficiency of the casting and the steel cleanness of the semi-finished goods. For estimation of these values the maximum bubble pressure method was introduced at the Institute of Iron and Steel Technology at Technical University Bergakademie Freiberg, Germany, were measurements are done in the melts without contact to ambient atmosphere. The method was now adapted in this work for the measurement of molten slags and industrial mold powder slags. First in the experimental work a binary system with 50 wt. % CaO and 50 wt. % Al_2O_3 and a synthetic CaO-SiO_2 system with different SiO_2 content were investigated followed by an industrial CaO-SiO_2-Al_2O_3 blast furnace slag system. Moreover investigation on industrial available mold powder slags with high transient CaF_2 (14 wt. %) content were initiated with step wise reduced Na_2O content. The results for density and surface tension were discussed in relation to the chemical composition and temperature of the melts.

Key words: molten slags, fluxes, thermophysical properties, maximum bubble pressure, high temperature measurements

1. Introduction

The experimental work was undertaken to provide thermophysical properties such as density and surface tension for mold powder fluxes and industrial slags related to their chemical composition. A wide range of process values can be taken from Slag Atlas [1]. As seen in experimental investigations below there are a wide scatter in process values for same slag systems and for new compositions of mold powder fluxes calculated values by theoretical models could be insufficient for precise surface tension and density data.

Determination of thermophysical properties is of major importance. For modeling of dissolution rate of oxide inclusions into slag precise values, e.g. of density, is needed [2]. Furthermore ladle glaze is marked out to provide major inclusions in steel processing, where slag penetration rate into refractory is dependent to materials properties such as interfacial tension and density [3]. According to *Janke* [4] density of metallurgical slags are needed to describe behavior of smelting of metals physically and chemically, description of slag structure and determination of slag properties such as surface tension. Furthermore in blast furnace process slag phase is important for separation of non-reducible components of ores and metallurgical work, whereby surface tension as slag property has main influence on draining of primary slag [5]. Density is also needed for calculation of thermal conductivity [6]. According to *Olivares* et al. [7] slag density measurements were used to observe changes in mold powder composition. Change in slag composition of about 0.1 wt % was experimentally observed in a change of slag density. Also mold fluxes used in continuous casting have large influence to oxidation of steel, thermal insulation and inclusion absorption [8]. Foaming behavior of silicate slags is dependent to thermophysical properties, surface tension and viscosity have main influence on it [9,10]. According to *Nexhip* et al. [11] draining rate of liquid in CaO-SiO_2-Al_2O_3 slag is mainly influenced by surface tension.

2. Experimental

2.1 Sample preparation

For verification of installed experimental setup a binary CaO-Al_2O_3 (50-50 wt. %) and a binary CaO-SiO_2 with two different SiO_2 contents was synthetic mixed before. The liquidus temperature $T_{liq.}$ were taken from FactSage 6.2 calculations corresponding to chemical composition of the slag type. Moreover an industrial blast furnace slag containing CaO-SiO_2-Al_2O_3 was used. As mold powder flux a standard composition was defined followed by different Na_2O steps in the chemical composition to obtain influence on surface tension. $T_{liq.}$ for mold powder fluxes was measured with heating microscopy corresponding to DIN 51730 (2006 09)/ISO 540 (1995-03) seen in Fig. 1.

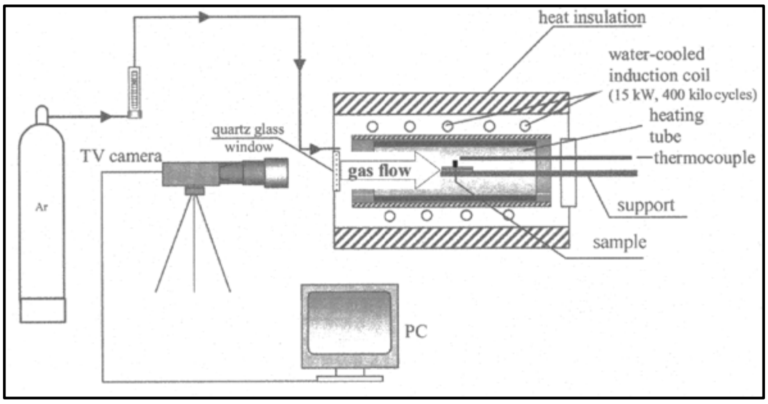

Fig. 1: Heating microscopy for measuring of liquidus temperature at IEST.

Before and after measurements of the slag systems all samples were premelted in an inductive furnace under protective atmosphere and slags and fluxes were chemical analyzed by X-ray fluorescence spectrometry. The chemical composition of all considered slag types are listed below where main changes in same slag type are grey marked in Table 1.

Table 1: Analyzed compositions of investigated slag samples.

Sample	Analyzed compositions (mass %)											$T_{liq.}$
	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	MnO	CaF_2	K_2O	P_2O_5	Na_2O	TiO_2	°C
$CaO-Al_2O_3$	50	0.09	0	0.19	50	0	0	0	0	0.02	0	1362
$CaO-SiO_2$, mod. 1	40.75	59.84	0.10	0.13	0.87	0.01	0.00	0.00	0.00	0.00	0.03	1489
$CaO-SiO_2$, mod. 2	38.48	63.98	0.09	0.11	0.15	0.01	0.00	0.00	0.00	0.00	0.03	1472
Blast furnace slag	39.58	35.47	0.61	8.59	12.16	0.19	0	0.39	0	0.22	0.57	1500
Mold powder flux, standard	30.96	44.00	0.26	0.93	0.70	0.06	13.97	0.03	0.02	8.60	0.04	1240
Mold powder flux, Na-2	32.66	45.00	0.25	0.90	0.70	0.06	13.56	0.04	0.02	6.40	0.04	1284
Mold powder flux, Na-6	34.60	46.90	0.27	1.00	0.70	0.06	13.77	0.04	0.02	2.40	0.03	1393
Mold powder flux, Na+2	30.60	42.80	0.22	0.90	0.60	0.06	13.77	0.03	0.02	10.60	0.03	1187

2.2 Measurement

The experimental investigations were performed after the maximum bubble pressure method MBP. An experimental device was settled up at the Institute of Iron and Steel Technology where results of surface tension and density measurements on liquid Cr-Mn-Ni systems were published [12,13]. In the investigation of liquid slag systems a modified furnace device was used and is shown in Fig. 2. A rod drilled molybdenum (wt. % Mo >99.97) capillary in dimension 3.175·0.381·400 was used. Slag systems with comparable filling height in Mo crucible were set in heating zone of inductive furnace. The capillary is fixed during measurements and furnace will move in vertical position to change the immersion depth of the capillary into the liquid slag with a margin of error of ± 0.005 mm. Temperature is controlled via Type B thermocouple (Pt-30 % Rh/Pt-6 % Rh) on the bottom of the furnace. Top and bottom purging of foaming gas (95 % N_2/5 % H_2) protect Mo-crucible to high temperature corrosion. The gas system inlet via flow bus system is connected to Mo-capillary and high purity argon 5.0 (≥99.999 % Ar) is used for bubble build up in the liquid. Bubbling rate is kept constant of 5-6 bubbles/min at 1.0 Ncm^3/min flow rate. Through analogous differential pressure signal of pressure sensor and the immersion depth of the capillary density and surface tension are obtained.

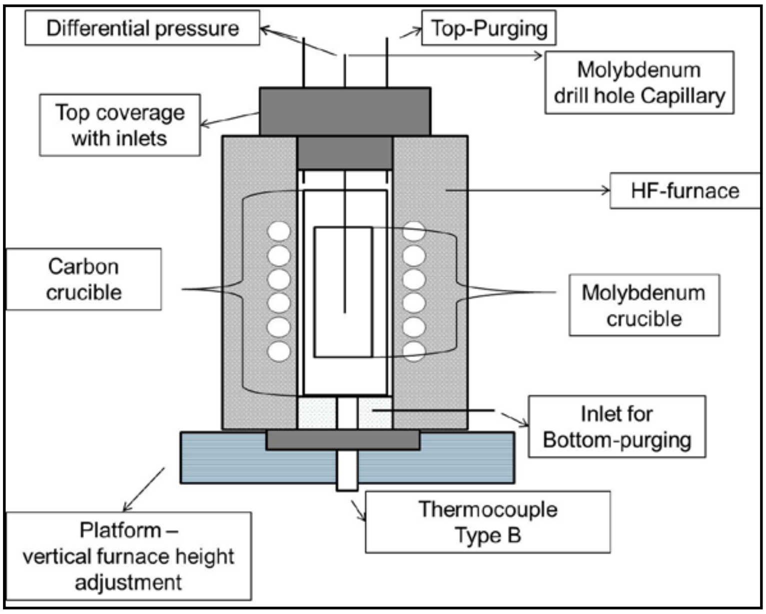

Fig. 2: Experimental setup MBP for determination of density and surface tension of slag systems.

Maximum bubble pressure at bubble rupture point correlates by an increasing immersion depth of the Mo-capillary into the liquid slag system. By increasing depths the static pressure increases leading to higher voltage signals of sensor as seen in Fig. 3. Due to linear behavior of voltage signal and depth, surface tension and density were obtained from process values.

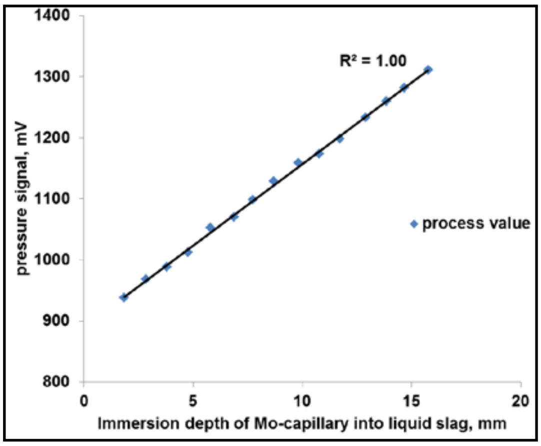

Fig. 3: Pressure signal vs. immersion depth of Mo-capillary.

The signal of pressure sensor is linear and calibrated in a pressure range and constant room temperature from 0 to 100 mbar respectively 0 to 10 V. Corresponding measurement of immersion depth (h) in the liquid the surface tension is calculated after following equation [14]:

$$\mathbf{p}_{max} = \mathbf{p}_{capillary} + \mathbf{p}_{static} \qquad \textbf{(1)}$$

Where p_{max} is maximum bubble pressure, $p_{capillary}$ is capillary pressure and p_{static} is static pressure from liquid. Capillary pressure is expressed as surface tension σ and inner capillary radius r of Mo-capillary. Static pressure p_{static} is product of liquid metal density ρ, acceleration of free fall g and immersion depth h of Mo-capillary into the liquid slag. At the surface level of the liquid slag the immersion depth h is zero where finally the maximum bubble pressure is expressed by capillary pressure:

$$\mathbf{p}_{\mathbf{max}} = \frac{\mathbf{2\sigma}}{\mathbf{r}_{\mathbf{capillary}}} + \boldsymbol{\rho} * \mathbf{g} * \mathbf{h}$$

$$\mathbf{p}_{\mathbf{max}}(\mathbf{h} = \mathbf{0}) = \frac{\mathbf{2\sigma}}{\mathbf{r}_{\mathbf{capillary}}} \qquad \textbf{(2)}$$

Surface tension is calculated as follows and is based on geometric spherical bubbles:

$$\boldsymbol{\sigma} = \mathbf{0.5} * \mathbf{p}_{\mathbf{max}}(\mathbf{h} = \mathbf{0}) * \mathbf{r}_{\mathbf{capillary}} \qquad \textbf{(3)}$$

For increasing capillary radius geometry of bubbles is not spherical and correction after *Schrödinger* [15] introduced. Non spherical behavior of ruptured bubbles is based on dependency of geometry to immersion depth [16]. In this experimental investigation spherical behavior of bubbles was estimated.

The density ρ of liquids is calculated by the slope of the linear regression ($\Delta p_{max}/\Delta h$) and acceleration of free fall g using following equation:

$$\boldsymbol{\rho} = \frac{\Delta \mathbf{p}_{\mathbf{max}}}{\Delta \mathbf{h} * \mathbf{g}} \qquad \textbf{(4)}$$

3. Results and Discussion

After experimental trials slag samples were chemically analyzed as shown in Table 2. It is seen that binary $CaO-Al_2O_3$ and $CaO-SiO_2$ slag systems are stable in their chemical composition; also for industrial blast furnace slag no significant change in composition was observed. For mold powder fluxes due to volatile behavior of fluorine, F_2 content equally CaF_2 in slag disappeared in gas phase.

Table 2: Analyzed compositions of investigated slag samples after experimental trials.

Sample	Analyzed compositions (mass %)										
	CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	MnO	CaF_2	K_2O	P_2O_5	Na_2O	TiO_2
$CaO-Al_2O_3$	50	0.06	0	0.2	50	0	0	0	0	0	0
$CaO-SiO_2$, mod. 1	40.78	59.53	0.09	0.12	0.29	0.01	0.00	0.00	0.00	0.00	0.03
$CaO-SiO_2$, mod. 2	38.57	63.30	0.13	0.10	0.33	0.01	0.06	0.00	0.00	0.00	0.04
Blast furnace slag	40.36	36.35	0.36	8.68	12.77	0.18	0	0.01	0	0.02	0.56
Mold powder flux, standard	33.08	45.71	0.19	0.89	0.61	0.02	10.23	0.00	0.01	8.24	0.02
Mold powder flux, Na-2	34.92	46.48	0.19	0.94	0.81	0.02	9.84	0	0.01	6.13	0.01
Mold powder flux, Na-6	36.17	48.66	0.19	1.01	0.88	0.03	10.99	0.00	0.00	2.12	0.02
Mold powder flux, Na+2	34.68	44.37	0.14	0.89	0.73	0.02	7.81	0.00	0.01	10.16	0.01

For verification of experimental setup $CaO-Al_2O_3$ slag systems was investigated. Experimental values for density and surface tension are shown in Fig. 4 and Fig. 5. Experimental values for density were compared with results from *Gammal* et al. [17], *Zielinski* et al. [18] and *Sikora* et al. [19]. Density will decrease by increasing temperature from approx. 2.87 10^3 kgm^{-3} at 1498 °C to 2.72 10^3 kgm^{-3} at 1648 °C. Values are in good agreement according to *Zielinski* et al. where maximum bubble pressure was used. In addition surface tension values where compared to *Ershov* et al. [20], *Krinochkin* et al. [21]. For model calculation after *Sato* [22] and *Salmang* [23] following values of surface tension coefficients were considered, Table 3 and Table 4.

Table 3: Surface tension coefficient according to *Sato* at 1400 °C [22].

	Cr_2O_3	CaF_2	Fe_2O_3	MnO	TiO_2	CaO	K_2O	SiO_2	Al_2O_3	MgO	Na_2O
σ_i in mN/m	575	283	550	650	380	610	155	290	650	525	300
Equation	$\sigma_{slag} = \sum N_i \times \sigma_i$ Where N_i is percentage of mol of component i in slag and σ_i surface tension coefficient of component i.										

Table 4: Surface tension coefficient according to *Salmang* [23].

	Cr_2O_3	CaF_2	Fe_2O_3	MnO	TiO_2	CaO	K_2O	SiO_2	Al_2O_3	MgO	Na_2O
σ_i	-5.9	3.7	4.5	4.5	3	4.8	0.1	3.4	6.2	6.6	1.5
Equation	$\sigma_{slag} = \sum X_i \times \sigma_i - 0.04 \times (T_{slag} - 1183K)$ Where X_i is weight percent of component i in slag and σ_i surface tension coefficient of component i.										

It is shown that there is wide range of surface tension values for same composition. Surface tension decreases with increasing temperature from approx. 0.62 Nm^{-1} at 1523 °C to 0.59 Nm^{-1} at 1648 °C and in good agreement with data from *Zielinski* et al. For stable binary $CaO-Al_2O_3$ slag system there is wide range of values for density and surface tension for equal temperature range.

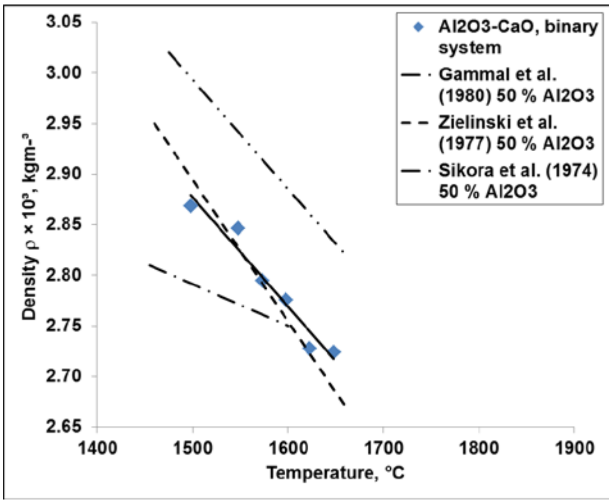

Fig. 4: Experimental values of density for $CaO\text{-}Al_2O_3$ slag system compared with references.

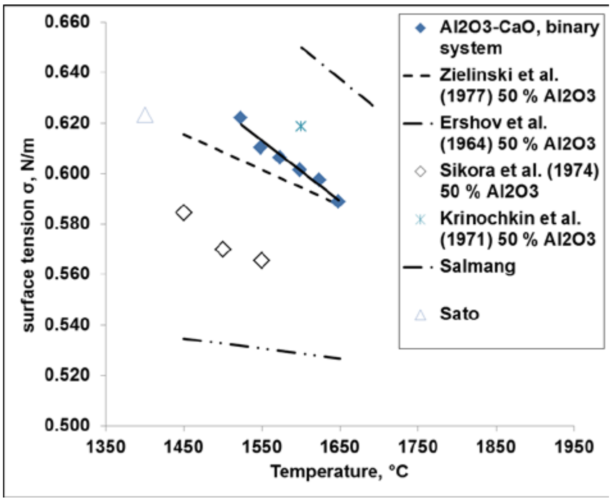

Fig. 5: Experimental values of surface tension for $CaO\text{-}Al_2O_3$ slag system compared with references.

It is shown in Fig. 4 that density decreases by an increase in temperature. There is good agreement for modification 1 corresponding approx. 60 wt. % SiO_2 content to *Popel* [24] and for modification 2 corresponding approx. 64 wt. %SiO_2 content to *Ono* et al. [25]. Model calculation according to *Tomlinson* et al. [26] showed increase of slag density at same temperature for decreasing SiO_2 content, but the step between both calculated values is lower than in experimental values observed. No significant increase of surface tension with higher SiO_2 contents and increasing temperatures was observed as seen in Fig. 7. Higher SiO_2 content in slag reduces surface tension from 0.40 Nm^{-1} for 60 wt. % SiO_2 down to 0.37 Nm^{-1} at 1668 °C respectively. Influence of SiO_2 content in slag to surface tension was also mentioned in [27]. From determined data, strong influence of SiO_2 content to density and surface tension was experimentally observed.

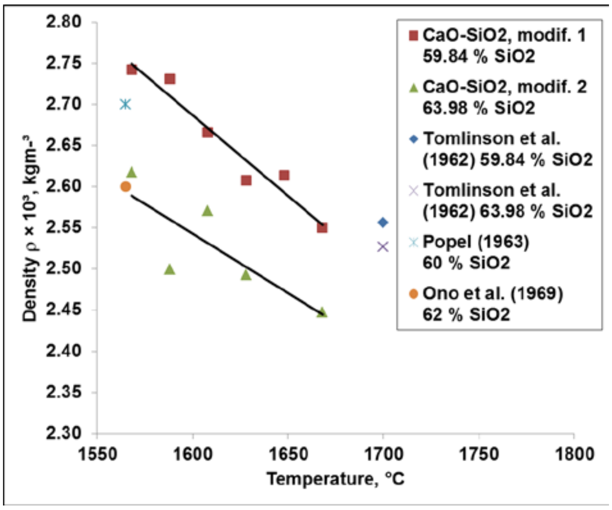

Fig. 6: Experimental values of density for $CaO\text{-}SiO_2$ slag system compared with references.

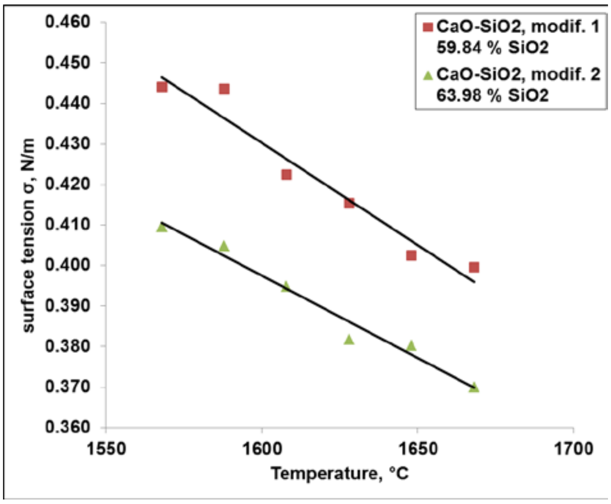

Fig. 7: Experimental values of surface tension for $CaO\text{-}SiO_2$ slag system.

Determined thermophysical properties for blast furnace slag can be taken from Fig. 8 and Fig. 9. Both density and surface tension show right tendency of decrease of values by increasing temperatures. Where density decreases from approx. 2.83 10^3 kgm^{-3} at 1498 °C down to 2.70 10^3 kgm^{-3} at 1648 °C and surface tension from 0.45 Nm^{-1} at 1498 °C to

0.42 Nm^{-1} at 1648 °C. *Inaba* et al. [6] also investigates blast furnace slag via maximum bubble pressure method, where surface tension value is higher than in this experimental work. The effect could be related to higher basicity in slags considered in [6].

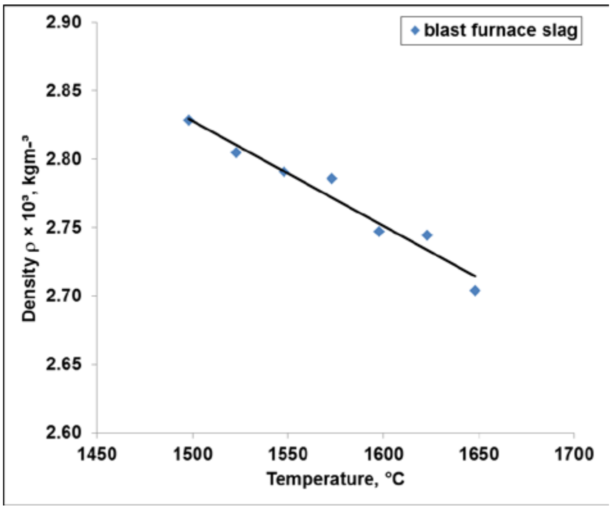

Fig. 8: Experimental values of density for blast furnace slag.

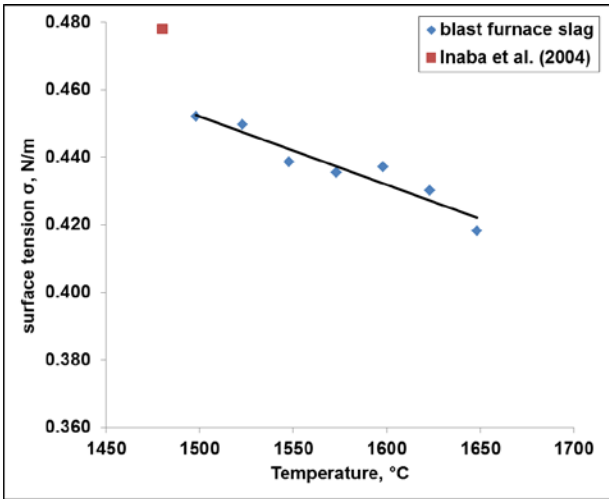

Fig. 9: Experimental values of surface tension for blast furnace slag.

Density values of mold powder fluxes at 1400 °C are linked to Na_2O contents. *Ivanov* et al. [28] showed tendency of density decrease by increasing values for Na_2O content in slag. Investigated values for mold powder fluxes are in agreement and decrease by increasing Na_2O wt. percentage. The drop of experimental values is less compared to *Ivanov* et al. For mold powder flux containing 2.12 wt. % Na_2O density is 2.75 10^3 kgm^{-3} continuously dropping to 2.68 10^3 kgm^{-3} at 10.16 wt. % Na_2O. Similar behavior for surface tension is seen in Fig. 11. By steady increase of Na_2O content in mold powder fluxes surface tension decreases from 0.362 N/m to 0.310 N/m, effect of Na_2O previously mentioned in [29]. Calculated values according to *Salmang* and *Sato* at 1400 °C are higher at same Na_2O content than experimentally observed. There is lack in model description for investigated mold powder fluxes with different Na_2O steps.

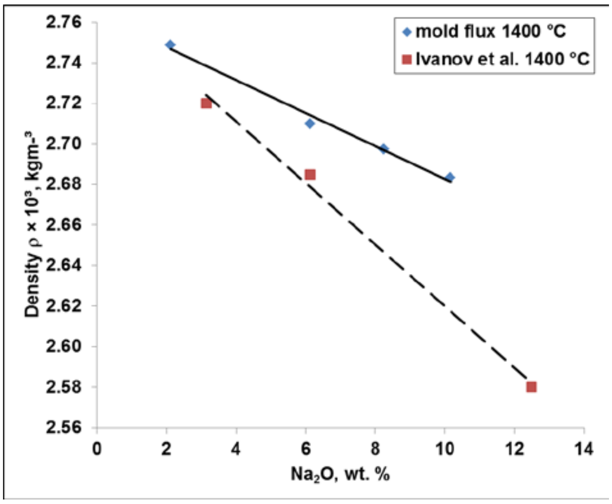

Fig. 10: Experimental values of density for mold powder fluxes and corresponding Na_2O content.

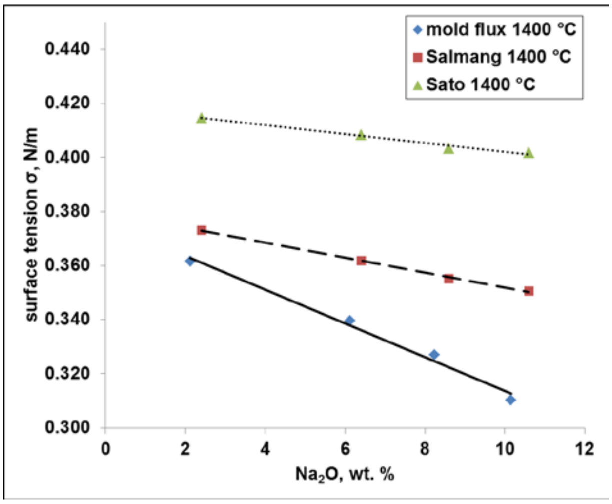

Fig. 11: Experimental values of surface tension for mold powder fluxes and corresponding Na_2O content.

Mold powder fluxes were measured at 1400 °C, all other slags were measured in selected temperature range, for binary systems there is strong temperature influence on density. Multi component slag, e.g. blast furnace slag has lower temperature influence on density. Temperature coefficient of surface tension for all synthetic slags and blast furnace slag is in dimension of 10E-04 which is in good agreement to literature [29], Table 5.

Table 5: Temperature coefficients of surface tension and density for investigated slags.

Investigated slag system	$\frac{d\rho}{dT}$ in $[\frac{kg}{m^3 \times K}]$	$\frac{d\sigma}{dT}$ in $[\frac{N}{m \times K}]$
CaO-Al_2O_3	-1.1	-2.4E-04
CaO-SiO_2, mod. 1	-1.9	-5.1E-04
CaO-SiO_2, mod. 2	-1.5	-4.1E-04
Blast furnace slag	-0.77	-2.0E-04

4. Conclusions

In this experimental investigation it was shown, that there is strong influence on temperature to density and surface tension for binary slag systems with non-surface active components in chemical composition. In addition influence of increasing Na_2O content in mold powder fluxes on thermophysical slag properties was verified. According to published data in literature it is seen that there is a wide range of values available for same slag compositions. By this, also model calculation is limited to certain chemical composition. Furthermore for new slag types of slag and mold fluxes values of density and surface tension in liquid slags are necessary to be obtained experimentally. Maximum bubble pressure method is a fundamental method for precise determination of thermophysical properties.

Acknowledgement

This work was founded by the European Social founds ESF and the free state of Saxony which are gratefully acknowledged. Furthermore the experimental investigations were supported by the technical workforce at the Institute of Iron and Steel Technology Freiberg, Saxony.

References

[1] Slag Atlas 2nd edition. Verlag Stahleisen GmbH, 1995.

[2] P. Rocabois, H. Saint Raymond, C. Gatellier. Physical and Theoretical Modelling of Alumnia Inclusions Entrapment by Slags. 2nd ICS, 2001, pp. 255-264.

[3] S. Riaz, K.C. Mills, K. Bain. Ladle Glazes. 2nd ICS, 2001, pp. 275-286.

[4] D. Janke. Physical Properties of slags. In Schlacken in der Metallurgie, 1984, pp. 31-60, in German.

[5] K. Koch, H.J. Renner, H. Schliephake. Slags in iron ferrous metallurgy. In Schlacken in der Metallurgie, 1984, pp. 175-189, in German.

[6] S. Inaba, Y. Kimura, H. Shibata, H. Ohta. Measurements of Physical Properties of Slag Formed around the Raceway in the Working Blast furnace. ISIJ International, 2004, 44 (12), pp. 2120-2126.

[7] R. Olivares, M.P. Brungs, H. Liang. Monitoring of Slag Composition Changes by Density Measurements. Metallurgical Transactions B, 1991, 22B (6), pp. 305-307.

[8] J. Elfsberg, T. Matsushita. Measurements and Calculation of Interfacial Tension between Commercial Steels and Mould Flux Slags. Steel research int., 2011, 82 (4), pp. 404-414.

[9] D. Skupien, D.R. Gaskell. The Surface Tensions and Foaming behavior of Melts in the System CaO-FeO-SiO_2. Metallurgical Transactions B, 2000, 31B (10), pp. 921-925.

[10] K. Koch, J. Falkus, R. Bruckhaus. Physico-chemical and physical properties of slags at steel making. Archive of Metallurgy, 1994, 39 (2), pp. 147-154, in German.

[11] C. Nexhip, S. Sun, S. Jahanshahi. Some Observations on the Draining of CaO-SiO_2-Al_2O_3 Slag Bubble Films. Metallurgical Transactions B, 2000, 31B (10), pp. 1105-1115.

[12] T. Dubberstein, M. Hötzel, R. Hagemann, P. Heller, P.R. Scheller. Some Thermophysical Properties of Liquid Cr-Mn-Ni-Steels. steel research int., 2011, 82 (9), pp. 1122-1128.

[13] T. Dubberstein, P.R. Scheller. Determination of density and surface tension of high manganese steels in liquid state. Werkstoffe und werkstofftechnische Anwendungen, Chemnitz, 2011, 63, pp. 325-332, in German.

[14] T. IIDA, R.I.L. Guthrie: The Physical Properties of Liquid Metals. Oxford Science Publications, New York, 1993, pp. 53-55.

[15] R. Schrödinger. Notes about capillary pressure in gas bubbles. Ann. Der Physik,1915, 46, p. 413, in German.

[16] K.J. Mysels. Colloids and Surfaces, 43 (2), 1990, pp. 241–262.

[17] T. El Gammal, R.D. Müllenberg. Archive of Metallurgy, 1980, 51 (6), p. 221.

[18] M. Zielinski, B. Sikora. Pr. Inst. Metall. Zelaza in St. Staszica. 1977, 29 (3-4), p. 157.

[19] B. Sikora, M. Zielinski. Hutnik. 1974, 41 (9), p. 433.

[20] G.S. Ershov, E.A. Popova. Russian Journal of Inorganic Chemistry. 1964, 9 (3), p. 361.

[21] E.V. Krinochkin, K.T. Kurochkin, P.V. Umrikhin. Fiz. Khim. Poverkh. Yav. Rasp. Naukova Dumka, 1971, pp. 179-182.

[22] R. Sato. Powered Mold Additives for Continuous Casting - Characteristic Properties of the Instructions for the Use of C-Series Teemix. Steelmaking Proc., ISS-AIME Detroit, 1979, 62, pp. 48-67.

[23] G. Salmang. Phyiscal and chemical basics of ceramics. Gosstroyizdat, 1959, in German.

[24] S.I. Popel. Sb. Bauchn. Tr. Ural'sk. Politckhn. Inst. 1963, 126, p. 5.

[25] K. Ono, K. Gunji, T. Araki. Nippon Kinzoku Gakkaishi / Journal of the Japan Institute of Metals. 1969, 33 (3), p. 299.

[26] J.W: Tomlinson, M.S.R. Heynes. J. Bockris. Transactions of the Faraday Society. 1958, 54, p. 1822.

[27] M. Askari, A.M. Cameron. Surface Tension of Some CaO-MgO-Al_2O_3-SiO_2 Slags. Canadian Metallurgical Quarterly, 1991, 30 (4), pp. 207-212.

[28] O. Ivanov, L. Savov, D. Janke. Alkali Capacity and Properties of Blast Furnace Type Slags. Steel research int., 2004, 75 (7), pp. 433-441.

[29] M. Hanao, T. Tanaka, M. Kawamoto, K. Takatani. Evaluation of Surface Tension of Molten Slag in Multi-component Systems. ISIJ International, 2007, 47 (7), pp. 935-939.