

## A STUDY OF THE HIGH-TEMPERATURE INTERACTION BETWEEN SYNTHETIC SLAGS AND STEEL

### ŠTUDIJA VISOKOTEMPERATURNE INTERAKCIJE MED SINTETIČNO ŽLINDRO IN JEKLOM

**Karel Gryc<sup>1</sup>, Karel Stránský<sup>2</sup>, Karel Michalek<sup>1</sup>, Zdeněk Winkler<sup>3</sup>, Jan Morávka<sup>4</sup>,  
Markéta Tkadlečková<sup>1</sup>, Ladislav Socha<sup>1</sup>, Jiří Bažan<sup>1</sup>, Jana Dobrovská<sup>5</sup>, Simona Zlá<sup>5</sup>**

<sup>1</sup>VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Metallurgy and Foundry, Czech Republic

<sup>2</sup>Brno University of Technology, Faculty of Mechanical Engineering, Institute of Materials Science and Engineering, Czech Republic

<sup>3</sup>Military Technical Institute of Protection in Brno, Czech Republic

<sup>4</sup>MATERIÁLOVÝ A METALURGICKÝ VÝZKUM s. r. o., Czech Republic

<sup>5</sup>VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Physical Chemistry and Theory of Technological Processes, Czech Republic  
karel.gryc@vsb.cz

*Prejem rokopisa – received: 2011-10-27; sprejem za objavo – accepted for publication: 2012-02-15*

The paper is devoted to selected aspects of the current issues of the high-temperature interaction of the synthetic multicomponent oxidic systems and selected grades of steel. Analysing the consequences of the interaction between slag and molten steel is an integral part of modern research that can be connected with subsequent, applied research in the field of producing and refining steel. The interactions between the synthetic slag and the molten metal is realized after the processing of the liquid steel in the primary metallurgical aggregates, i.e., at the beginning of refining processes of secondary metallurgy. The addition of these synthetic systems (slag) significantly affects many technological processes and indirectly affects the final quality of the cast steel. This influence can be seen on two levels: the metallurgical and the metallographic. Both of these levels of evaluation complement each other.

For the evaluation of the metallurgical aspects of refining processes a number of thermodynamic relations were used, supplemented by empirically established formulas and coefficients. Metallographic analyses utilize modern tools in the study of the structure and the chemical composition of materials, i.e., from light microscopy to sophisticated systems of microanalysis of elemental composition using a scanning electron microscope combined with an energy-dispersive X-ray micro-analyser. It is obvious that this area deserves more focused research and more attention, particularly in the context of the on-going needs for the identification and quantification of phenomena taking place in the following metallurgical innovations.

Keywords: synthetic slag, interaction with steel, saturation

Članek obravnava izbrane vidike aktualnih vprašanj o visokotemperaturni interakciji sintetičnih večkomponentnih oksidnih sistemov v izbranih vrstah jekel. Analiziranje posledic interakcije med žlindro in talino je sestavni del potekajočih raziskav in se lahko poveže z uporabnimi raziskavami na področju proizvodnje in rafinacije jekla. Do interakcije med sintetično žlindro in staljeno kovino pride po izdelavi taline jekla v primarni metalurški peči, na začetku postopka rafinacije v sekundarni metalurgiji. Dodatek sintetične žlindre močno vpliva na številne tehnološke procese in neposredno vpliva na končno kvaliteto ulitega jekla. Ta učinek se kaže na dveh nivojih: na metalurškem in metalografskem. Oba nivoja ocene sta med seboj komplementarna.

Za oceno metalurških vidikov postopka rafinacije je bilo uporabljeno več termodinamskih odvisnosti, dopoljenih z empirično določenimi enačbami in koeficienti. Metalografska analiza uporablja sodobna orodja za študij strukture in kemijske sestave materiala – od svetlobne mikroskopije do zapletenih sistemov mikroanalize, elementne sestave z uporabo vrstičnega elektronskega mikroskopa v kombinaciji z energijsko disperzijsko rentgensko spektroskopijo. Očitno to področje zahteva bolj usmerjene raziskave in večjo pozornost, posebno v kontekstu zahtev, identifikacije in kvantifikacije pojavov, ki so posledica metalurških inovacij.

Ključne besede: sintetična žlindra, interakcija z jeklom, nasičenje

## 1 INTRODUCTION

It is necessary to continuously optimize the production of steel in steel mills. Such an optimization of the metallurgical processes is often connected with operational challenges that could be solved by changes in the slag regime. An integral part of the steel-making process is the use of different types of synthetic slag. These, together with other slag materials, facilitate the successful course of the metallurgical reactions that are necessary to achieve the desired chemical and metallurgical purity of the steels.

In addition to plant experiments, which are an essential and major part of the slag-optimization regimes

and whose results are crucial for the innovations in the final steel production process, there is the possibility of studying the interaction of metal and oxidic systems, e.g., under laboratory conditions.<sup>1-4</sup>

This paper focuses on a discussion of the results of the oriented research that was realized within the grant project ID No. 106/09/0969 with the financial support of the (GACR) Czech Science Foundation. The presented results are not directly tied to any specific operating conditions in a steel plant.

The studied synthetic slags react in real conditions with steel, especially together with pre-existing slag and/or with currently added slag-forming materials. Al-

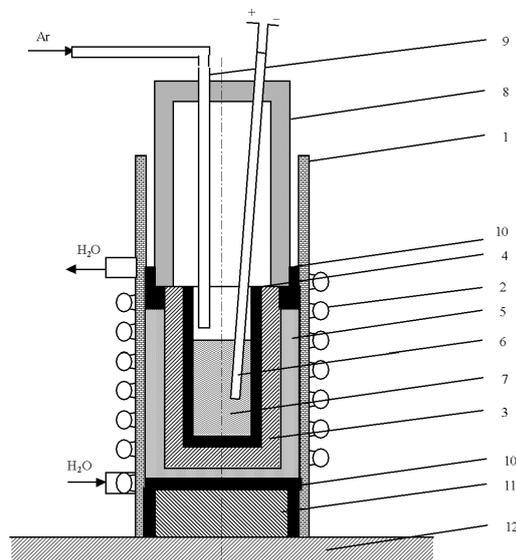
though this study of the high-temperature interactions between synthetic oxidic melts and steels lies outside the field of applied research, its results can extend current knowledge about the mechanisms associated with these systems of melts. The methods used could provide guidance to address the challenges associated with solving the practical aspects of steelmaking technology.

A series of interesting results was obtained in the course of this project. That is why the focus of this paper will be only on an analysis of the changes in the chemical composition of the studied synthetic oxidic mixtures, depending on the chemical composition of steel, with which these compounds reacted during the laboratory heats.

## 2 EXPERIMENTAL CONDITIONS AND CHARACTERISATION OF THE STUDIED MELTS

Heats designed for the study of the interaction between liquid metal and synthetic oxidic melts were carried out under laboratory conditions at the Department of Metallurgy in an induction furnace (**Figure 1**) connected to a GV 22 high-frequency generator.

Each 300 g sample of steel (**Table 1**) was melted in a corundum crucible under the continuous maintenance of a protective atmosphere (Ar, flow rate of 0.5 L min<sup>-1</sup>). One of the following synthetic oxidic mixtures (**Table 2**) was added (30 g) after reaching the temperature of



**Figure 1:** Diagram of the experimental equipment; 1 – protective cylinder of SiO<sub>2</sub>, 2 – water-cooled inductor, 3 – graphite block, 4 – working crucible, 5 – protective Al<sub>2</sub>O<sub>3</sub> powder, 6 – PtRh6 – PtRh30 thermocouple, 7 – molten metal, 8 – protective cover, 9 – supply of argon, 10 – TERMOVIT cotton, 11 – insulating brick, 12 – fireclay base

**Slika 1:** Shematski prikaz eksperimentalne opreme: 1 – zaščitna obloga iz SiO<sub>2</sub>, 2 – vodno hlajen inductor, 3 – grafitni blok, 4 – talilni lonec, 5 – zaščitni Al<sub>2</sub>O<sub>3</sub> prašek, 6 – PtRh6 – PtRh30 termočlen, 7 – staljena kovina, 8 – zaščitni pokrov, 9 – dovod argona, 10 – TERMOVIT preja, 11 – izolacijska opeka, 12 – ognjevarna obloga

1600 °C. The melting process of oxidic mixtures requires approximately 2.5 min. However, a stable temperature (1600 °C) was kept for an additional 10 min. Then, the generator was stopped. The solidified steel and slag were removed from the crucible after cooling down. Subsequently, samples were prepared to perform the appropriate analyses.

**Table 1:** The content of the monitored elements in the selected steels  
**Tabela 1:** Vsebnost analiziranih elementov v izbranih jeklih

Identification of steel	Chemical composition in mass fractions, w/%					
	C	Mn	Si	P	S	Cr
1	0.19	1.16	0.14	0.015	0.033	1.100
2	0.21	1.04	0.13	0.033	0.170	0.054
3	0.12	1.20	<0.01	0.060	0.340	0.080
4	0.19	1.34	0.18	0.015	0.015	0.055

**Table 2:** Content of selected oxidic mixture components

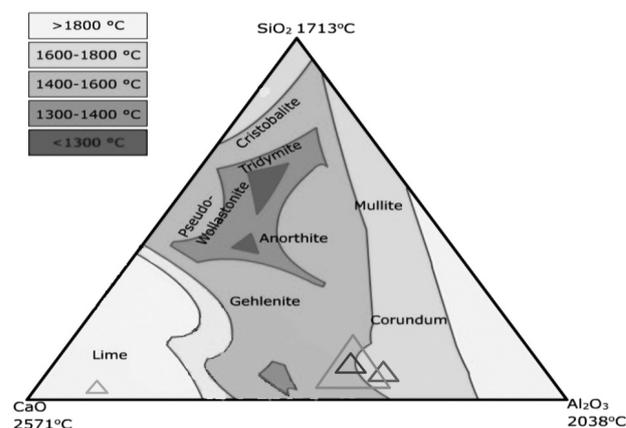
**Tabela 2:** Vsebnost komponent v izbranih mešanica oksidov

Identification of oxidic mixture	Chemical composition in mass fractions, w/%								
	Fe <sub>tot</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	S	P <sub>2</sub> O <sub>5</sub>	MgO	MnO	Cr <sub>2</sub> O <sub>3</sub>
A	0.42	83	11	1	0.05	0.44	1.91	0.81	0.49
B	0.79	48	46	2	0.12	0.39	1.08	0.2	0.41
C	1.96	34	47	9	0.19	0.55	1.58	0.23	0.31
D	1.21	49	39	5	0.32	0.39	1.68	0.07	–
E	0.63	31	56	5	0.67	0.12	3.84	0.02	0.02

It is obvious (**Table 1**) that the steels were selected based on such a chemical composition in order to assess the impact of significant changes in the content of the significant elements on the result of the metallurgical refining process.

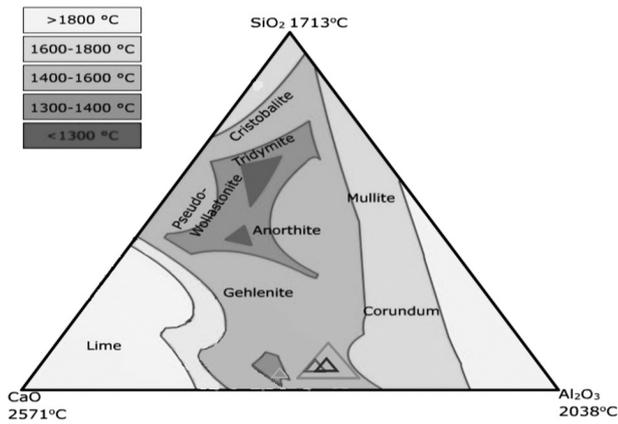
## 3 DISCUSSION

The contents of the elements in the steel and slag components listed in this paper in **Table 1** and **2** were determined using standard methods.



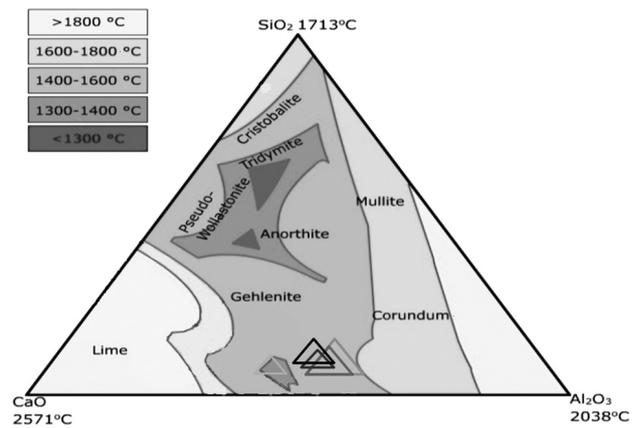
**Figure 2:** Ternary diagram for the starting oxidic mixture (A) and the slag obtained after the reaction with molten steels

**Slika 2:** Ternarni diagram začetne mešanice oksidov (A) in žilindra, ki je nastala po interakciji s staljenimi jekli



**Figure 3:** Ternary diagram for the starting oxidic mixture (B) and the slag obtained after the reaction with molten steels

**Slika 3:** Ternarni diagram začetne mešanice oksidov (B) in žlindra, ki je nastala po interakciji s staljenimi jekli



**Figure 5:** Ternary diagram for the starting oxidic mixture (D) and the slag obtained after the reaction with molten steels

**Slika 5:** Ternarni diagram začetne mešanice oksidov (D) in žlindra, ki je nastala po interakciji s staljenimi jekli

Analyses of the elements in the steel:

- C, S using a CS 230 LECO combustion analyser,
- Mn, Si, P, Cr using a PW 1400 Philips X-ray spectrometer.

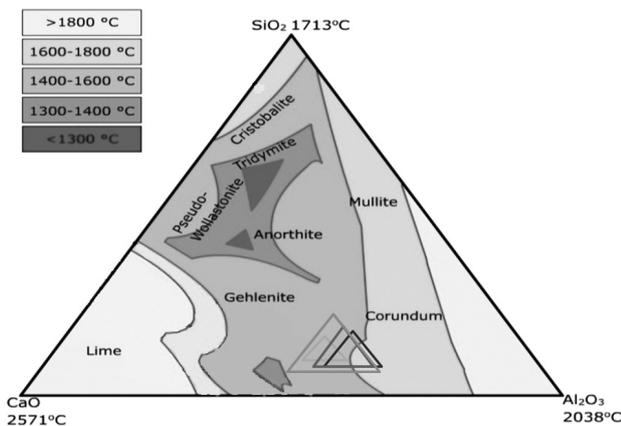
The analysis of the content of the monitored slag components was implemented using the analytic complex formed by the EDAX PHILIPS energy-dispersive micro-analyser in conjunction with the PHILIPS scanning electron microscope. A detailed description of the apparatus and the applied methods can be, together with the results of the analysis, found in the report<sup>5</sup>.

The results of the analyses are summarized in the simplified CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary diagrams (Figures 2 to 6). It is obvious that in terms of securing good kinetic conditions of the refining processes (low viscosity of the oxidic systems), it is advantageous to have a chemical composition of oxidic systems with a melting point below the working temperature of steel during its processing in a given technology node.

The ternary diagrams (Figures 2 to 6) show the chemical composition of the initial oxidic mixture (green) and the slag after laboratory heats with different steels (1 – dark blue, 2 – red, 3 – light blue, 4 – black).

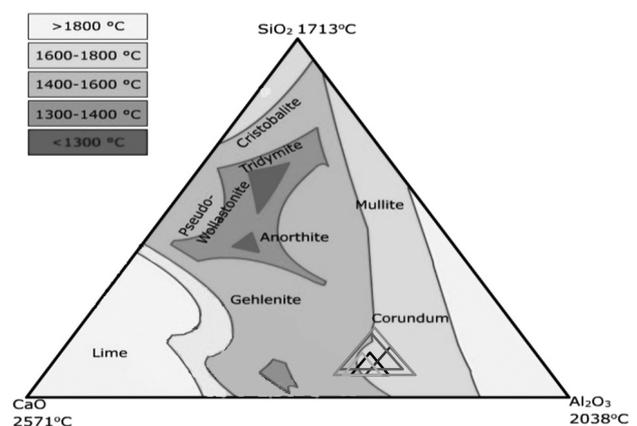
Figure 2 shows a ternary diagram with plotted areas for the oxidic mixture A (83 % CaO-11 % Al<sub>2</sub>O<sub>3</sub>-1 % SiO<sub>2</sub>) and the slag after the reaction with molten steels 1 to 3. It is obvious that there is a significant change in the chemical composition due to the interaction of an oxidic mixture with steels. The resulting oxidic melt contains mass fractions of Al<sub>2</sub>O<sub>3</sub> from 51 % to 60 %. The chemical composition of the resulting slag, in the case of an interaction with the steels 1 and 3, ensures that the slag was liquid at temperatures above 1600 °C. In contrast, the resulting slag for the interaction with steel No. 2 occurs in an area that does not guarantee its liquid state.

The initial, synthetic slag B (48 % CaO-46 % Al<sub>2</sub>O<sub>3</sub>-2 % SiO<sub>2</sub>) occurs in the ternary diagram area that is characterized by melting temperatures in the interval



**Figure 4:** Ternary diagram for the starting oxidic mixture (C) and the slag obtained after the reaction with molten steels

**Slika 4:** Ternarni diagram začetne mešanice oksidov (C) in žlindra, ki je nastala po interakciji s staljenimi jekli



**Figure 6:** Ternary diagram for the starting oxidic mixture (E) and the slag obtained after the reaction with molten steels

**Slika 6:** Ternarni diagram začetne mešanice oksidov (E) in žlindra, ki je nastala po interakciji s staljenimi jekli

1300 °C to 1400 °C (**Figure 3**). The chemical composition of the reaction products, is after the interaction of the (B) oxidic mixture with steels No. 1 to 3, close to the original one. However, due to the increasing  $\text{Al}_2\text{O}_3$  content, the steels have increased their melting temperature, to the 1400 °C to 1600 °C interval, which still guarantees their high reactivity in order to maintain their relatively low viscosity.

The initial oxidic mixture C (34 % CaO-47 %  $\text{Al}_2\text{O}_3$ -9 %  $\text{SiO}_2$  – **Figure 4**) contains the most silica compared with the previous slag (**Figures 2 and 3**). The CaO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  final slag remains in the ternary diagram, mostly in the same area, which is characterised by the melting-temperature interval from 1400 °C to 1600 °C after the reaction with steels 1 to 3. The melting temperature exceeds 1600 °C only partially.

The initial chemical composition of the oxidic mixture D (49 % CaO-39 %  $\text{Al}_2\text{O}_3$ -5 %  $\text{SiO}_2$  – **Figure 5**) is very close to the chemical composition of the mixture B (**Figure 3**). Its position in the ternary diagram is also located in areas with a relatively low melting point (1300–1400 °C). The oxidic interaction products have, compared to the oxidic mixture B ( $w = 2\text{--}4\%$ ) a higher content of silica ( $w = 5\text{--}7\%$ ).

The oxidic mixture E (31 % CaO-56 %  $\text{Al}_2\text{O}_3$ -5 %  $\text{SiO}_2$  – **Figure 6**) with its initial chemical composition, differs from the previous ones (B, C, D) in terms of a higher content of  $\text{Al}_2\text{O}_3$  to the extent that it already appears in the area with a relatively high melting point (above 1600 °C) in the ternary diagram. The products of the mixture interaction with the metal melt no longer contain the higher content of  $\text{Al}_2\text{O}_3$ , and are located at the identical area in the ternary diagram.

#### 4 CONCLUSION

The analysis of the interaction of synthetic oxidic mixtures with steels having different contents of the major metallurgical elements C, Mn, Si, P, S, Cr resulted in the following conclusions.

The interaction of the above-discussed oxidic systems and selected steels led to a final content of  $\text{Al}_2\text{O}_3$  in

the interval ( $w = 46\text{--}60\%$ ). Although the content of  $\text{Al}_2\text{O}_3$  in the initial oxidic mixture (A) was the lowest (11 wt.%), in comparison with the other mixtures the  $\text{Al}_2\text{O}_3$  content was the highest of all ( $w = 60\%$ ) after its interaction with the steel (2). These facts lead to the hypothesis that the settings of the experiments enabled the saturation of the resulting slag with  $\text{Al}_2\text{O}_3$  content in the interval 46 % to 60 %. This saturation occurs within 10 min of the dissolution of the added oxidic mixtures. Furthermore, we can say that a clear dependence of the resulting chemical composition of the oxidic mixture on steels, with which they interacted, has not been proved. The content of  $\text{SiO}_2$  did not increase above 9 % in all the studied cases and its influence on the change of the melting temperature of the oxidic mixtures was not significant.

#### Acknowledgement

The presented research focused on the high-temperature interactions between synthetic slag and steel was carried out with financial support from GACR (Czech Science Foundation) under project ID No. 106/09/0969.

#### 5 REFERENCES

- <sup>1</sup> B. Smetana, S. Zlá, M. Žaludová, J. Dobrovská, P. Kozelský, Application of High Temperature DTA to Micro-Alloyed Steels, *Metalurgija*, 51 (2012) 1, 121–124
- <sup>2</sup> B. Smetana, S. Zlá, J. Dobrovská, P. Kozelský, Phase transformation temperatures of pure iron and low alloyed steels in the low temperature region using DTA, *International Journal of Materials Research*, 101 (2010) 3, 398–408
- <sup>3</sup> R. Dudek, E. Dobrovský, J. Dobrovská, Interpretation of Inorganic Melts Surface Properties on The Basis of Chemical Status and Structural Relations, *International Journal of Materials Research*, 99 (2008) 12, 1369–1374
- <sup>4</sup> K. Gryc, B. Smetana, K. Michalek, V. Sikora, M. Tkadlečková, S. Zlá, M. Žaludová, J. Dobrovská, Connecting of Basic and Applied Research in the Field of Thermo-Physical Study of the Properties of Steels, Slag and Ferro-Alloys, In 20<sup>th</sup> Anniversary International Conference on Metallurgy and Materials – METAL 2011, 125–131
- <sup>5</sup> K. Stránský, J. Janová, Chemical analysis of slags realized in laboratory of Brno University of Technology, FME in 2010. Technical report. BUT, FME, Brno 2010. [in Czech]