THE STUDY OF MOLTEN ZINC INTERACTION ON THE SURFACE OF REFRACTORIES IN THE PRODUCTION OF ZINC OXIDE

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Resume

This paper is closely connected with the complete process of indirect production of ZnO as well as with the problems which occur during the metallurgical process. Purity of raw materials has an important influence on the final quality of ZnO and the occurrence of slag that remains stuck on the walls of furnace linings. ZnO is generally produced in the melting furnaces with different types of ceramic linings. Input materials have to be analyzed and investigated in the order to the predict behavior from the aspect of the complex production process. Moreover, analysis of occurrence of undesirable phases in the batch, the output materials, character of furnace linings and waste material have to be evaluated and observed. Mutual interaction of all components will have a significant impact on the final quality of the ZnO. The result of the investigation of interaction occurring in the components will be used for the proposal of the suitable surface for furnace lining while the mentioned result is mainly obtained on the principle of chemical reactions and bonds. This surface for lining should have a minimum adhesion of the zinc and its alloys relating to production of ZnO.

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1. Introduction

Zinc oxide is used as a semi-product in many fields of production. The most important industries are the rubber, pharmaceutical and glass industries, manufacture of paints etc. Zinc oxide can be also characterized as a semiconductor of type n [1]. Recently, considerable attention has been paid to zinc oxide as a material for the UV LED (Ultraviolet Light-emitting diode), varistors, transparent actuators, piezoelectric transducers and gas sensors, and furthermore it has been considered as suitable material for the construction of liquid crystal displays as well as for production thermal insulation of windows and thin film solar cells [2]. Zinc oxide can be produced by variety of ways, but the most common method of production which is used in Slovak republic is indirect, i.e. pyrometallurgical combustion of zinc and zinc alloys. This method is also called "French process". Nowadays, production of ZnO by French process includes the biggest scale of production in industrial society. Indirect production of ZnO starts by melting zinc and subsequent oxidation with oxygen from the air and it was developed by Le Clair in France in the years from 1840 to 1850 [3].

The process of production is based on batching of metal zinc into the rotary furnace where this metal zinc is molten and then evaporated. The raw or input material for this production method is the metallic zinc and its alloys. The quality of ZnO depends on the starting (raw) materials. There is the occurrence of slag (waste material) which negatively affects the total production process of ZnO and final product during processing of the waste zinc (approx. purity of Zn is 90 wt. %) from galvanic process containing other elements, such as Pb, Fe and Al. According to the fact that zinc (with its higher weight percentage - more than 90 wt. % Zn) occurs as a compound with other elements, we can call this raw material as a zinc alloy.

The coke generator produces thermal energy for oxidation combustion of zinc and the zinc vapors are the result of this process. The given process occurs at temperature which is higher than 1000 °C. Rate of zinc vapor is 8 - 12 $m.s^{-1}$ and leads to a rapid oxidation with atmospheric oxygen and this reaction is indicated by flame of green and white color at the temperature from 1000 up to 1400 °C [4]. The production process in a strong reducing atmosphere is performed according to chemical reactions (1) and (2).

$$Zn_{(s)} \rightarrow Zn_{(l)} \rightarrow Zn_{(g)} \qquad (1)$$

$$Zn_{(g)} + ½O_{2\ (g)} \xrightarrow{+CO/CO_2} ZnO_{(s)} \qquad (2)$$

Small amount of coal dust has been added into the rotary furnace in the favor of final product. A coal is used as reducing agent and its excess separates particles of concentrate and prevents creating blends which can be meltable easily. The different types of coke e.g. the casting coke, the blast furnace coke or a wood coal are commonly used to create the required energy.

However, the mutual chemical reactions of the present elements and compounds in the furnace aggregates cause premature rupture of refractory linings and high adhesion in relation to the walls of the ZnO furnace linings. Zinc oxide has the ability to interfuse into cracks, pores of wall linings and it causes major damage [5]. The impact of environment on the object is the function of a surface while the object is made of given materials. Reaction of the surfaces can be created on the basis of the initiation of rupture or development of degradation and it can be evaluated as an acceptable or an unacceptable fact in relation to technical facility.

It is also well known that the presence of ZnO in a blast furnace causes degradation of coke and iron ore (the given process runs mainly during the recycling a steel scrap metal with impurities of zinc, zinc dust and zinc ash).

2. Experimental materials

2.1. The microstructure of zinc and zinc alloys

Zinc samples were selected on the basis of their similarity to the raw material. Phases were investigated in the microstructure of zinc alloy.

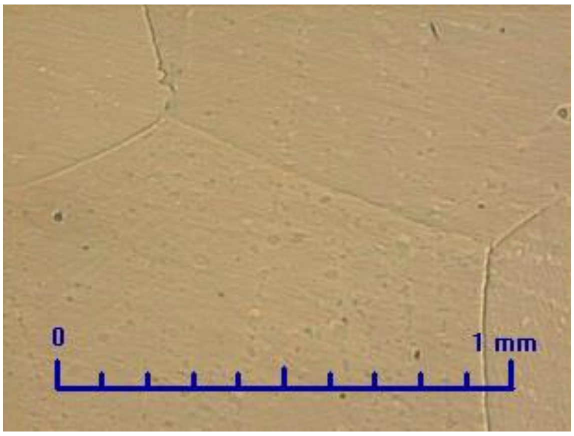

Fig. 1. Microstructure of chemically pure zinc

The detailed analysis and study of input materials is published in paper [6]. It is a relatively soft metal (similar to cadmium), with a good corrosion resistance. Protective oxidic layer that occurs on a surface has a suitable resistance in atmospheric conditions. We investigated samples prepared metallographically by LOM and SEM. We could conclude that the microstructure of the pure metal is formed by monolithic large grains (Fig. 1). Elements which occur in combination with zinc are Fe, Pb, Cd, Sn, etc. and these mixed combinations create

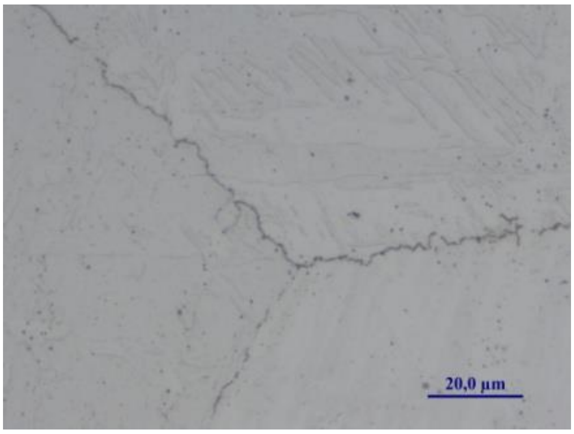

Fig. 2. Cracks in the structure of zinc alloy

various phase types. It is known that pure iron has the highest influence on the structure recrystallization. Crystallization process of zinc occurs when there is the 0.01 wt. % of Fe at 70 - 100 °C. The elements contained in zinc compound have significant effects on its mechanical properties. Lead, cadmium, tin and zinc form easy meltable eutectics which occur at the grain boundaries. They cause decohesion in the hot processing and they are initiators of cracks in the structure of zinc [7] (see Fig. 2 crack formed by casting of molten zinc alloy into an ingot form).

2.2. Zinc oxide

For the better understanding of problem of the technological process in relation to production of zinc oxide, it is necessary to define the output segment - white powder ZnO (Fig. 3). From the chemical point of view, zinc oxide is white inorganic compounds [1]. Layers occupied by zinc atoms alternate with layers occupied by the oxygen atoms. Pure ZnO crystallizes in the hexagonal (wurzite) crystal structure [1] with a lattice parameters $a = 3.25\ 10^{-10}$ m and $c = 5.12\ 10^{-10}$ m [7]. Character of crystal shape depends not only on the crystal lattice, but it also depends on the method of production ZnO associating with the primary crystallization [4]. High attention is paid to research in the modern development of ZnO. ZnO is amphoteric oxide, i.e. oxide reacting with water and it has properties, such as hydroxide as well as acid.

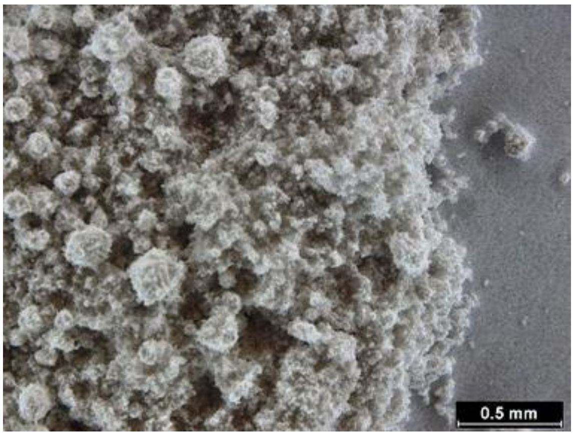

Fig. 3. The zinc oxide powder

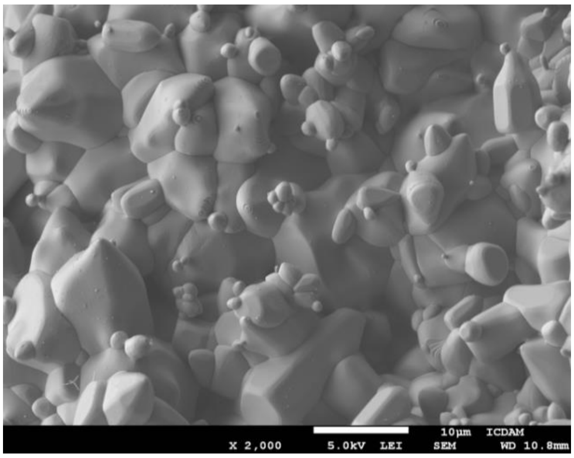

Fig. 4. The grain of recrystallized zinc oxide

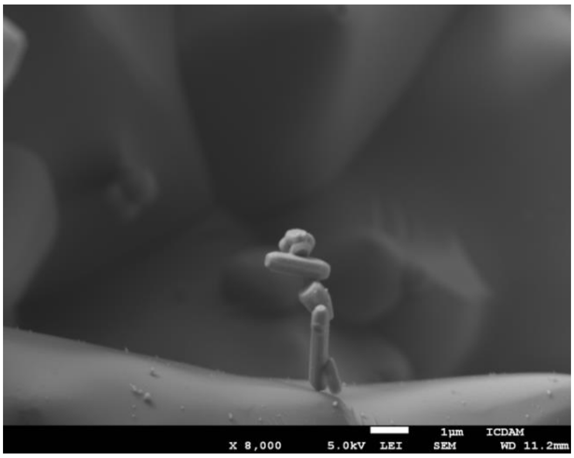

Fig. 5. The detail of ZnO "Stick Figure"

More detailed investigations of re-crystallized mineral - zincit (Fig. 4) enabled us to obtain morphological formations (Fig. 5), where they showed a gradual increase of crystallization in dependence on temperature and rate of crystallization.

2.3. Refractories

The refractories as furnace lining (Fig. 6) are in the direct contact with the hot metal in rotary furnace.

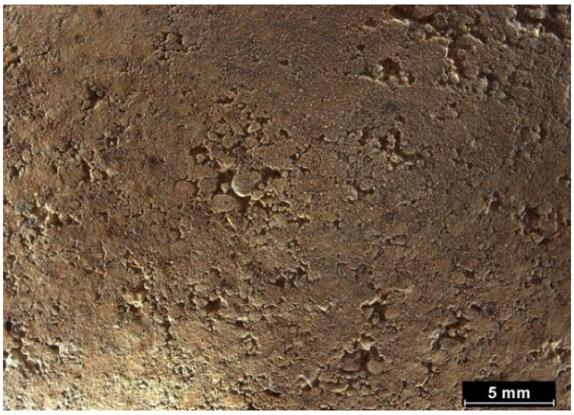

Fig. 6. The view of the surface of chamotte
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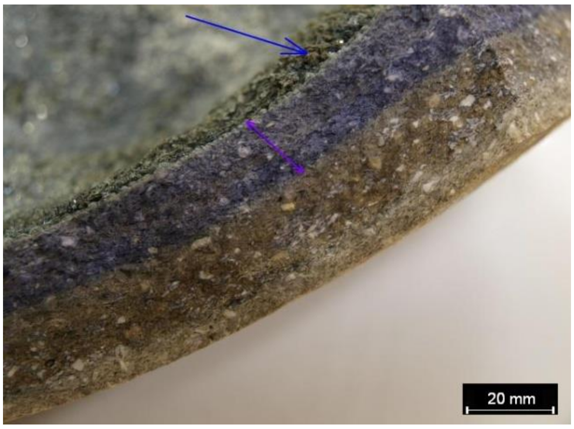

Fig. 7. The chamotte sample
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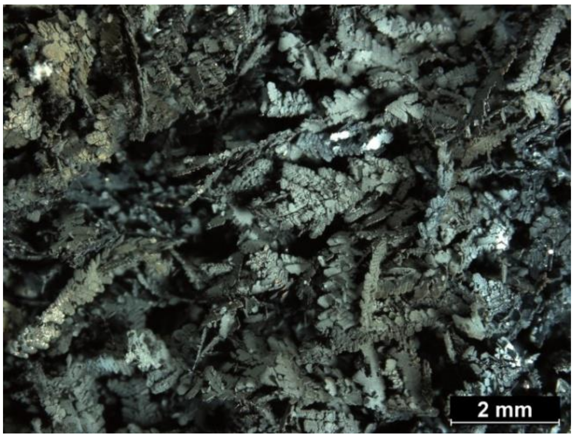

Fig. 8. The zinc slag in form of dendrides

The high melting point and thermodynamic stability at high temperatures are the elementary requirements for completing all the process [8].

Compounds Zn_2SiO_4 and $ZnAl_2O_4$ are created on the basis of the chemical reaction of ZnO and chamotte if this chamotte is used as lining of furnace. Mullite (3 Al_2O_3 + 2SiO_2) is not resistant chemically to the action of zinc oxide [9]. The mullite reacts with zinc oxide to form $ZnAl_2O_4$ and SiO_2 (Fig. 7 - the blue arrow points the remains of the zinc slag on the lining of the sample shown in Fig. 8) and it is at temperature 900 °C.

3. Technology of measurement

The measurements were performed using the stereomicroscopic device NIKON SMZ 1500 (CVUT in Prague, Czech Republic), SEM - JSM 7600F (CVUT in Prague, Czech Republic), AAS –AA 240 VARIAN (SlovZink, a.s. Koseca, Slovakia) and X- Ray diffraction Brűcker 8, KalfaCo with Co-lamp (SAV Bratislava, Slovakia). Setting the measurement - time to step is set up in different cps (counts per second).

4. Results and discussion

Reffering to work [9], refractory materials containing 61.5 wt. % SiO_2, 34.4 wt. % Al_2O_3, 3.18 wt. % Fe_2O_3, 0.25 wt. % CaO, 0.62 wt. % MgO were used for investigation of ZnO interaction with chamotte which was made from Morsk clay. X-ray analysis of the mixture of chamotte and zinc oxide showed that at 1200 - 1300 °C, that is, temperatures of maximum possible reaction (3), there is an important change in the phase composition of the chamotte refractories. Willemite (Zn_2SiO_4) and gahnite ($ZnAl_2O_4$) are formed on the principle of the reaction of the chamotte with the zinc oxide. With a comparatively small (10 wt. %) addition of zinc oxide to the chamotte the following reaction takes place [9]:

$$3\,ZnO + 3\,Al_2O_3.2\,SiO_2 \rightarrow$$

$$\rightarrow 3\,ZnAl_2O_4 + 2\,SiO_2 \qquad (3)$$

In this case, the phase composition of the mixture consists of gahnite, a small quantity of residual mullite, and cristobalite contained in the original chamotte.

Mullite was not observed in the mixture containing 20 wt. % ZnO. With large content of ZnO (30 - 50 wt. %) there was also no mullite. The quantity of Zn_2SiO_4 with the increase in the content of zinc oxide increases, and there is a corresponding reduction in the quantity of cristobalite, as indicated by the intensity of the lines for these phases.

The work [9] presents that cristobalite does not remain in the sample containing 60 wt. % zinc oxide, and the phase composition of the mixture consists of two compounds: $ZnAl_2O_4$ and Zn_2SiO_4. The samples, containing more that 60 wt. % ZnO, together with the gahnite and willemite contained free zinc oxide.

We have come to a little bit different conclusions by the analysis of investigated chamotte and zinc slag. The presence of cristobalite in 10 selected samples was proved by AAS analysis and X-ray diffraction analysis. The repeated analyzes showed that samples should not be prepared by conventional methods of chemical analysis of slag - the evaporation of H_2SO_4 (1:3) but they should be only dissolved in HCl (1:1) and the given solution should be heated to the boiling point. After dissolution and following chemical analysis, differences were found in the results of the analysis (Pb = 10.49 wt. %, Cu = 6.43 wt. %, Fe = 5.6 wt. %, Ni = 11.0 wt. % and Zn was undetectable). These differences could be caused by insufficient dissolving of the sample in boiling acid.

X-ray diffraction showed that the samples contained about 50 wt. % $AlFe_3$ as well as other compounds (or minerals), such as Pb, ZnO (zincit), Al_2O_3, Pb_3O_4, PbO_2 (platnerite) and SiO_2 (cristobalite). Analysis of results is shown in table 1 and in the diffraction diagram (fig. 9).

It is clear that some substances including Al_2O_3 (melting point 2040 °C, boiling point: 2977 °C), SiO_2 (melting point: 1713 °C), Pb (melting point: 327.5 °C, boiling point: 1750 °C), Pb_3O_4 (melting point: 500 °C, boiling point: 800 °C), Zincite (ZnO) (melting point: 2690 °C, sublimation point: 1800 °C) and others elements or components remain in the slag because their boiling point is higher than the temperature of the production process of ZnO (about 1400 °C).

Slag samples contained a significant amount of ZnO which was not transferred to the final product but its residues were stuck in the form of slag on the walls of the furnace. This effect causes a great loss of the final product. There have been some compounds, such as zincit (ZnO – fig. 4), plattnerit (PbO_2), cristobalit (SiO_2), magnetit (Fe_3O_4) and other and all these compounds were recrystallizated at high temperature and low underpressure.

Table 1

The average XRD analysis of samples of waste material (wt. %)

Substances	**Content of substances (wt. %)**
$AlFe_3$	53.05
Pb	21.86
Pb_3O_4	8.16
ZnO	6.07
SiO_2	4.46
PbO_2	3.34
Al_2O_3	2.45

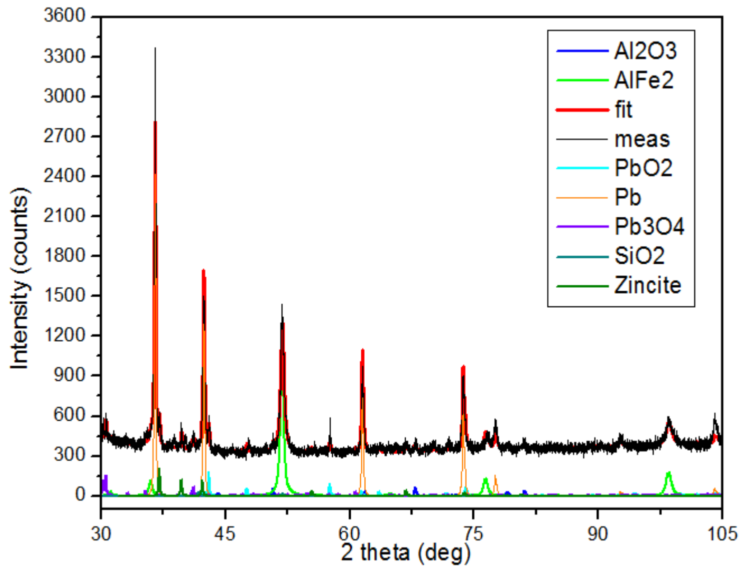

Fig. 9. The difractogram of selected samples for waste material
(full colour version available online)

5. Conclusions

From the study, the following conclusions can be drawn:

- Slag samples contained an enormous amount of ZnO, which does not pass into the final product, but remains stuck as the slag on the furnace lining – more zinc, more losses in relation to final product.
- High temperature and low pressure lead to re-crystallization of some compounds, such as *zincit* (ZnO), *plattnerite* (PbO_2), *cristobalite* (SiO_2), *magnetite* (Fe_3O_4) and other compounds or minerals.
- Slag contains the residues of iron and aluminum which have a higher melting point and boiling point. Iron and aluminum are evaporated at a temperature from 2520 °C to 2862 °C while zinc has boiling point 907 °C. Then it follows that the resulting eutectics on the basis of Fe-Zn-Al and Zn-Al can have boiling point over 1000 °C and it is connected with increase in fuel consumption.
- The analysis of samples of slag should not be performed by method - chemical way for AAS because of insufficient dissolution of the waste material either in HNO_3 or by evaporation of H_2SO_4. Suitable analysis is the X-ray diffraction using Co lamp. Usage X-ray diffraction in crystals can be understood as the non-destructive method for determination of the internal structure of crystals and their qualitative and quantitative analyses can be done using obtained diffraction pattern.
- Investigated phases which occur in the slag sample revealed that the resulting phase is not different from the phases that are in the raw material. Then it follows that at high temperature (about 1 400 °C) there is not any change of the structure of the raw material which remains in the process as slag.
- Sprayed ceramic coatings can be utilized for the prediction of occurred critical states as well as degradation processes. Ceramic and metal-ceramic coatings on the basis of selected elements have excellent resistance to high temperature as well as to acid and hot metal, wear resistance and low thermal and electrical conductivity. This is the reason to use these choose materials as the furnace linings.
- In this case, the composition of the coating should have the basic matrix on

the basis of tungsten carbide (WC) and tungsten carbide (WB) in the order to perform all needed mechanical, physical and chemical requirements. The removal of the step interphase between the substrate and the surface coating (i.e. minimizing of differences of thermal expansion, elastic modulus, the crystallographic structure, the mutual solubility, the difficulty of diffusion etc.) can be achieved by the creation of suitable intermediate layers, such as „sandwich" coatings or graded coatings.

- As a solution, it is recommended to find a suitable method of cleaning of the furnace after three days of continuous operation and the pure zinc (marked SHG or HG) have to be used to furnace instead of hard Zn (less than 95 wt. % Zn) while the hard zinc contains such negative substances as iron, lead and aluminum and other elements.

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