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THE STUDY AND MICROSTRUCTURE ANALYSIS OF ZINC AND ZINC OXIDE

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The given paper is closely connected with the process of the manufacturing of ZnO. The purity of the metal zinc has crucial influence on the quality of ZnO. ZnO can be produced by pyrometallurgical combustion of zinc and hard zinc. But this mentioned method of preparation leads to the creation of the enormous amount of waste including chemical complexes. On the basis of the occurrence of the residual content of other elements, it is possible to make prediction about the material behavior in the metallographic process. The input and finally materials were investigated and this investigation was done from the aspect of structural and chemical composition of the materials.

Key words: zinc, production of zinc oxide, mivrostructure, chemical composition, zinc slag

INTRODUCTION

Zinc oxide has been an important industrial material for centuries and is currently the subject of considerable new interest [1, 2]. ZnO is used by several 100 000 tons per year [2]. Zinc oxide is a white solid inorganic powder, non-flammable, stable and insoluble in water. Size can vary between 0,5 and 5 μm, but typical size is around 1μm. Zinc oxide occurs in nature as mineral zincite. However, in most cases zinc oxide is obtained through a technical process from zinc [1, 3, 4]. ZnO commonly occurs in the wurtzit structure. Layers occupied by zinc atoms alternate with layers occupied by the oxygen atoms. This fact closely related to its tetrahedral bond symmetry and its prominent bond polarity [2, 5]. However, zinc oxide is mainly used in a powder state, when not only classic dimensional effects, but al characteristics of surface states of phonons can manifest themselves, which requires a special study [6].

Zinc oxide is used as a semi-product in many fields of production. The multiplicity of Zinc oxide is used as a semi-product in many fields of production. The multiplicity of processes by which ZnO can be produced is a potential source of confusion, however, the process used has a large influence on the properties of the oxide, and hence on its suitability for various applications. Zinc oxide powder has traditionally been used as a white pigment and as an additive to rubber. While it has largely been displaced as a pigment in paints, its usage in rubber remains very important [1]. Everyday items zinc or zinc compounds are used in paint pigments and coating, plastics, rubbers, cosmetics, medical etc. [3]. Recent investigations reveal that zinc oxide convert sun´s is rays into chemical energy in a manner similar that of chlorophyll. Zinc oxide is the only inorganic material known to act in that manner [7].

Production of zinc oxide by burning zinc in air was developed by Le Clair in France in 1840, hence the French Process. The production of ZnO via French process is based on high speed of zinc vapor at speeds 0,1 Mach or higher [1] and temperature is in the range from 1 300 °C to 1 400 °C.

The production process is performed according to chemical reactions [8]:

$$Zn_s \rightarrow Zn_l \rightarrow Zn_g \quad (1)$$

$$Zn_g + ½O_{2g} \xrightarrow{+CO/CO_2} ZnO_s$$

French process is concern only to metallic zinc content in raw material and raw material is deciding factor for quality of zinc oxide formed [9]. In this case, the character of determination of occurred phases of cast is not such important but on the other hand, the chemical composition as well as content of elements seems to be the most important.

EXPERIMENTAL MATERIALS

Zinc

After iron, aluminum and copper, zinc is usually the fourth-most used metal. Zinc is a relatively soft metal with a good corrosion resistance. A protective surface layer of oxide and carbonate ($Zn_5(OH)_6(CO_3)_2$) forms as the zinc corrodes. This protection lasts even after the zinc layer is scratched but degrades through time as the zinc corrodes away [10]. Structure of pure zinc is monotonous and consists of large grains [11].

To understand the phases, which are forming in the zinc alloys (Zn content min. 90 %), several types of

N. Luptáková, Academy of Sciences of Czech Republic, Institute of Physics of Materials, Brno, Czech Republic
F. Pešlová, University of Alexander Dubcek in Trencin, Slovakia
J. Kliber, VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Ostrava, Czech Republic

chemically different zinc were selected (chemical composition is in Table 1); this zinc is also known as a “hard zinc”. Samples were collected and processed from ingots. The attention was paid to the selected sample of metal zinc for investigation of the microctructural phases which occur in the zinc with additions. This given selected sample is different from other input materials as well as it is inhomogeneous from the chemical aspect. It is commonly fulfilled that the hard zinc created by intermetallic compounds, such as aluminium-saturated δ ($FeZn_7$) phase or ζ phase which is determined by x-rays diffraction analysis [12].

Table 1 **Chemical composition of samples /wt. %**

No.	Cd	Ni	Al	Fe	Zn
1.	0,00031	0,0025	1,52	1,30	96,15
2.	0,00052	0,0015	0,74	5,10	92,36
3.	0,00130	0,0001	0,06	0,002	99,75

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 - ZnO (Figure 1). Samples of zinc oxide which was prepared by French process have been chosen in the order to investigate and study the morphology of materials. The primary materials were zinc with additions (approx. 90 wt. % Zn). Selection of zinc oxide samples represents the given process of production and output material. The chosen samples were from samples and crystallized minerals whose composition was corresponding to primary element of the production process. Zinc oxide is also created on the surface of metal zinc at the temperature over 419,5 °C (Figure 2) as well as by casting molten zinc into the ingot.

ZnO occurs naturally under the name zincite - (Zn, Mn^{2+}, Fe^{2+})O. Pure, synthetic ZnO is colourless and clear in agreement to the gap in the near UV. Owing to the incorporation of impurity atoms such as Mn of Fe,

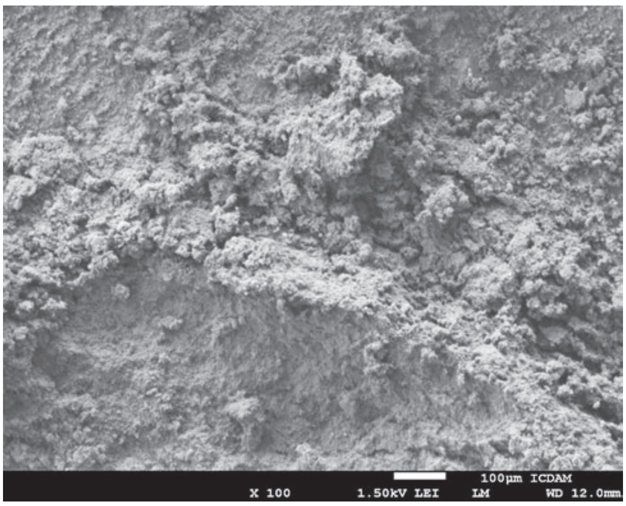

Figure 1 SEM micrograph illustrating the powder zinc oxide (magnification 100x)

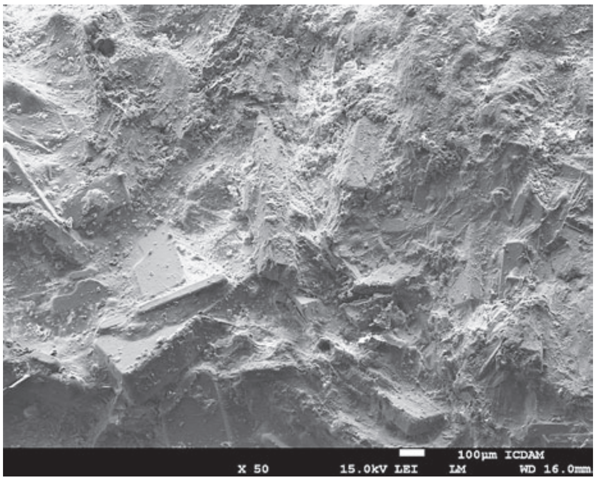

Figure 2 SEM micrograph of created zinc oxide on the surface of metal zinc (magnification 50x)

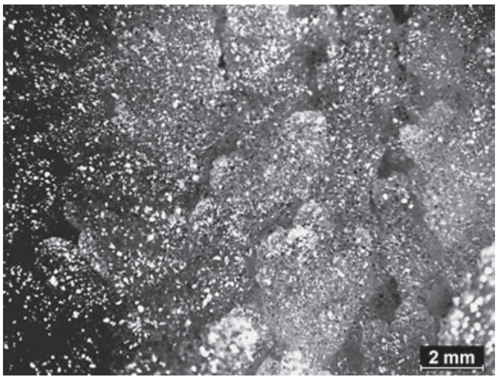

Figure 3 Optical micrographs of mineral zincite as slag from production ZnO by French process

zincite looks usually yellow to red [2]. These minerals (Figure 3) were obtained via pyrolytic combustion of zinc and hard zinc in graphite crucibles.

Testing methodology

The microstructures and the fracture surface of the samples were investigated by optical and scanning electron microscopy. The measurements were performed using the stereomicroscopic device NIKON SMZ 1500, SEM - JSM 7600F, AAS –AA 240 VARIAN and X- Ray diffraction Brűcker 8, KalfaCo with Co-lamp. Setting the measurement- time to step is set up in different cps (counts per second).

RESULTS AND DISCUSSION

The samples of microstructure which contained elements such Zn, Al, Fe, Ni, Cu etc. (Figure 4 - 8, chemical composition is in Table 1) were investigated. In Figure 4 is LOM micrograph of carbides containing inclusion. It is mosaic structure of grains where there are the carbides (content of carbon is 85,51 %). The ratio of pale and dark areas is 5,4/2 with high content of Cr, Fe and Ni seemed to be unusual. Nonuniform grain distribution in the microstructure of sample zinc with a phase formed at the

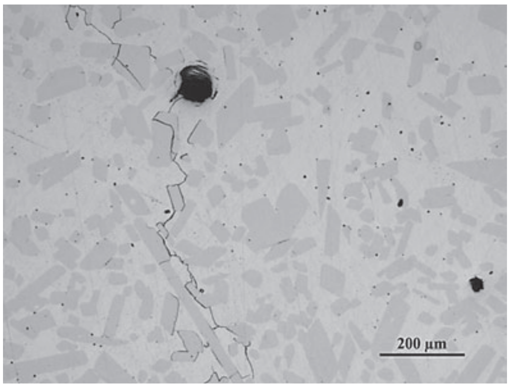

Figure 4 Sample No. 1, LOM micrograph of carbid containing inclusion (magnification 100x)

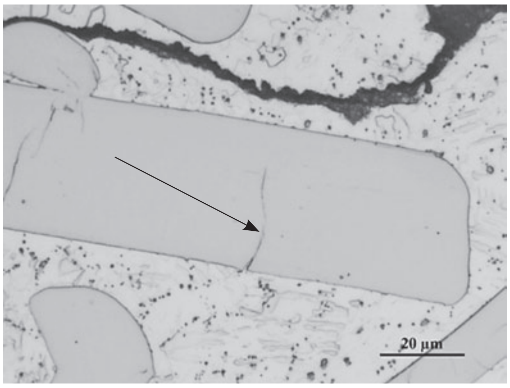

Figure 5 Sample No. 1, LOM micrograph showing the crack initiation by the matrix/particle decohesion, particle cracking and the localization of deformation at the tip of the inclusion causing an evident notch effect, (magnification 500x)

grain boundaries in combination with a number of carbides showing the same tendency (Figure 4). One of such areas is shown in the Figures 5 and 6 with identified the crack initiation by the matrix/particle decohesion.

There are also some differences visible in form of micro-structure morphology changes of the phases and precipitations occurred in the investigated alloys (Figure 7).

The more detailed image of the grain boundaries of samples No. 3 (Figure 8) represented the morphological arrangement of individual carbides of iron. Next, these carbides were investigated in the more detailed way. Analysis of sample No. 3 showed that the particular phases are mutually different from the chemical aspect (Table 2).

More detailed investigations of re-crystallized mineral - zincite enabled us to obtain morphological formations, where they showed a gradual increase of crystallization in dependence on temperature and rate of crystallization (Figure 9). From the chemical analysis, the composition of the crystal was obtained - the matrix is formed by the majority of Zn (99,87 wt. %) and other elements, such as Pb (0,003 wt. %), Fe (0,001 wt. %), and one thousandth of wt. % relating to Cu, Ni and Cd, which will subsequently affect their following growth.

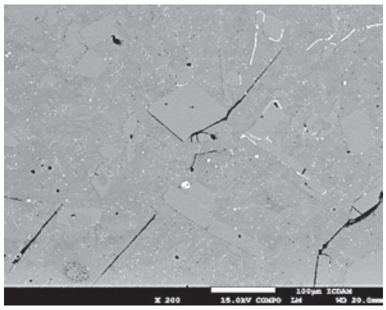

Figure 6 Sample No. 1, scanning electron microscope micrograph illustrating the crack propagation initiated by the matrix/inclusion decohesion (magnification 200x)

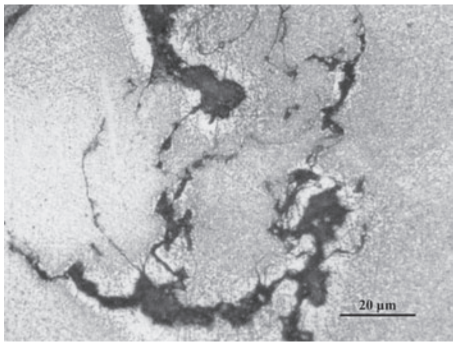

Figure 7 Sample No. 2, hot cracking caused by the presence of oxides formed by casting process (magnification 500x)

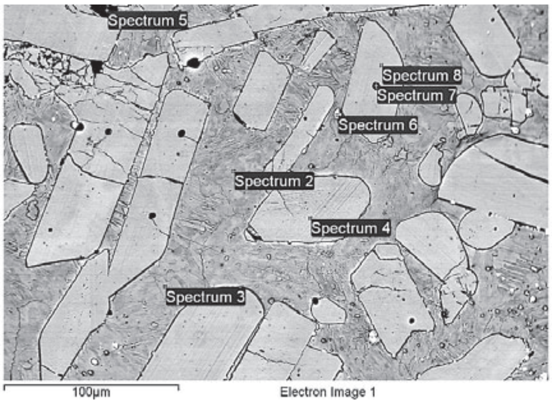

Figure 8 Sample No. 3, semi-quantitative analysis (EDS) showed the presence of zinc, iron and other elements and their oxides and carbide

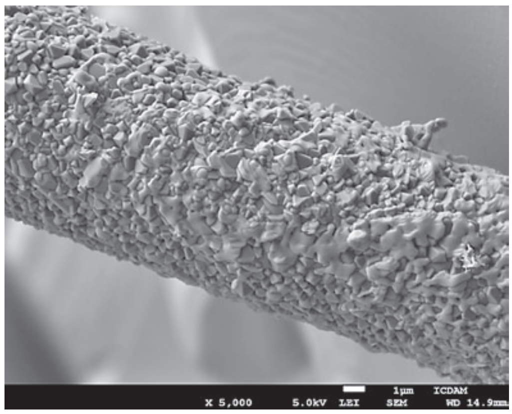

Figure 9 SEM images of re-crystallized mineral – zincite (magnification 5 000x)

Table 2 **EDS spectrum analysis of the sample No. 3 shown in Figure 8 /wt. %**

Number of Spectrum	C	O	Fe	Zn
Spectrum 2	66,98	5,42	6,20	20,53
Spectrum 3	66,90	5,73	5,86	20,57
Spectrum 4	32,53	1,03	53,14	12,93
Spectrum 5	22,96	0,40	68,06	8,29
Spectrum 6	59,82	5,16	11,55	22,43
Spectrum 7	33,72	1,05	52,35	12,46
Spectrum 8	32,74	1,15	52,89	12,82
Sum Spectrum	39,10	1,67	44,21	14,55

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CONCLUSION

Conclusions can be summarized in the following points:

- During the production of the ZnO, the primary raw material is seriously influenced by the other additives, The occurrence of the additive or impurities as well as other unsuitable phases will have the significant influence on the whole technological process therefore the attention must be paid to the input raw materials;
- High temperature and low pressure lead to re-crystallization of some compounds as zincite (ZnO) and others compounds or minerals;
- The resulting final product - zinc oxide in an imperfect production process of ZnO can contain Fe_2O_3 and Al_2O_3 which cause that ZnO can be yellow-brown colors;
- Zinc 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 2 520 °C to 2 862 °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 1 000 °C and it is connected with increase in fuel consumption;
- In this case, the coke can be used to reduce the boiling point in the furnace and it means merging the French process with the American process;
- There is the recommendation to perform much more detailed analysis of the input material as well as research interactions of the molten secondary zinc with the other elements and with aggregates of furnace case.

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Note: The responsible for English language is Silvia Koišová (Faculty of Industrial Technology, University of Alexander Dubček in Trenčín, Slovak Republic)