N. LUPTÁKOVÁ, P. DYMÁČEK, F. PEŠLOVÁ, Z. JURKOVIĆ, O. BARBORÁK, J. STODOLA
ISSN 0543-5846
METABK 55(3) 407-410 (2016)
UDC – UDK 669.5: 620.18:541.451.669.5.002.2=111

IMPACT OF RESIDUAL ELEMENTS ON ZINC QUALITY IN THE PRODUCTION OF ZINC OXIDE

Received – Primljeno: 2015-06-18
Accepted – Prihvaćeno: 2015-12-26
Preliminary Note – Prethodno priopćenje

The paper is focused on zinc oxide manufacturing process. The present work deals with the character and morphology of the input material for the production of ZnO by the indirect pyrometallurgical process. Undesirable phases in the feedstock can be identified through profound recognition of the source material and the nature of its microstructure. If these compounds diffuse into the lining during thermal processes, they become the cause of stress in metallurgical ceramics. The emergence of these chemical reactions may subsequently affect the entire metallurgical zinc smelting process. The results obtained by analysis are used to minimize waste - zinc slag and to eliminate the conditions which enable the formation of the undesired product, thereby increasing the productivity of the ZnO production.

Key words: zinc, metallography, microstructure of zinc, zinc oxide, production of zinc oxide

INTRODUCTION

Zinc oxide (ZnO) has attracted much attention within the scientific community as a „future material". This is however, somewhat of a misnomer, as ZnO has been widely studied since 1935 [1], with much of our current industry and day-today lives critically reliant upon this compound. Zinc oxide is already widely used in our society, and indeed it is key element in many industrial manufacturing processes including paints, cosmetics, pharmaceuticals, plastics, batteries, electrical equipment, rubber, soap, textiles, and floor coverings to name just a few [2].

Zinc oxide can be produced by variety of ways (for example the direct - American process, hydrometallurgical synthesis, the production of active zinc oxide by decomposition of hydrozincite etc.) [3]. European production of ZnO is based on the indirect process. This indirect method was popularized by LeClaire (France) and therefore is commonly known as the French process.

Nowadays, production of ZnO by French process includes the biggest share of production in industrial society [4]. The production of ZnO via French process is based on high speed of zinc vapour at speeds 0,1 Mach or higher and temperature in the range from 1 300 °C to 1 400 °C [3, 4]. The feedstock of this production method is the production of metallic zinc and its alloys as-received state. Zinc and its alloys are combusted in the muffle or rotary furnaces. The production process is performed according to chemical reactions (1) and (2) [5].

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

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

where are: *s* solid phase, *l* is liquid phase and *g* is gas phase. Indirect process is considered to be the fastest and most productive method for industrial production of ZnO [6], but according to the practical experience, this type of production ZnO is not optimal for utilization of the product in all technological applications. The quality of ZnO depends on the feedstock. During processing of the waste zinc (approx. purity of Zn is 90 wt. %) from galvanic process containing other elements, such as Fe, Cd and Al, there is the occurrence of slag which negatively affects the total production process of ZnO and final product.

For better understanding of the technological process problems challenges in the production it is necessary to characterize the output product – ZnO. From the chemical point of view, zinc oxide is white inorganic compound. Zinc oxide compound has anisotropic character. The character of crystal shape is dependent not only on the crystal lattice, but it also depends on the method of production ZnO associating with the primary crystallization. High attention is paid to research in the modern development of ZnO [2, 3].

The objective of this paper is to investigate the effect of residual elements on quality of metal zinc in the production of zinc oxide. According to the works [7-10], the feedstock as well as the technology has been studied. There was investigated the morphology, chemical composition, particle-size of different Zn samples. These studies have shown interesting correlations be-

N. Luptáková, P. Dymáček, CEITEC IPM, Institute of Physics of Materials, Academy of Sciences of the Czech Republic Brno, Czech Republic
F. Pešlová, Faculty of Faculty of Industrial Technology, University of Alexander Dubček in Trenčín, Slovak Republic
Z. Jurković, Faculty of Engineering, University of Rijeka, Rijeka, Croatia
O. Barborák, Faculty of Special Technology, Trencin University of Alexander Dubcek in Trencin, Slovak Republic
J. Stodola, Faculty of Military Technology, University of Defence Brno, Czech Republic

tween morphology and chemical composition of Zn samples.

Detailed investigation will help in predicting the behavior of the material in the metallurgical process. This knowledge can be used as prevention of slag occurrence or it can even help us to find a way for easier removal from the furnace aggregates.

EXPERIMENTAL

Material

Structure of pure zinc is monotonous and consists of large grains. To understand the phases, which are forming in the zinc alloys (Zn content min. 90 %), four types of chemically different metal zinc were selected (chemical composition is shown in Table 1). Samples were removed 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.

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

Sample	Cd	Ni	Al	Cu	Fe	Zn
1	0,00031	0,0025	2,52	0,02	1,5	Balance
2	0,00052	0,0031	0,95	0,01	3,5	Balance
3	0,0013	0,0015	3,52	0,025	0,2	Balance
4	0,0012	0,06	4,5	0,03	0,8	Balance

Methods

Four selections of samples represent the indirect process of production of zinc oxide. The microstructure and the surface of the samples in the as-received state were examined with LOM applying the optical microscope Zeiss Neophot 32 as well as SEM equipped with an energy-dispersive X-ray analysis system (EDX) using microscopes Jeol JSM 5410 and Tescan Lyra 3. The samples were prepared by standard methods. A solution of NaOH (10 ml) + H_2O (90 ml) was used as the etchant.

EXPERIMENTAL RESULTS

Chemically pure zinc

Chemically pure zinc - SHG (Special Hight Grade) has a composition according to international standards ISO752-2004 and European standards (see Table 2). Chemically pure zinc is a relatively soft metal with the ability of forming hard oxide coating on its surface. The studies of Zn samples by LOM and SEM showed that the microstructure of pure metal grains displayed the occurrence of different phases with more or less oxygen content. Microstructure of chemically pure zinc consists of large grains (average grain size is 650 μm).

The different oxygen content in these areas (depending on the change of temperature gradient) possibly also minimum hardly-identifiable content of additional elements influence the final polyhedric microstructure. Atomic-sized residual elements from metal melting influenced the character of solid solutions or stress-strain states in microareas of the solidified microstructure.

Table 2 **Chemical composition of SHG Zinc/ wt. %**

Al	Sn	Cu	Fe	Pb	Cd	Zn
max. 0,001	max. 0,001	max. 0,001	max. 0,002	max. 0,003	max. 0,003	min. 99,995

Zinc with residual elements

The structure of zinc samples labelled No. 1 (Figure 1, 2) is characterized by the occurrence of unevenly spaced, relatively large grains, where a phase rich in silicon (see Figure 1), designated by EDX analysis, precipitated at the zinc grain boundaries. The microstructure shown in Figure 2 presents the precipitation of pure residual elements and different phases which are rich in undesirable elements (e.g. Al, Fe, Pb, Cd) within the grains of zinc as well as crack initiation by the matrix/ particle decohesion and particle cracking. The localization of deformation at the tip of the inclusion causes an evident notch effect (see Figure 2 red arrow). They can be in the form of excluded segregates at the zinc grain boundaries, which can be converted into new grains as the newly formed phase that represents of about 40% the microstructure. The morphology of these phases is variable from ovules to angular formations that cause notch effect increasing stress-strain conditions.

The microstructure of the zinc sample No. 2, see Figures 3, 4, has the character of a mosaic arrangement of grains. This microstructure was observed from the viewpoint of chemical analysis. Furthermore, the microstructures of sample, in which angular phases occurred, were observed. All these particles as well as the fine ones (contained in the phases or outside) were analyzed by the EDX method. The chemical analysis showed that the selected microlocations were rich in oxide, fermium and aluminum. It can be expected that they can be Al_2O_3 and Fe_2O_3.

The observed sample No. 3 had a lamellar structure, keeping the orientation of lamellas, with the remnant of dendritic microstructure of the primary crystallization. The size of the lamellas is different; their length mostly varies, see Figure 5. This microstructure was more chemically pure, but the grain boundaries were partially disturbed, probably by releasing the phases previously located in the vicinity of the boundaries. The elimination of secondary phases and their subsequent arrangement may result in forming certain locations with different strain. It can be assumed that this condition will be contingent on the change of temperature and pressure during the cooling of the casting. It is known that the cooling causes the occurrence of crystallization nucleons on the walls of the chill molds and in areas with the highest content of impurities. Figure 6 shows decohesion of grains, which could have arisen in the process of solidification and forming the structure by cooling and draining the molten zinc from the ingot.

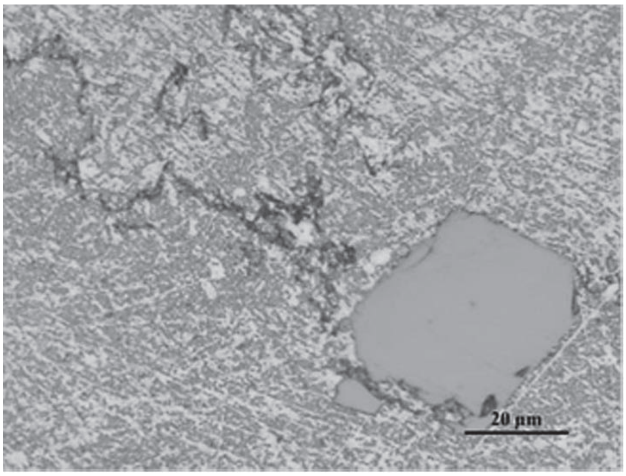

Figure 1 Microstructure of the sample No. 1 with the of SiC-based inclusion (LOM)

Typical microstructure of the sample No. 4, see Figures 7 and 8, containing about 60 % oxide complexes and other phases and with only about 40 % zinc arises during usual zinc smelting without remelting. If these microstructures contain „oxide membranes”, they are not recommended for producing ZnO due to their high melting point.

Oxygen occurrence in the vicinity of zinc, leads to Zn oxidation while producing $Zn_5(OH)_6(CO_3)_2$ which form passivating barriers (see Figures 8). The passivation of metallic zinc subsequently prevents further oxidation. Observation of the metallic zinc surface by SEM shows that a differently thick layer with its uneven coverage arises, see Figure 8. The analyzed surface is chemically pure zinc which was re-melted and slowly cooled. The surface was formed unevenly, creating various reliefs and was wrapped immediately with carbon-based ZnO detected by EDX analysis.

CONCLUSION

Conclusions can be summarized in the following points:

1) The best choice for other processing of the metallic zinc is to use chemically pure zinc. Because of the

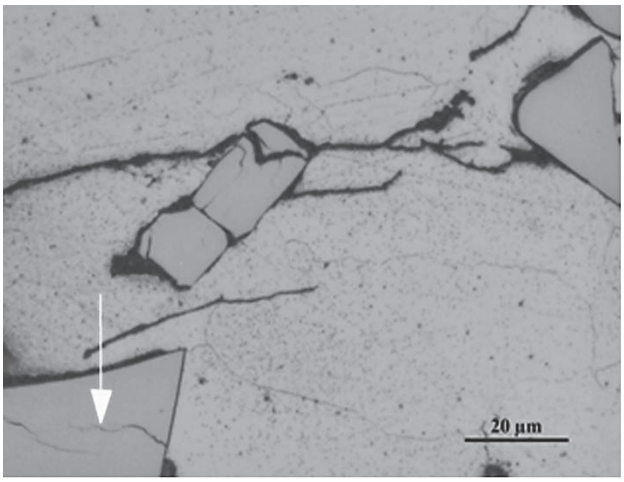

Figure 2 Microstructure of sample No. 1 with precipitation of other elements and cracks (LOM)

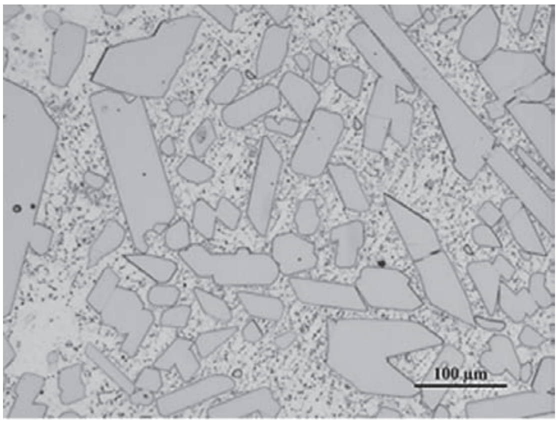

Figure 3 Microstructure of the sample No. 2, mosaic arrangement of grains (LOM)

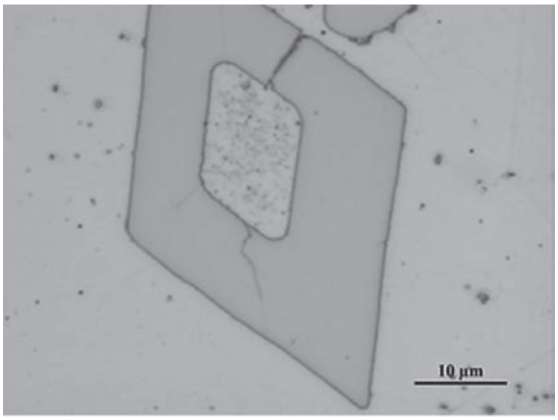

Figure 4 Microstructure of sample No. 2, detail of mosaic shape of grain (LOM)

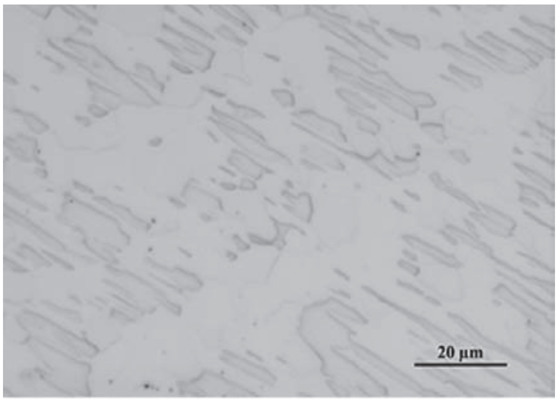

Figure 5 Lamellar microstructure of the sample No. 3, (LOM)

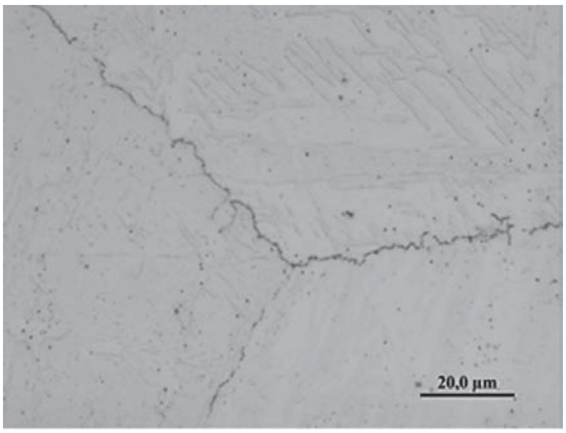

Figure 6 Microstructure of sample No. 3 with grain decohesion (LOM)

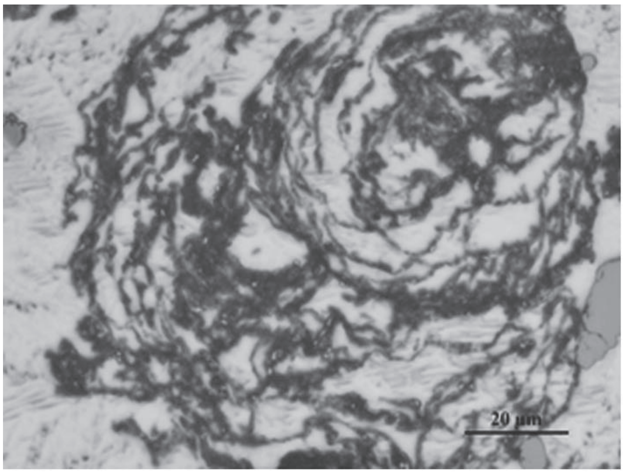

Figure 7 Microstructure of the sample No. 4 with oxide membranes (LOM)

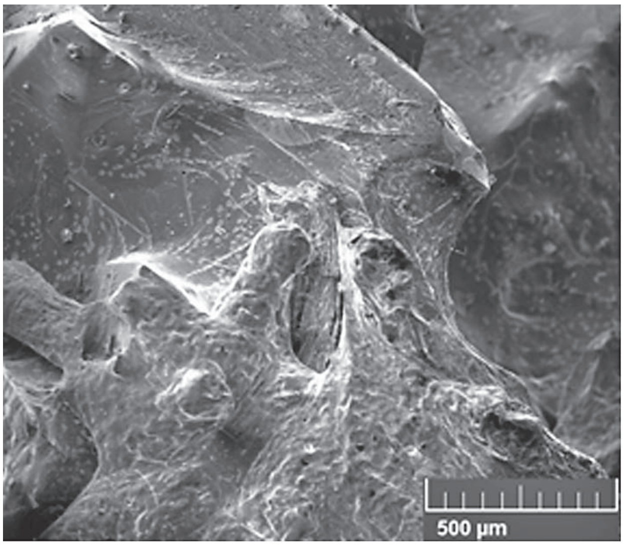

Figure 8 Crystallized chemically pure zinc coated with oxide (SEM)

price and technological difficulties, it is necessary to evaluate processing of the waste zinc in relation to galvanizing process because the French method for production of the zinc oxide in rotary furnaces is very effective.

2) During the production of the ZnO, the primary raw material is seriously influenced by the residual elements. This fact is closely connected with the decrease of lifetime of furnace aggregates as well as increase of the fuel consumption. The occurrence of the additives or impurities as well as other unsuitable phases will have the significant influence on the whole technological process; therefore careful attention must be paid to the input raw materials.
3) The resulting final product 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.
4) The recommendation is to provide sufficient amount of CO (> 25,0 vol. %) in the furnace atmosphere to create reducing atmosphere which ensures that ZnO will not form in the space of the rotary kiln but in the oxidation shaft as well as add a precisely defined amount of charcoal to the feedstock to create a suitable reducing atmosphere.

Acknowledgements

This work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the Project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund. This work has been supported also by the Project VEGA No. 1/0385/14 and with the support of the Ministry of Defence of the Czech Republic, Partial Project for Institutional Development, K-202, Department of Combat and Special Vehicles, University of Defence, Brno.

REFERENCES

[1] C. W. Bunn, The lattice dimensions of zinc oxide, Proceedings of the Physical Society 47(1935)5, 835-842, doi:10.1088/0959-5309/47/5/307

[2] Ü. Özgür, H. Morkoç, Optical properties of ZnO and related alloys, Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications, C. Jagadish, S. Pearton, (ed.), Elsevier, Oxford 2006, pp. 175-240.

[3] A. Moezzi, A. M. McDonagh, M. B. Cortie, Zinc oxide particles: Synthesis, properties and applications, Chemical Engineering Journal 185-186(2012), 1-22, doi:10.1016/j.cej.2012.01.076

[4] G. Auer, W. D. Griebler, B. Jahn, White Pigments, Industrial Inorganic Pigments, G. Buxbaum, G. Pfaff (ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2005, pp. 51-97, doi: 10.1002/3527603735.ch2

[5] L. Koudelka, J. Horák, P. Jariabka, Morfology of polycrystalline ZnO and its physical properties, Journal of Materials Science 29(1994)6, 1497-1500, doi: 10.1007/BF00368915

[6] S. Mahmud, M. J. Abdullah, G. A. Putrus, J. Chong, A. K. Mohamad, Nanostructure of ZnO fabricated via French process and its correlation to electrical properties of semiconducting varistors, Synthesis and Reactivity in Inorganic and Metal-Organic and Nano-Metal Chemistry 36(2006)2, 155-159, doi: 10.1080/15533170500524462

[7] N. Luptákova, F. Pešlová, J. Kliber, The study and microstructure analysis of zinc and zinc oxide, Metalurgija 54(2015)1, 43-46.

[8] N. Luptákova, E. Anisimov, I. Janotová, P. Švec, F. Pešlová, The study of molten zinc interaction on the surface of refractories in the production of zinc oxide, Materials Engineering 20(2013)2, 91-97.

[9] R. S. Lehto, Zinc, The encyclopedia of the chemical elements, Reinhold Book Corporation, New York 1968, pp. 822-830.

[10] G. Vourlias, N. Pistofidis, El. Pavlidou, G. Stergioudis, E.K. Polychroniadis, Study of structure of hot-dip galvanizing byproducts, Optoelectronics and Advanced Materials 9(2007)9, 2937-2942.

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