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IMPACT OF RESIDUAL ELEMENTS ON QUALITY OF METAL ZINC

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Summary: The paper is closely connected with the morphology of the raw material for the production of metallic zinc which is used in the production of ZnO by indirect pyrometallurgical processes. The input material is the key parameter in the production of high-quality zinc oxide. Currently is zinc oxide the subject of considerable interest. ZnO has attracted much attention within the scientific community as a "future material". ZnO is an essential part of the aerospace industry. For the prediction of complex production process when problematic situation may occur, the systematic analysis of the input zinc materials is needed. Undesirable phases in the feedstock can be identified through profound recognition of the source material and the nature of its microstructure. Undesirable phases in the feedstock can form (with zinc and other elements) hard and brittle compounds. 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 zinc oxide production.

Key words: zinc, zinc oxide, waste material, metallography, chemical analysis, phases

INTRODUCTION

Zinc oxide is widely used in our society, and indeed it is key element in many industrial manufacturing processes including paints pigments and coating, cosmetics, pharmaceuticals, medical and dental, plastics, batteries, electrical equipment, rubbers, soap, textiles, floor coverings, miscellaneous applications to name just a few (1-3). So, zinc oxide is used as a semi-product in many fields of production and its world-wide use is in excess of 100 000 tons per year (4). With improvements in growth technology of ZnO nanostructures, epitaxial layers, single crystal and nanoparticles, we are now moving into an era where ZnO devices will become increasingly functional (2).

Zinc oxide can be also characterized as a semiconductor of type *n*. 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 (5).

Moreover, when the US National Aeronautics and Space Administration (NASA) scientists needed a coating that could withstand the extreme temperatures of space travel, they

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turned to zinc oxide. Researchers were able to develop a zinc-based coating capable of withstanding thermal cycling between +180° C and -180° C, and the bombardment of ultraviolet exposure equivalent to 19 000 sun hours. This zinc oxide coating is now routinely used to protect components of spacecraft, which are some of the most technically advanced and complex machines ever made.

The Cassini space (Fig. 1) probe left earth in 1997 on a seven-year voyage to Saturn. Upon arrival at Saturn, the probe will conduct a four-year mission with fifty orbits and numerous satellite encounters. Several parts of the Cassini probe, not least of which its four-meter diameter High Gain Antenna system, are protected by thermal control paint based on zinc oxide. This zinc-containing thermal coating is of critical importance to the probe because extreme temperatures will be encountered as the probe approaches within 0.61 astronomical units (AU[1]) of the sun, during Venus flybys, and will be as far as 10 AU from the sun as it orbits Saturn. A number of coatings were evaluated for the project, but the zinc oxide formula best met Mission requirements, including the ability to withstand extreme temperatures and ultraviolet exposure (6).

French process is considered to be the fastest and most productive method for industrial production of ZnO (7), 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 starting materials. 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, there is the occurrence of slag (waste material) which negatively affects the total production process of ZnO and final product.

The work is focused on the enormous amount of slag material. It is closely connected with the previous work (8-10) in which the primary material has been studied. Detailed investigation of waste material will help in predicting the behavior of the material in the metallurgical process. This knowledge can be used as prevention of occurrence slag or it can even help us to find a way for easier removal from the furnace.

Source: NASA

Fig. 1 - The Cassini spacecraft, with the Huygens probe seen on the right, sits atop a Titan IVB/Centaur expendable launch vehicle at the Cape Canaveral Air Station (11)

1. EXPERIMENTAL MATERIALS

1.1 ZINC OXIDE

From the chemical point of view, zinc oxide is white inorganic compounds. Compound ZnO has anisotropic character (12). Pure ZnO crystallizes in the hexagonal (wurzite) crystal structure (13) with a lattice parameters a = 3.25 Å and c = 5.12 Å (12). 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 (15). High attention is paid to research in the modern development of ZnO.

Zinc oxide can be produced by variety of ways (for example the direct - American process, hydrometallurgical synthesis, the production of zinc oxide by decomposition of hydrozincite enc.). Indirect production of ZnO or French process was developed by Le Clair in France in the years from 1840 to 1850 and therefore is commonly known as the French process. By weight, most of the world's zinc oxide is manufactured via French process. European production of ZnO is based on the indirect or French process (1, 15).

The production of ZnO is based on high speed of zinc vapor at speeds 0.1 Mach (30 $m.s^{-1}$) or higher and temperature is in the range from 1 300 °C to 1 400 °C. Sublimation temperature of ZnO is 1 725 °C. Zinc vapor reacts with the oxygen in the air to give ZnO, accompanied by a drop in its temperature and bright luminescence. The production process is performed according to chemical reactions (15):

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

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

The raw material for the production of ZnO can be various kinds of zinc material. Investigation of microstructural phases that form zinc with different additives was carried out on samples that represented a random selection of input materials. Zinc samples were collected and processed from different ingots and molds, in which hard zinc is cast as a waste of the galvanizing process. Study samples of zinc have been chosen on the base of chemical composition (Tab. 1).

Tab. 1 - Chemical composition of the elements of the samples

Number of Samples	Cd	Ni	Cu	Pb	Al	Fe	Zn
1	0.00033	0.0015	0.00041	0.0006	1.74	1.2	96.14
2	0.00062	0.0035	0.0035	0.56	0.52	5.5	92.63

3	0.0011	0.00031	0.00031	0.0037	0.086	0.0019	99.36
4	0,0002	0,0004	0,0005	0,005	1,2	6,5	92.21

Source: Authors

2. TESTING METHODOLOGY

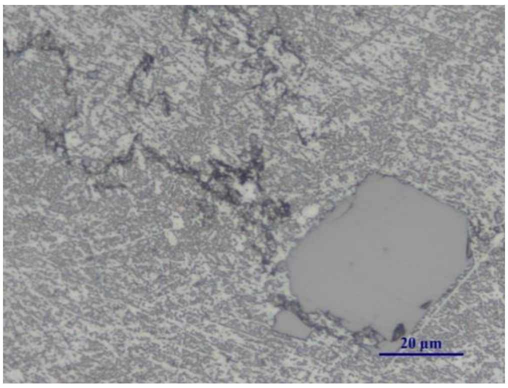
The phase composition and the microstructure were studied using by light optical microscopy (LOM) and by a scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray analysis system (EDX). The chemical composition of the elements of samples was observed using by atomic absorption spectroscopy (AAS).

The measurements were performed using the stereomicroscopic device NIKON SMZ 1500, SEM - JEOL JSM-7600F and AAS - AA 240 VARIAN. A solution of NaOH (10 ml) + H_2O (90 ml) was used the etchant. Photo documentation of microstructure is shown in Figs. 2 to 6. The microstructure is imaged at various magnifications.

3. RESULTS AND DISCUSSION

3.1 MICROSTRUCTURE EVALUATION OF SAMPLES BY LOM AND SEM

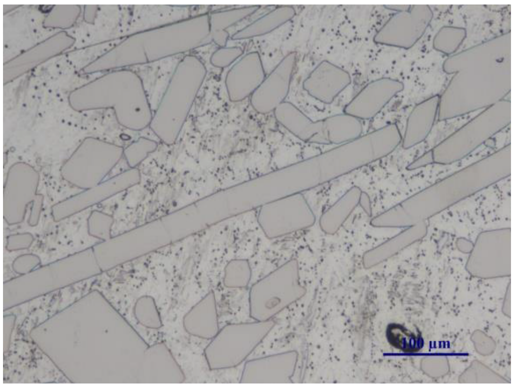
The emergence of various phases in the zinc (Zn content is min. 90 wt. %) was observed in metallographically prepared microstructures of various types of waste zinc. The selected samples of zinc microstructures are shown in Figures 2 to 6 at 500x magnification. The structure of zinc samples labelled No. 1, Fig. 2, is characterized by the occurrence of unevenly spaced, relatively large grains, where a phase rich in silicon excreted at the zinc borders.



Source: Authors

Fig. 2 - LOM image of the sample No. 1 with the inclusion of SiC-based

The microstructure in Fig. 5 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 (16). 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 (about 40% in the structure). The structures are characterized by the appearance of darker and lighter areas which can characterize the distribution of different additives enriching the originally formed phases. 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, Fig. 3, has the character of a mosaic arrangement of grains. This structure was observed from the viewpoint of chemical analysis.



Source: Authors

Fig. 3 - LOM image of the sample of zinc No. 2 with mosaic arrangement of grains

Furthermore, the structures of zinc alloys, 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 (17). The chemical analysis showed that the selected microlocations were rich in O, Fe and Al; it can be expected that they can be Al_2O_3 and Fe_2O_3 oxides. The observed sample No. 3 had a lamellar structure, keeping the orientation of lamellas, with the remnant of dendritic structure of the primary crystallization. The size of the lamellas is different; their length mostly varies (Fig. 4). This microstructure was chemically purer, 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 in 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. The spot indicated by the arrow in Fig. 5 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.

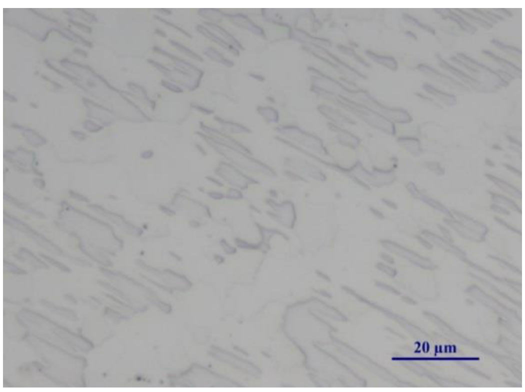


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Fig. 4 – LOM image of microstructure of sample No. 3 containing lamellar phases

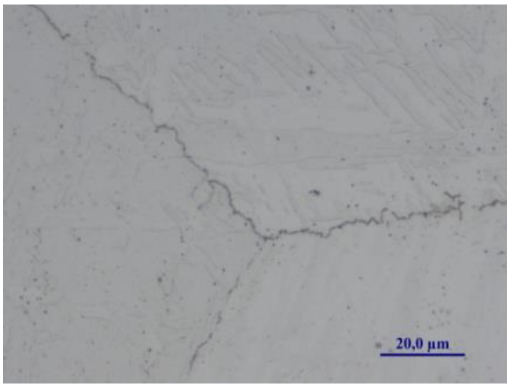

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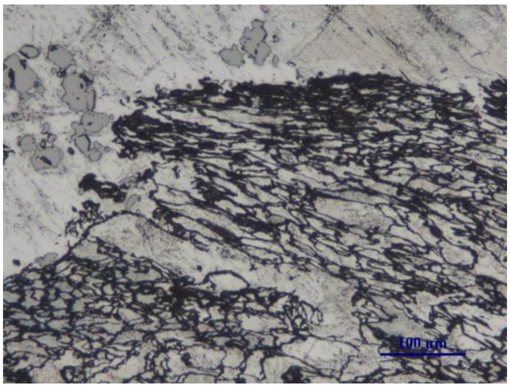
Fig. 5 – LOM image of microstructure of sample No. 3 with grain decohesion

Typical microstructure of the sample No. 4, Figure 6, containing about 60% oxide complexes and other phases and with only about 40% zinc arises during usual zinc smelting without remelting. If these structures contain "oxide membranes", they are not recommended for producing ZnO due to their high melting point.



Source: Authors

Fig. 6 - LOM image of zinc No. 4 with oxide membranes

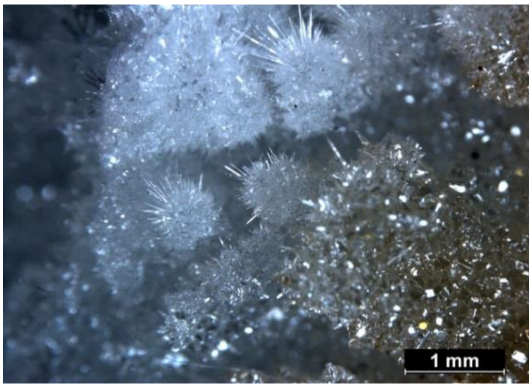
3.2 THE EVALUATION THE FINAL PRODUCT - ZINC OXIDE

For better understanding the problem of the technological process in relation to the zinc oxide production, it is necessary to define the output segment - white powder ZnO. From the chemical point of view, zinc oxide is a white inorganic compound. Layers occupied by zinc atoms alternate with layers occupied by oxygen atoms.

If the furnace space violates thermodynamic equilibrium, for example by changing the temperature gradient, pressure drop, etc., secondary crystallization of ZnO occurs during the production which will be affected by the surroundings, i.e. ambient elements. Acicular morphology of new crystals is shown in Figures 7 to 9.

Source: Authors

Fig. 7 - Acicular zincit crystals (ZnO) of different sizes



Source: Authors

Fig. 8 - Local crystallization of zincit crystals (ZnO)

Chemical analysis showed that even a tiny percentage of other elements such as zinc affect the formation and morphology of the emerging crystals. It appeared that the majority matrix is composed of Zn (99.88 wt. %) and other elements: Pb (0.0028 wt. %), Fe (0.0013 wt. %) and thousandths wt. % Cu, Mn, Ni and Cd will subsequently influence the course of further growth or disappearance of new nucleation.

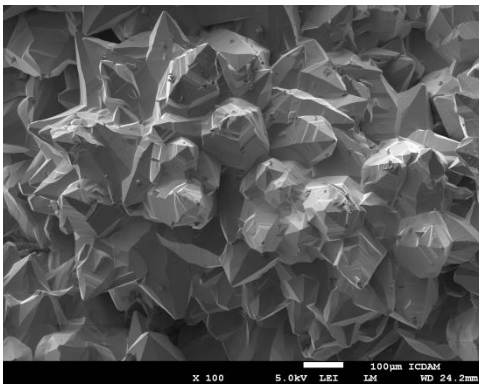


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Fig. 9 - Dendritic formations of zincit crystals (ZnO) with pyramidal (magnification 100x)

CONCLUSIONS

The briefly described solution is based on the needs and requirements of the chemical industry focused on the production and processing of zinc, zinc alloys and zinc compounds. Theoretical knowledge gained from national and international scientific studies were the basis of the authors' own research and design solutions for the development of technologies for the production of zinc oxide. The results of experimental research are an asset that can be exploited by companies dealing with ZnO production technology and by metallurgical companies processing zinc and zinc alloys. Diversified information that emerged from the research can be used to change the particle morphology by modifying selected technological parameters. In terms of practical design the crucial part is the one where the authors present a possible solution of selected technological problems, which can be used to enhance the quality of output products, or to reduce costs.

The conclusions obtained from this study as well as suggestions and recommendations can be summarized in the following points:

- zinc oxide production processes are heavily dependent on the chemical reactions in the furnace chamber; if temperature or pressure fluctuate in this area, other phases besides ZnO will likely occur and will degrade the final product;
- the quality of the resultant ZnO is heavily dependent on the chemical composition of the metallic zinc regardless of the technology of obtaining the feedstock;
- residual elements present in the zinc raw material, even a minimal amount, affect the character of the microstructure of zinc and become the activators for the deposition of other phases in the microstructure rich in a specific element;
- based on the nature of the input microstructure of zinc, the quality of the final product can be predicted, i.e. the occurrence of harmful impurities and phases will affect all subsequent process of the production of ZnO;
- implement detail analysis of the input material.

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