SOME PROPERTIES OF ZINC OXIDE BODIES¹

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ABSTRACT

Melting Point of ZnO.—The melting point of ZnO is above 1800°C and may be above its normal sublimation point.

Volume Shrinkage and Porosity of ZnO Bodies.—A very hard and dense body composed of pure ZnO can be prepared. At high temperatures it exhibits the unusual phenomenon of volume shrinkage accompanied by an increasing porosity.

Zinc Retort Bodies.—In the discussion the possible advantages of incorporating zinc oxide in a zinc retort body are mentioned.

1. Introduction.—The data presented below constitute part of an investigation which had for its purpose the determination of the Phase Rule diagram for the system $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. It was found, however, that, using pure materials, most of the temperatures of the diagram were beyond the range of any furnace equipment which the Department possessed and the investigation was therefore abandoned. The few data which were obtained, however, may be of some value to others interested in the behavior of zinc oxide and it seems, therefore, worth while to place them on record.

2. Material Employed.—The zinc oxide employed was a “chemically pure” material having the following analysis:

Fe.....	trace
Cu.....	none
Cd.....	none
Mn.....	none
Pb.....	0.01%

3. The Sintering of Zinc Oxide.—The material employed was in the usual form of a light fluffy powder which, on heating to a bright yellow heat, volatilized rather rapidly. Since the vapor pressure of a substance increases with increase in the convexity of the evaporating surfaces, it seemed probable that the high volatility of ordinary zinc oxide is caused by the combination of a great surface exposed and a high vapor pressure due to the smallness of the individual particles.

In order, therefore, to reduce the surface and to increase the size of the crystals, a sample of the zinc oxide was first placed in a desiccator and allowed to stand over damp filter paper until it had absorbed about 20 per cent of water. This moist material was found suitable for pressing, and cylinders 1.5 cm. in diameter by 5 cm. long were pressed out in a hardened-steel die, using a large hand operated screw press. These cylinders were then dried and the surface layer removed to eliminate any possible contamination with iron from the surface of the die. The cylinders

¹ Received March 8, 1922.

were then placed in a small platinum box with a tightly fitting cover and heated in a platinum resistance furnace to a temperature of 1400°C and held there for several hours.

Upon cooling, the cylinders were found to be extremely hard and stone-like. The outer surface was dark brown and numerous crystals, some as wide as 0.5 mm., had developed. The brown coating was found to be confined entirely to the surface, the inner portions of the cylinder showing a sparkling, coarsely crystalline aggregate. The dark superficial layer was

FIG. 1.

ground off and upon analysis was found to contain 0.07 per cent Fe_2O_3 , the source of which was probably the platinum box in which the sticks were fired. The interior portions of the cylinder after crushing and grinding in an agate mortar gave a yellow, heavy, crystalline powder, having the following analysis:

Fe.....	trace
Pb.....	0.01%
Cd.....	none
SiO_2	0.03%, probably from the agate mortar
Al_2O_3	trace, probably from the alundum furnace tube

It was estimated that if the yellow color of the powder was due to iron not more than 0.0005 per cent Fe_2O_3 was present. No attempt was made to determine the crystallographic properties of the crystallized material,

but its general appearance under the microscope as well as its density (5.4) indicated that it was the mineral zincite.

4. Melting Point of Zincite.—A sample of material held for 48 hours at 1710°C showed no signs of fusion. A stick of the material was then heated in an oxyacetylene flame, using the apparatus and method described in a previous paper.¹ It was possible in this way to heat the end of a stick to a black-body temperature of 1800°C. It is not improbable therefore that the melting point of zincite is above 2000° and it may be that its sublimation temperature under atmospheric pressure is lower than its melting point.

5. The Burning Behavior of Zinc Oxide Bodies.—Cylinders of commercial zinc oxide were prepared by the dust-press process described above. After drying, their bulk volumes were obtained with a small mercury volumeter of the Seger type. They were then placed in an alundum-tube furnace wound with a platinum heating coil and were fired at the rate of 200°C per hour, trials being drawn at the following temperatures, 1000°, 1100°, 1200°, 1300°, 1400°, 1500° and 1600°C, respectively. The heating curve of the furnace as indicated by a platinum-platinum-rhodium thermocouple was recorded on a Hoskins automatic recorder.

The burning shrinkages and porosities are shown in Fig. 1. The porosities were obtained by means of the Washburn-Bunting porosimeter.²

6. Discussion of the Volume and Porosity Changes.—The volume shrinkage curve shows that the material shrinks uniformly with rising temperature, but the curve shows no breaks or peculiarities corresponding to the peculiar changes that are found in the porosity curve. The porosity-temperature curve shows that the porosity decreases gradually to a minimum at 1350°C and thereafter increases. This peculiar behavior is apparently due to the gradual growth of large crystals at the high temperatures, these crystals being very dense, but being separated from one another by small cracks or interstices which grow in size with the crystals, consequently producing an increase in the porosity. It is probable that a body made from pure zinc oxide would gradually disintegrate at high temperature, owing to this slow crystallization.

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Discussion

By E. W. WASHBURN:—During use a zinc retort body gradually changes in composition owing to the absorption of zinc oxide and the resultant body contains a large amount of this material. Zinc oxide itself, as Mr. Libman's results show, is a good refractory and it is practically certain that from

¹ Washburn and Libman, *Jour. Amer. Ceram. Soc.*, **3**, 637 (1920).

² Washburn and Bunting, *Ibid.*, **5**, 112 (1922).

the substances Al_2O_3 (introduced as fire clay) SiO_2 and ZnO a highly refractory zinc retort could be manufactured. There is also the additional possibility of being able to obtain a retort body which would be practically unattacked by the charge during operation. The principles to be followed in meeting this condition are known but in order to apply them the Phase Rule diagram of the system is required and this has not yet been worked out. The construction of this diagram offers no insurmountable difficulties and the requisite furnace equipment is on the market. If the zinc industry would coöperate in supporting research in this field some extremely valuable and fundamental scientific data would result which would enable us not only to understand exactly what happens in a zinc retort during usage but would also point the way toward the scientifically ideal retort body.