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Discussions and Notes

PbO Transformation Induced by Water

CHARLES A. SORRELL

ALTHOUGH tetragonal PbO transforms readily to orthorhombic PbO near 500°C, the reverse transformation is not instantaneous. Soederquist and Dickens¹ reported that single crystals of orthorhombic PbO (size not specified) transform in hours or days at room temperature to the tetragonal modification; however, very small crystals, as in powders, persist indefinitely as the orthorhombic modification unless external forces are applied.

The transformation of orthorhombic to tetragonal PbO by grinding was studied in detail by Clark and Rowan,² who found that ball-milled material was distorted and had greatly enhanced catalytic properties. Dachille and Roy³ and White *et al.*,⁴ who also investigated transformation by grinding, concluded that isostatic pressures determine the equilibrium phase, with shear stresses contributing to transformation kinetics only. Lewis *et al.*,⁵ however, concluded that the equilibrium assemblage is a mixture of both modifications and that shear stresses modify the pressure-temperature diagram. Senna and Kuno⁶ studied the kinetics of the orthorhombic-tetragonal transformation by isothermal wet ball-milling, obtaining a first-order relation between fractional conversion and milling time. They concluded also that a mechanical effect has a fundamental role.

Lead monoxide is basic; soon after it is added to water a white precipitate appears and, on drying, coats the material. The precipitate has been reported⁷ to be a highly basic carbonate but has not been characterized.

The present note reports that complete conversion of powdered orthorhombic PbO to tetragonal PbO can be induced merely by water treatment and that the precipitate has been identified as basic lead carbonate.

Commercial PbO, prepared by oxidation of molten Pb in a reverberatory or cupel furnace,⁸ is normally a mixture of the modifications. Reagent-grade PbO,⁹ which contains 85±3% orthorhombic PbO, the remainder being tetragonal, transformed to 100% tetragonal PbO at all temperatures between 22° and 100°C in the presence of sufficient water to wet all the particles during the time required for wetting, decanting, and drying. Reagent-grade PbO converted to 100% orthorhombic PbO by heating at 600°C exhibited appreciable densification and grain growth and did not undergo the transformation in water within a year. Very fine-grained orthorhombic PbO, produced by vapor deposition, transformed in water within 48 h. All analyses were obtained by X-ray diffractometry, using CuK α radiation, with a scanning rate of 0.2°2 θ /min.

Enough precipitate was separated by repeated decanting to establish its identity as basic lead carbonate, 2PbCO₃·Pb(OH)₂; it was identified by comparing the X-ray diffraction data with those of Katz and Lefker¹⁰ and by comparing the DTA curves with those of commercial basic lead carbonate. Mass spectrometric determination of the dissociation products and measurement of weight loss on dissociation to PbO at 700°C confirmed the identification. To determine if CO₂ in aqueous solution is involved in the transformation, reagent-grade PbO

was covered with an excess of distilled water, boiled, purged with N₂, and decanted and dried in an N₂ atmosphere. Basic lead carbonate did not precipitate, but transformation to litharge occurred as in air.

It seems probable that water causes the transformation through interaction of the polar molecule with the particle surface, resulting in relief of strain in the metastable orthorhombic layers. It is also possible that the mechanism is one of solution and reprecipitation, with nucleation of tetragonal PbO on the surface followed by inward transformation. It was observed, however, that less polar liquids, e.g. acetone, ethanol, and 1-propanol, do not induce the transformation even though the solubility of PbO is appreciable. In mixtures of water with acetone, ethanol, or 1-propanol both phases were present, apparently in dynamic equilibrium with the liquid.

Another possibility is that the two phases have different compositions and that water plays a role in changing the stoichiometry. If, for example, tetragonal PbO has a higher O:Pb ratio than orthorhombic PbO, the transformation could be a consequence of addition of oxygen atoms, i.e. OH ions, to the phase. Until the O:Pb ratios of the phases have been further investigated, the question remains open.

Regardless of the mechanism, particle size and the presence of tetragonal PbO are important factors in the transformation in water. Relatively large particles, produced by sintering, did not transform; on the other hand, very fine particles, produced by vapor deposition, transformed slowly. The transformation was fastest in relatively fine-grained material containing some tetragonal PbO, which apparently accelerates the nucleation and growth process.

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