HEAT TREATMENT OF TIN POWDER

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Powdered tin [1] is widely used in the national economy [2], in particular in the manufacture of chemical reagents [3, 4]. In this connection, the present work was undertaknen with the aim of studying the processes occurring during the production of SnO_2 from a tin powder [1]. Because of its properties (high corrosion resistance, good electrical conductivity, and the like [5]), tin dioxide (IV) is used for making mixers, crucibles, electrodes, radio components, and various other parts. There is therefore considerable interest in exploring new ways of synthesizing SnO_2 and studying conditions under which it is obtained. At the present time the most advanced direction in the tin dioxide (IV) manufacturing technology is high-temperature oxidation of powdered tin metal [6].

The main methods of investigation were x-ray phase analysis (XPA) (DRON-2.0 diffractometer, filtered copper radiation) and thermography (OD-103 derivatograph, heating rate 10°C/min, batch weight 1.25-1.35 g). The material investigated was a mixture produced by thorough mixing in a mechanical mortar and consisting of OP1 tin metal powder [1] and grade ChDA (pure for analysis) tin dioxide (IV) [7]. Tin dioxide (IV) is added to such a charge in order to separate the tin metal particles from one another, which melt during heating, but, because of the presence of SnO_2 in the mixture, cannot join together [3]. Consequently, during a subsequent temperature rise the tin (0) oxidizes separately in each particle (drop), which creates the most favorable conditions for obtaining the required product (SnO_2). Heat treatment of a mixture consisting of tin (0) and tin dioxide (IV) powders produces the same effect that is usually achieved in the preparation of SnO_2 by the atomization of molten metal with compressed air [6]. However, as has been shown by experiments, simple mechanical mixing of the powdered components eliminates the operation of molten tin (0) disintegration by an air stream (at a high temperature and a pressure of several atmospheres). Special apparatus for this operation is then no longer necessary, and the number of stages in the SnO_2 production process is reduced.

In our experiments heat treatment was performed on mixtures containing tin (0) and tin dioxide (IV) in a wide range of concentrations, but Fig. 1 shows only heating curves for specimens of the optimum composition, i.e., an equimolar $Sn—SnO_2$ mixture. From the DTA and TG curves it can be concluded that, as would be expected, during the heat treatment (at up to 900°C) of this mixture in the absence of of atmospheric oxygen no oxidation of metallic tin took place. An endothermic effect with a 232°C maximum was due to melting of metallic tin. This conclusion is borne out by XPA data for specimens calcined (in sealed quartz capsules) in the 200-900°C temperature range: No new phase formation was detected [8]. The DTA curve for an $Sn—SnO_2$ specimen heated in air shows two thermal effects: an endothermic effect with a 232°C maximum, due to heat absorption during the melting of tin, and an endothermic effect with a 590°C maximum, linked with oxidation of molten tin and borne out by appriciable specimen weight gains observed at temperatures up to 880 ± 10°C (TG curve). According to XPA data, an equimolar mixture specimen calcined at 900°C was a virtually single-phase tin dioxide (IV) [8] with the rutile lattice (a = 0.473 and c = 0.318 nm). Further investigation established that the behavior of specimens containing 25-50 mole % SnO_2 during heating was identical, single phase tin dioxide (IV) alone being present at a temperature of 900°C [8].

The XPA method was employed for studying the phase formation and distribution behavior during the heating of the equimolar $Sn—SnO_2$ mixture at a steadily rising temperature. The data obtained revealed the character of the chemical transformations taking place in this system. It was found that up to 200°C no changes whatsoever occurred in the $Sn—SnO_2$ mixture and that it was only at 250°C that a new phase, tin dioxide (II), appeared as a result of incipient oxidation of molten tin (0). As no separate molten tin (0) phase formation was then detected (even visually), it is reasonable to assume that tin (0) oxidized on the sur-

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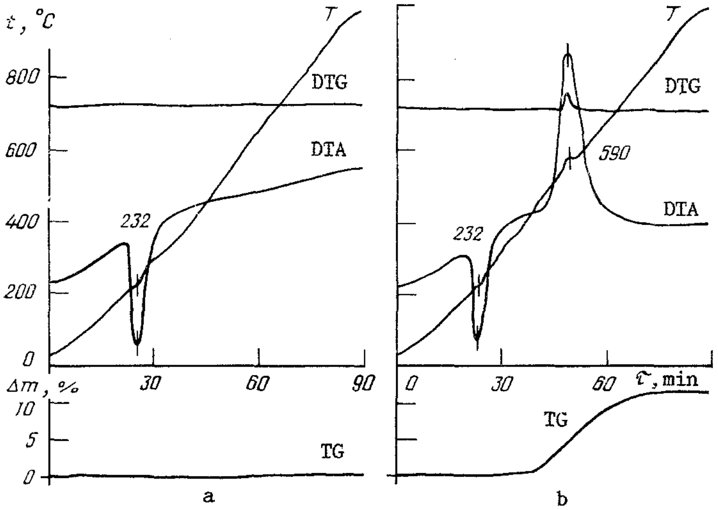

Fig. 1. Derivatograms of equimolar $Sn-SnO_2$ powder mixture heated in nitrogen (a) and air (b): T) specimen temperature variation curve; DTG) differential thermogravimetric curve; DTA) differential thermal curve; TG) specimen weight loss curve.

face of each of its individual droplets, with the formation of an intermediate phase, i.e., SnO. However, because of the instability of tin dioxide (II), the oxidation of tin during heating in the 400-500°C range was accompanied by the tin dioxide (II) disproportionation reaction

$$SnO \xrightarrow{400+500\,°C} SnO_2 + Sn + Sn_3O_4 + SnO. \quad (1)$$

Phase composition of equimolar $Sn-SnO_2$ mixture specimens heat-treated in air*

Temp., °C	Phase composition
200	SnO_2, Sn
250	SnO_2, Sn, SnO (Tr.)†
300	SnO_2, Sn, SnO
350	
400	SnO_2, Sn, SnO, Sn_3O_4
450	
500	SnO_2, Sn, Sn_3O_4, SnO (Tr.)
600	SnO_2, Sn (A. a.)
700	SnO_2, Sn (A. a.)
800	SnO_2, Sn (A. a.)
850	SnO_2, Sn (Tr.)
900	SnO_2

*Holding time at each temperature 3 h.
†Tr. = traces, A. a. = appreciable amount.

At temperatures of 500°C and higher direct oxidation of the powdered metallic tin powder predominated in the mixture. The oxidation process was finally completed at a temperature of about 900°C.

Phase compositions of tin-containing products* calculated in air for 2 h

Temperature, °C	Phase composition
350	SnO tetr
400	SnO, SnO_2, Sn, Sn_3O_4
450	SnO, SnO_2, Sn, Sn_3O_4
500	SnO_2, Sn, Sn_3O_4, SnO (Tr.)

*Grade ChDA SnO (TU 6-09-1503-76 was used.

Thus, the heat treatment of a mixture of tin and 25-50 mole % SnO_2 is accompanied by the following processes:

$$Sn + SnO_2 \xrightarrow{230+350\,^{\circ}C} SnO_2 + Sn + SnO \xrightarrow{400+500\,^{\circ}C} SnO_2 + Sn + Sn_3O_4 + SnO \xrightarrow{550+850\,^{\circ}C} SnO_2 + Sn \xrightarrow{900\,^{\circ}C} SnO_2. \quad (2)$$

It should be noted that the end product fully meets the grade CbDA requirements for SnO_2 [7].

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