ESTIMATION OF THE REACTIVITIES OF SOME IRON(III)OXIDES
BY EMANATION THERMAL ANALYSIS

V. Balek

Nuclear Research Institute, 250 68 Řež, ČSSR
(Received December 8, 1976)

Dedicated to Mrs. K. B. Zaborenko, Professor at the Moscow State University and leader of a research group developing emanation thermal analysis in the USSR, in honour of her anniversary.

A new method for estimating the reactivity of iron(III) oxide in a solid-state reaction is proposed. The method is based on the release of radioactive inert gas atoms ($^{222}$Rn emanation) from a mixture of solids previously labeled with the inert gas atoms. By measuring the rate of release of emanation as a function of temperature, information can be obtained about the solid-state reaction and the final reaction product. The reactivities of some iron(III) oxide samples of different thermal histories and origins have been estimated in the solid-state reaction with zinc oxide labeled with the parent isotope of the emanation, $^{228}$Th. The results of the proposed method, found more objective than common methods, are compared with surface area measurements on the tested samples.

The reactivity of iron(II) oxide is of great importance as regards the technology of ferrite materials, and the manufacture of catalysts and inorganic pigments. The reactivities of finely-dispersed powders are commonly estimated by the measurement of specific surface area, solubility in acids or catalytic activity.

However, as practical experience has shown, these parameters cannot adequately characterize the actual ability of the solid material to react with another solid. Emanation thermal analysis (ETA) [1, 2] permits the reactivities of oxides or other materials to be tested directly during solid-state reactions.

Experimental

Preparation of iron(III) oxide samples: Samples used in this investigation were obtained a) by the decomposition of basic iron carbonate, followed by its further heating for 2 hours at 700, 900 and 1100°, and b) as commercial chemicals denoted "For ferrites", "PPG" and "A.R." (made in USSR), the modes of preparation of which were not known. The powder characteristics of the iron(III) oxide samples are given elsewhere [3]; it was established by means of X-ray diffraction that all samples were $\alpha$-$Fe_2O_3$. 
Zinc oxide labeled with $^{228}\text{Th}$ was prepared by decomposition of zinc hydroxide at 800°C for 2 hours. A trace amount of $^{228}\text{Th}$ (10 pg per gram of sample) was introduced into the zinc hydroxide by co-precipitation. $^{220}\text{Rn}$ was produced in the sample by the radioactive decay: $^{228}\text{Th} \rightarrow ^{224}\text{Ra} \rightarrow ^{220}\text{Rn}$.

The iron(III) oxide sample intended for testing was mixed in a stoichiometric ratio (1 : 1) with another component of the ferrite mixture (zinc oxide in this case) which had been labeled previously with $^{228}\text{Th}$. The same zinc oxide was used in the reaction mixture for all the tested samples of iron(III) oxide. The reaction mixtures were ground together for 5 min under acetone in a mortar and 100 – 300 mg of the mixture was put into a quartz crucible and placed in a metal block of an electric furnace. The temperature of the furnace was raised to 1000°C at a rate of 10 – 12 K min$^{-1}$. A stream of air (flow-rate 200 ml min$^{-1}$) passed over the heated sample and carried the radioactive inert gas into a scintillation chamber. The count-rate measurement of the released radioactive inert gas $^{220}\text{Rn}$, as well as the temperature rise during heating, were automatically recorded. A detailed description of the apparatus used is given elsewhere [2, 4].

**Results and discussion**

*Reaction between ZnO and Fe$_2$O$_3*$

Results of ETA, DTA, dilatometry and chemical analysis of the ZnO – Fe$_2$O$_3$ mixtures are shown in Fig. 1. The ETA curves of the starting compounds ZnO and Fe$_2$O$_3$ were checked [2, 4] and were exponential over the temperature range studied.

![Fig. 1. Thermoanalytical study of ZnO + Fe$_2$O$_3$ reaction in air. (1) Dilatometric curve, (2) DTA curve, (3) ETA curve, (4) ETA curve during re-heating of mixture. Percentage of ZnO reacted is shown for samples I–VI](image-url)