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

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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(III) 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 α-Fe_2O_3.

Zinc oxide labeled with ^{228}Th was prepared by decomposition of zinc hydroxide at 800° for 2 hours. A trace amount of ^{228}Th (10 pg per gram of sample) was introduced into the zinc hydroxide by co-precipitation. ^{220}Rn was produced in the sample by the radioactive decay: $^{228}\mathrm{Th} \xrightarrow{\alpha} {}^{224}\mathrm{Ra} \xrightarrow{\alpha} {}^{220}\mathrm{Rn}$.

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}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° 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}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_2O_3

Results of ETA, DTA, dilatometry and chemical analysis of the ZnO – Fe_2O_3 mixtures are shown in Fig. 1. The ETA curves of the starting compounds ZnO and Fe_2O_3 were checked [2, 4] and were exponential over the temperature range studied.

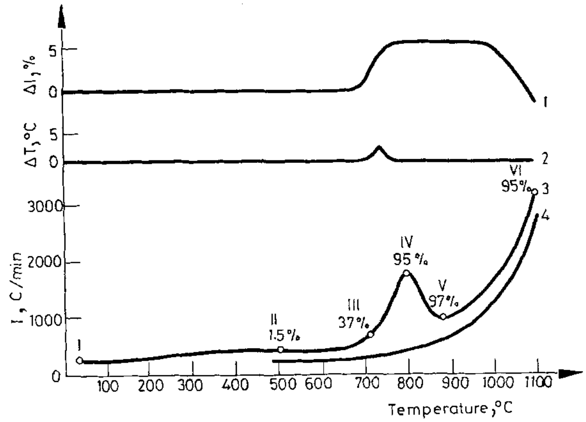

Fig. 1. Thermoanalytical study of ZnO + Fe_2O_3 reaction in air. (1) Dilatometric curve, (2) DTA curve, (3) ETA curve, (4) ETA curve during re-heating of mixture. Percentage of ZnO reacted is shown for samples I – VI

Zinc and iron oxides interact in a series of well-studied stages [5–7]. Results obtained in this paper confirm earlier conclusions [5–7]. The initial layers of the product begin to form by surface diffusion at the most favorable sites at 250 and 400°; their formation is reflected in an increase in the rate of emanation release (Fig. 1, curve 3). The DTA and dilatometric curves did not exhibit any change at these temperatures.

At 500°, 1.5% of the ZnO had reacted (the accuracy of the chemical analysis was ±1%). A sharp change in all the curves of Fig. 1 was observed at 670 to 700°. X-ray diffraction patterns of the mixture heated to 730° contain the characteristic zinc ferrite line at 25.3 nm, which correlates with the sharply increased quantity of zinc oxide (37%) reacting. The DTA curve shows a small exothermic effect, the dilation curve an expansion of the sample, and the ETA curve the maximum rate of ferrite formation.

Interaction of the basic mass of the initial oxides occurs by volume diffusion above 750°: 95% of the ZnO reacts at this temperature; in the ETA curve a sharp maximum occurs at 790°, after which the emanation release rate decreases, indicating that the reaction is completed. The dilation of the sample, which is probably caused by the formation of very fine reaction products, ceases at this point, and at high temperatures (up to the sintering temperature of the ferrite) the volume remains constant. The increase of the emanation release rate above 900° is determined by the diffusion release of ^{220}Rn from the specimen.

The ETA curve of the mixture of $ZnO-Fe_2O_3$ during the second heating (Fig. 1, curve 4) is of exponential form, being determined by the diffusion of ^{220}Rn from zinc ferrite. From the emanation rate, $\log E_D$ can be plotted as a function of $1/T$, and the activation energy Q for diffusion determined. The diffusion characteristics can be evaluated from the following expression [2, 8]:

$$\log(E - E_0) = (D_0/\lambda)^{1/2}\rho \quad S \exp(-Q/2\,RT) \tag{1}$$

where $(E - E_0)$ is the part of the emanation release rate corresponding to radon diffusion from the specimen, calculated from the total emanation release rate E measured at a given temperature and the emanation release rate E_0 measured at a temperature at which the radon diffusion in the solid can be neglected, (e.g. 25°). In expression (1) D_0 is the diffusion constant, λ the radon decay constant, S the specific surface area, ρ the density, Q the activation energy of radon diffusion in the solid, R the gas constant, and T the absolute temperature.

Estimation of reactivity of iron(III) oxide

As follows from Fig. 1, curve 3, the ETA curve sensitively reflects all the processes taking place during the solid-state reaction between iron(III) and zinc oxides. The temperature of the peak at 790° can be used as the parameter characterizing the reactivity of the $ZnO-Fe_2O_3$ mixture.

The reactivities of a series of iron(III) oxide samples can be estimated on the bases of the ETA curves of $ZnO-Fe_2O_3$ mixtures, when the ZnO component (labeled with ^{228}Th) used is the same in all the mixtures.

Figure 2 shows the ETA curves of $ZnO-Fe_2O_3$ mixtures; the Fe_2O_3 samples used in the mixtures were prepared by heating to 700 (1), 900 (2) and 1000° (3).

From Fig. 2 it follows that increasing temperature of iron(III) oxide treatment leads to rising temperatures of the ETA peaks, which represents the decrease of the iron(III) oxide reactivity with respect to the oxide.

The temperatures of the ETA peaks and the specific surface areas of the iron(III) oxide samples tested are listed in Table 1.

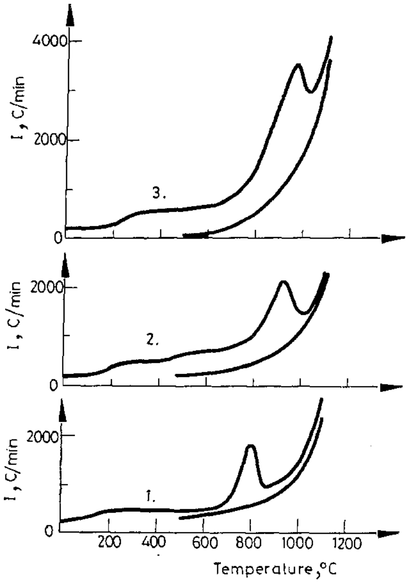

Fig. 2. ETA curves of the $ZnO-Fe_2O_3$ mixture, the ZnO labeled by Řež; the Fe_2O_3 was prepared by heating basic iron carbonate to (1) 700°, (2) 900° and (3) 1100°.

Table 1

Comparison of reactivities of iron(III) oxide samples

	Fe_2O_3 (ex carbonate) heated to °C			Commercial samples		
	700	900	1100	"For ferrites"	"PPG"	"A. G"
Specific surface area, $m^2 \cdot g^{-1}$	5.9	0.9	0.3	3.8	14.8	7.8
Peak in ETA curve, °C	790	925	980	720	880	920

By comparing the ETA results obtained and the specific surface areas, we can see that the iron(III) oxide (ex carbonate) loses its reactivity with decreasing surface area. With the commercial iron(III) oxide samples, however, the relatively highest reactivity is exhibited by the iron(III) oxide "For ferrites", even though its surface area is relatively low (3.8 $m^2 g^{-1}$). The reactivities of the three commercial iron(III) oxide samples decrease in the sequence: "For ferrites", "PPG", "A.G.". No dependence between the reactivities and specific surface areas of these samples has been found.

Conclusion

Emanation thermal analysis has been shown to be a suitable method for estimation of the reactivity of iron(III) oxide. The method makes it possible to investigate the details in the solid-state reaction, and especially the first stages of the reaction. The reactivity estimation of iron(III) oxide is provided directly during the solid-state reaction in the mixture, where the reaction components and the reaction atmosphere can be chosen according to the technological prescriptions.

The ETA method also yields valuable information about the diffusion properties of the final products of the solid-state reaction. It has been shown that the method proposed yields more objective results than the surface area measurements commonly used for estimation of the reactivities of powders.

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Résumé — On propose une nouvelle méthode pour estimer la réactivité de l'oxyde de fer(III) dans les réactions en phase solide. Elle repose sur le dégagement des atomes du gaz inerte radioactif ^{220}Rn (radon) du mélange des solides préalablement marqués par les atomes de gaz inerte. En mesurant la vitesse de dégagement du radon en fonction du temps on peut obtenir des renseignements sur la réaction dans l'état solide ainsi que sur le produit final de la réaction. On a pu estimer la réactivité en phase solide de quelques échantillons d'oxyde de fer(III), d'histoire thermique et d'origine différentes, vis-à-vis de l'oxyde de zinc marqué avec l'isotope parent du radon: ^{228}Th. On a comparé les résultats de la méthode proposée, estimée plus objective que celles habituellement utilisées, à ceux des mesures de surfaces spécifiques des échantillons étudiés.

ZUSAMMENFASSUNG — Eine neue Methode zur Abschätzung der Reaktivität von Eisen(III)oxid in der Festphasenreaktion wird vorgeschlagen. Die Methode beruht auf der Freisetzung radioaktiver Inertgasatome ^{220}Rn (Emanation) aus dem Gemisch ursprünglich mit Inertgasatomen markierter Festkörper. Durch Messung der Geschwindigkeit der abgegebenen Emanation in Abhängigkeit von der Temperatur können Informationen über die Festphasenreaktion und die Reaktions-Endprodukte erhalten werden. Die Ermittlung der Reaktivität einiger Eisen(III) oxid-Proben verschiedener Wärmegeschichte und verschiedenen Ursprungs wurde in der Festphasenreaktion mittels Zinkoxid durchgeführt, das mit dem Ausgangsisotopen der Emanation, ^{228}Th, markiert worden war. Die Resultate der vorgeschlagenen Methode, welche den üblichen gegenüber für objektiver gefunden wurde, werden mit den Oberflächenmessungen der geprüften Proben verglichen.

Резюме — Предложен новый метод для оценки реакционной способности окиси железа (III) в твердофазной реакции. Метод основан на выделении радиоактивных атомов инертного газа ^{220}Rn (эманация) из смеси твердых тел, ранее меченных атомами этого инертного газа. Путем измерения скорости выделения эманации в зависимости от термпературы, можно получить информацию о реакции в твердом теле и конечном продукте реакции. Оценка реакционной способности некоторых образцов окиси железа (III) различной термической предыстории и происхождения была доказана в твердотельной реакции с окисью цинка, помеченного материнским изотопом эманации — ^{228}Th. Результаты предложенного метода, который является более объективным, чем обычно методы, сопоставлены с измерениями удельной поверхностной исрользуемые исследованных образцов.