

COMPARISON OF VARIOUS ANALYTICAL METHODS IN THE STUDY OF THE REACTION BETWEEN ZINC OXIDE AND Fe(III) OXIDE

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Abstract

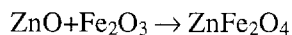
The paper deals with the possible application of various methods to follow the course of reaction between zinc oxide and Fe(III) oxide with respect to various kinds of Fe(III) oxides used (Fe(III) pigments – red, yellow and black). Differential thermal analysis and chemical analysis can be recommended as the most suitable methods for following reactions leading to spinel formation. The possibilities of determining the activation energy of the studied processes are discussed. When Fe(III) red pigment is used as a reactant and therefore no reaction occurs except spinel formation, conductometric thermal analysis was found to be suitable and more sensitive for the evaluation of differences in reactivities.

It has also been observed that the kind of Fe(III) pigment, due to its individual reactivity significantly affects the colouring properties of the final product (e.g., of the ceramic stain).

Keywords: conductometric TA, DTA, evaluation of methods of TA, formation of reactivity of Fe(III) oxides, kinetics of ferrite formation, reactivity, thermal dilatometry, Zn ferrite

Introduction

A very important group of oxidic materials are the mixed double oxides showing a spinel-like structure, which are prepared by the reaction between two oxides in a solid phase at high temperatures (1000–1250°C) [1, 2]. The spinel $ZnFe_2O_4$ is formed via the following reaction:



This compound is mainly used in the production of ceramic pigments [1, 2] and ferrites [1], and most recent uses of spinels include anticorrosive pigments [3, 4].

The course of formation of this spinel was reported by Paulik [5]. The process was followed by thermodilatometry (TD) and differential thermal analysis

(DTA) procedures. In the temperature range of 300–400°C the catalytic activity and the adsorption capacity were observed to increase, and the catalytic effect of ZnO and Fe₂O₃ on the reaction $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ also increased. As the DTA curves do not indicate any heat changes in this temperature range, it can be assumed that the changes are connected with a conversion to spinel only at the surface of the particles. Nucleation starts at 300°C, and the surface is gradually covered by the nuclei of a new phase. There are many active sites in this layer which cause an increase in the catalytic activity.

The second stage of change starts at 570°C, when the main role is played by bulk diffusion. This is indicated by effects shown by the DTA and TD curves. The reaction ends at 750°C [5]. The authors of [7] report the reaction to occur in the temperature range of 635–780°C.

Depending on the nature of the starting material (e.g., Fe₂O₃ as Fe(III) red precipitate product of thermal reaction, Fe(III) yellow or Fe(III) black), on the treatment applied (e.g. overfiring at a definite temperature), or occasionally, on the use of other activation procedures, the component concerned will have varying reactivity in the reaction of interest [1, 9–11]. Differences in the reactivity determine the degree of reaction, the presence of structural defects, the microstructure of the product grains and thus usually also the final properties of the product [12, 13].

The reactivity of the starting material (in the case of interest the Fe(III) oxide) can be evaluated by examining the behaviour of the starting material in the reaction for which the material is destined (the so-called destructive method), i.e. in the reaction with ZnO. A number of methods are available for following the course formation of ZnFe₂O₄. These methods include thermal analysis [5, 8, 13–15], chemical analysis [6, 7, 16], and X-ray diffraction analysis [6, 8] procedures. The present contribution is devoted to evaluate the applicability of the mentioned methods for following the reaction of ZnO with Fe₂O₃, aiming at differentiating among different properties like reactivities of the same kinds of Fe(III) pigments (different charges), technologies of production, etc.

Experimental

Starting compounds

Altogether 7 commercial pigments with the following designations were tested: Fe(III) red TP 303 (Precheza Joint – stock Company, Přeřov, Czech Republic), Fe(III) red TD 202 (Precheza, Přeřov, Czech Republic), Fe(III) red FB 110 (Bayer AG, Germany), Fe(III) red FB 130 (Bayer AG, Germany), Fe(III) yellow Hrušov (Hrušov Chemical Company, Czech Republic), Fe(III) yellow B 920 (Bayer AG, Germany), and Fe(III) black B 316 (Bayer AG, Germany). As a ZnO source, zinc white GR (a product of the Heubach Company, Germany) was used.

Devices and methods used

The reaction mixtures of ZnO and Fe₂O₃ (the amounts of Fe(III) yellow and black related to the corresponding Fe₂O₃ amounts) were wet homogenized in a Fritsch planetary mill Pulverisette 5 for 1 h. In milling process 50 ml agate mortars and 6 agate balls of 1–1.5 cm diameter were used. The reaction mixture was dried in a drier at 100°C and pulverized in a porcelain mortar.

Chemical analysis for the unreacted zinc was started by leaching the calcined reaction mixture with a saturated ammoniacal NH₄Cl solution. The zinc content was determined by chelatometric titration.

X-ray diffraction analysis was performed with a HZG-4B diffractometer. As a source of radiation and X-ray tube with a copper anticathode was used, the K_β radiation being reduced by means of a nickel filter.

DTA curves were recorded with a Derivatograph C (MOM, Hungary) under the following conditions: sample mass: 300–600 mg, temperature range: 25–950°C, linear heating rate: 10 K min⁻¹, air atmosphere, and aluminium oxide of the thermal analysis grade as a reference substance. The samples were placed in an open corundum crucible, and the temperature was measured by means of a Pt–PtRh thermocouple. The characteristic temperatures were determined using the TAS program [17].

Conductometric thermal analysis (CTA) was carried out using an equipment consisting of a vertical furnace, an LCRG bridge (Tesla BM 591, Czech Republic), and a programming unit Chinotherm (LP 849, Hungary). The sample to be measured was poured and compressed into a corundum crucible fitted with an electrode system and positioned at a thermocouple joint. The measurement was run in the temperature range of 200–900°C, at a heating rate of 2 K min⁻¹.

The changes in longitudinal expansion were followed by thermomechanical analyser TMA CXO3RA/T (R.M.I. Electronic Measuring Instruments Co., Czech Republic) under the following conditions: heating rate 5 K min⁻¹ maximum temperature 800°C (Pt–PtRh thermocouple), force acting on the sample 10 mN, and a sample pastille of 3 mm in diameter.

The chromatic properties of the pigments applied in a glaze (at a pigment concentration of 10 wt%) were measured using a Miniscan Hunter Lab instrument operating in the wavelength range of 400–700 nm and expressed by means of the trichromatic L* a* b* system CIE Lab coordinates.

Results and discussion

The reaction between ZnO and Fe₂O₃ can be followed by a number of methods. From the point of view of equipment, standard chemical analysis procedures are the most simple: the content of unreacted zinc is determined in calcined reaction mixtures. In addition to the evaluation of the reactivity of Fe(III) oxides at a given temperature, the method enables us to follow also the reaction kinetics

under isothermal or non-isothermal conditions and to calculate the activation energy of the process.

The advantage of the method is a satisfactory accuracy of the determination and the possibility of an easy evaluation of the reproducibility of determination. The major disadvantage of the procedure is its lengthiness due to the necessity of igniting the samples subjected to analysis followed by a subsequent leaching of the reaction mixture with an ammoniacal NH_4Cl solution and determining the content of zinc by chelatometric titration. In [7] a leaching procedure is described using a 0.5 M H_2SO_4 solution; however dissolution of the spinel in the leaching process can falsify the results of analysis. Preliminary experiments have shown that the amount of spinel dissolved increases with the temperature and concentration of the acid solution used. By the chemical analysis procedure the reactivities of all Fe(III) pigments (i.e. Fe(III) reds, Fe(III) yellows, and Fe(III) blacks) can be evaluated.

A further method used for following the formation of ZnFe_2O_4 is X ray diffraction analysis, which is applied to the fired reaction mixture. The formation of ZnFe_2O_4 is characterized by new diffraction peaks appearing in the diffractograms obtained, the peak intensities increasing with increasing degree of reaction. Thus, if we know the diffraction peak intensities in the reaction mixture ignited at a higher temperature, (therefore characterized by a high degree of reaction) we can determine the corresponding degree of conversion from the diffraction peak intensities obtained for the given reaction mixture. Comparison between the degrees of reaction found by the chemical analysis procedure and those found by the X-ray diffraction procedure for different firing temperatures was performed by Duncan [6]. The comparison shows that the value sets determined by these two methods exhibit a difference in the range of 2–4%. The X-ray diffraction method can be, however, recommended especially for determining the crystal line phases in the reaction mixtures.

Methods of thermal analysis are popular for following reaction of which CTA, TMA, and DTA procedures will be discussed below.

In CTA the course of reaction is followed by measuring changes in the dependence of conductivity on the reciprocal of temperature and determining the onset temperature of the reaction (T_{onset}) [15]. The method is sensitive and can be used for following the reaction even when small sample amounts are available. A disadvantage is the long time of measurement, as the reaction is recommended to be run at a low heating rate (as a rule of 2 K min^{-1}). Due to its high sensitivity, this method can be recommended for following the reactivities of various kinds or charges of Fe(III) red. For Fe(III) yellows and blacks further effects were observed and the reaction onset temperature could not be determined unambiguously. Figure 1 shows an example of the record obtained for the reaction of ZnO and Fe(III) red FB 130.

CTA permitted evaluation of changes in the reactivity of Fe(III) red due to activation by grinding; the reaction onset temperature was thus reduced by 20–30°C.

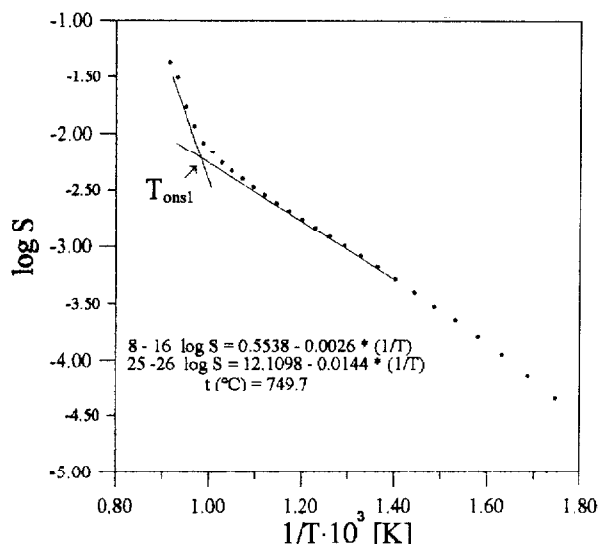


Fig. 1 CTA curve obtained with ZnO and Fe(III) red FB 130, $T_{\text{onsl}} = 750^{\circ}\text{C}$

Whereas in CTA the course of reaction is followed by measurement of changes in electric conductivity, TMA identifies the course of reaction on the basis of changes in linear expansion of the reaction mixture investigated. Again, it is possible to use a small amount (a pellet of 3 mm diameter). The course of reaction is characterized by a step, which allows the onset and end of the reaction to be determined. On cooling and subsequent repeated heating of the reacted mixture no changes occur in the thermal expansion (Fig. 2, curves 2 and 3). It is not possible to follow the reactivities of Fe(III) yellow and black again, as during the dehydration or, occasionally, oxidation thereof larger changes in the linear expansion would take place. Fe(III) yellows and blacks can be used only when changed to the Fe(III) red via, e.g., firing at 350°C for an hour. An example of TMA measurements is shown in Fig. 2, wherein, as a source of the Fe(III) pigment, the Fe(III) red TD 202 was used.

Reactions of this kind are most frequently followed by DTA procedures, which enable heat-induced changes occurring during sample heating to be followed. It is possible to evaluate the onset temperature of reaction, maximum and end of the reaction peak for the real reaction (exothermal effect) on the one hand and for the peaks corresponding to the dehydration or oxidation processes involving Fe(III) yellows or Fe(III) blacks on the other. The principle can be used advantageously also for determining the activation energies [19]. For Fe(III) reds the reaction peaks are rather small and the measurement requires a large amount (400–500 mg) of material. With some kinds of Fe(III) red even rates of heating as high as 15 K min^{-1} produce no effect. When using the present advanced instruments allowing possibility use of small sample amounts (10–100 mg), the

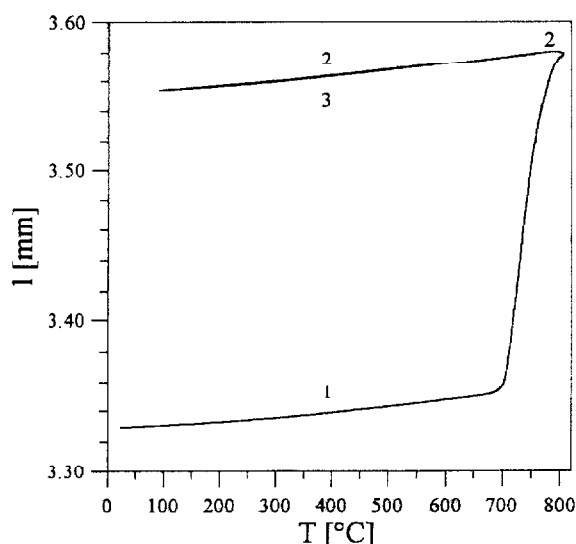


Fig. 2 TMA curves of the ZnO+Fe(III) red TD 202 system. Conditions of heat treatment (1) heating at a rate of 5 K min^{-1} up to 800°C , (2) cooling at a rate of 5 K min^{-1} down to 100°C , and (3) heating at a rate of 5 K min^{-1} up to 800°C (dashed line)

analysis is to be run at a relatively high heating rate, which results in a rather rapid wearing of the thermocouple and furnace heating coils. From the point of view of the sensitivity of measurement it seems to be advisable to use the so-called Roberts block (in principle, by a thermocouple in direct contact with the sample); thus, the reaction peaks obtained become more distinct.

In Table 1 the reaction onset temperatures (T_{ons1}) are compared as determined by chemical analysis, CTA, TMA, and DTA procedures using Fe(III) reds TP 303 and TD 202 (produced by the Precheza Company, Přerov, Czech Republic).

Table 1 Extrapolated reaction onset temperatures for Fe(III) reds TP 303 and TD 202 obtained by means of various methods

	Chemical analysis	CTA	TMA	DTA
	$T_{\text{ons1}}/^\circ\text{C}$			
Fe(III) red TP 303	734	600	730	746
Fe(III) red TD 202	710	551	702	714

The Table shows clearly that when the chemical analysis, TMA, and DTA procedures are applied, the extrapolated onset temperatures do not differ significantly. CTA yields much lower onset temperatures, which reflects differences in the methods. The CTA method, as it indicates more sensitively the start of the reaction, gives therefore greater differences in the T_{ons1} values of reactants of vari-

ous reactivities. Whereas in the CTA procedure the first steps of reaction onset as running in the surface layer are recorded, in the DTA procedure the temperature effects taking place in the sample bulk are measured.

Comparison of all the methods mentioned clearly shows that the course of the reaction of Fe(III) pigments with zinc oxide can be followed best by means of DTA. CTA cannot be recommended to evaluate the reactivities of Fe(III) yellows, blacks or other Fe₂O₃ sources, because their decomposition processes leading to Fe₂O₃ are very close to the ferrite formation reaction and it is nearly impossible to evaluate the intersection of the linear parts of the log σ vs. $1/T$ plot. On the other hand, CTA is a more sensitive method, therefore it is suitable when only small changes or treatments with Fe₂O₃ reactants were done (another batch of reactants, changes in the milling of the reaction mixture etc.).

As it has been mentioned above, the chemical analysis and DTA procedures can be used for calculating the activation energy and, occasionally, the kinetic reaction model. When using the chemical analysis method of approaching the problem, the procedure is based on determining the rate constants for the reactions corresponding to the presumed models (in the present case the diffusion models) at varying temperatures of firing [18] (isothermal kinetics) or, occasionally, on determining the time necessary for achieving a certain degree of conversion (mostly $\alpha=0.5$) [18]. On the other hand, with the DTA method, the temperatures of peak maxima obtained at various heating rates (non-isothermal kinetics) are followed, and the calculations are made most frequently using the Kissinger method [19].

Table 2 Activation energy E values for the Fe₂O₃+ZnO reaction system as determined by chemical analysis and DTA procedures

Source of Fe ₂ O ₃	Chemical analysis	DTA
	$E/\text{kJ mol}^{-1}$	
Fe(III) yellow Hrušov	139	205
Fe(III) red TP 303	182	282
Fe(III) red FB 130	330	475

Table 2 contains the activation energy values obtained by the two methods for various Fe(III) pigments.

It is evident that the values thus obtained differ from each other. In a previous paper [7] the dependence of the experimental activation energy on the method used has been discussed. The values were found to vary in a range as broad as 58–461 kJ mol⁻¹.

So far the methods identifying differences among Fe(III) pigments on the basis of changes taking place on heating or, occasionally, by means of following the unreacted zinc content have been discussed. In practice, however, it is necessary

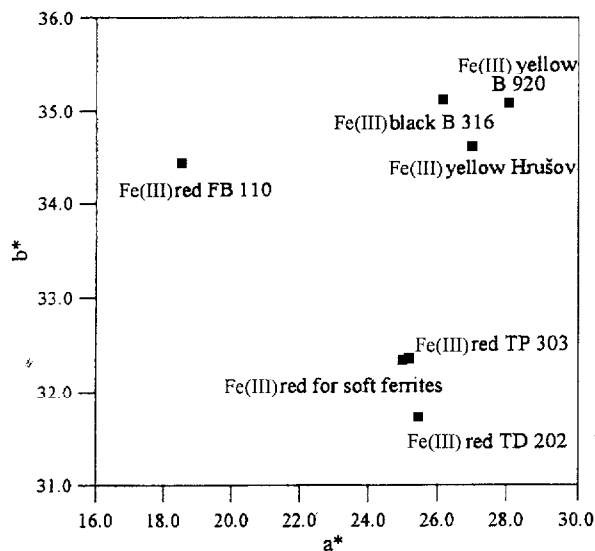


Fig. 3 Chromatic properties of the colouring pigment applied in transparent glaze (ZP 6474) with a molar composition of $4.94\text{ZnO} \cdot 1.14\text{Cr}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ for Fe(III) pigments of various kinds

to evaluate the properties of pigments, especially with respect to potential applications thereof. One of the applications of Fe(III) pigments is in the field of production of ceramic pigments (stains). It is shown by the example of a ceramic-colouring pigment with a molar composition of $4.94\text{ZnO} \cdot 1.14\text{Cr}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ that the kind of Fe(III) pigment affects heavily the chromatic properties of the colouring pigment (Fig. 3) which is, to a certain degree, connected with the history, preparation and therefore the reactivity thereof. The higher the reactivity of the Fe_2O_3 used for the production of the above mentioned ceramic stain applied in commercial transparent glazes, the greater the shift of the resulting colour in CIE $L^*a^*b^*$ system to reddish hue of brown colour.

Further application possibilities of Fe(III) pigments (especially of Fe(III) reds) are in the field of preparing environmentally positive anticorrosive pigments [3, 20]. This concerns namely the pigments containing mixed oxides, such as $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ and $\text{CaO} \cdot \text{Fe}_2\text{O}_3$.

Conclusions

For the purpose of following the reaction of ZnO and Fe_2O_3 the choice of the appropriate method depends on the kind of the Fe(III) pigments (Fe(III) reds, Fe(III) yellows, and Fe(III) blacks) used, the equipment applied, and on the purpose of measurement. To follow the reaction of all kinds of Fe(III) pigments differential thermal analysis can be recommended, although, due to the small

amount of tested material used in modern instruments the effects are not very large. Therefore the DTA method can be supplemented by chemical or X-ray diffraction analysis. For Fe(III) reds used for the production of ferrites where only one reaction occurs, the method of conductometric thermal analysis was suitable and more sensitive for testing the differences in reactivities.

As there are great differences in the reactivities of Fe(III) pigments, it is necessary to consider this aspect when thinking of the proper use of Fe(III) pigment kinds and of the evaluation of the changes in the properties of products when using different starting materials.

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