

USE OF EMANATION THERMAL ANALYSIS, DTA AND TG/DTG FOR ZIRCONIA REACTIVITY TESTING DURING ZIRCON PREPARATION

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(Received 28 June 1988)

ABSTRACT

Emanation thermal analysis, DTA and TG/DTG are used to distinguish between the reactivities of three commercial zirconia specimens, ZrO₂-7 (Goldschmidt, F.R.G.), CRO-1 (U.S.S.R.) and ZrO₂-S (MEL, U.K.), in the high temperature reaction with silica (Austria) in the presence of admixtures (NaCl–NaF) as mineralizers for zircon (ZrSiO₄) formation. The possible mechanisms of the zircon formation are discussed.

INTRODUCTION

Zircon pigments, used in the ceramic industry for the colouring of glazes, are based on zirconium(IV) silicate (ZrSiO₄) which has a crystal structure corresponding to the mineral zircon.

Previously published reports [1–7] dealing with the formation of zircon pigments explain the transfer of the silicate component during this high temperature reaction. However, there is no satisfactory explanation for the behaviour of zirconia in the reaction mixture with silica. Nor has the reactivity of the feed zirconia in the mixture with silica been evaluated.

In refs. 8 and 9, the applicability of DTA to the study of zircon preparation was mentioned; in ref. 10, DTA was used to study the influence of various admixtures on the high temperature reaction between zirconia and silica.

In this paper, several thermoanalytical techniques, including emanation thermal analysis (ETA) [11], DTA and TG/DTG, are used to distinguish between the reactivities of various commercial zirconia specimens and to describe the mechanism of the reaction between zirconia and silica in the presence of a mineralizer.

EXPERIMENTAL

Three types of zirconia powders, ZrO₂-7 (Goldschmidt, F.R.G.), CRO-1 (U.S.S.R.), and ZrO₂-S grade (MEL, U.K.), and one type of silica, quartz modification (Austria), were used as feed products for the zircon preparation. An equimolar mixture of NaCl–NaF was used as the mineralizing admixture; the chemical composition of the feed reaction mixture being 44 mol% ZrO₂, 44 mol% SiO₂, 6 mol% NaF and 6 mol% NaCl.

The DTA and TG/DTG measurements were carried out in air at a heating rate of 5 K min⁻¹ using Derivatograph equipment, type Q-1500 (MOM Hungary), the mass of the samples being 1.5 g. The inner walls of the furnace were protected with corundum coatings against the corrosive effect of gaseous halogenides. The sensitivity of the DTA measurement was 1/2, that of DTG 1/2 and that of TG was 20 and 50 mg. After the formation of ZrSiO₄, as indicated by the exothermic effect on the DTA curves, the heating run was stopped and the samples were cooled and then chemically analysed, and the conversion degree of ZrSiO₄ was determined. From the DTA results, the onset and end of the ZrSiO₄ formation reaction, T_i and T_f temperatures respectively, the reaction enthalpy ΔH and the activation energy of the reaction E_a were evaluated [12–13,15].

ETA [11,14] of 0.1–0.3 g of the reaction mixture was performed using an ETA thermoanalyser (NRI Řež, Czechoslovakia). The same experimental conditions were used as for the DTA measurements. The zirconia components were previously labelled by impregnation with trace amounts of ²²⁸Th and ²²⁴Ra radionuclides. By spontaneous radioactive decay, radon ²²⁰Rn is formed in the sample



The release of radon atoms was continuously measured during sample heating. The ETA curves are expressed as the temperature dependences of the radon release rate related to the total radioactivity of the labelled samples.

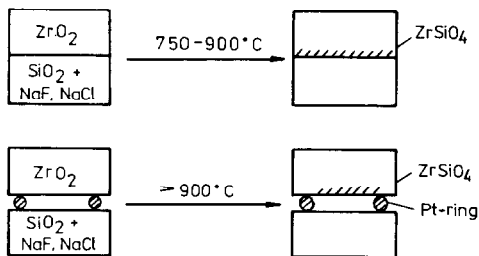


Fig. 1. Scheme of the investigation of the reaction mechanism by means of the Pt-labelled-tablets method.

The Trojan method of the Pt-labelled tablets [16] was used to investigate the movement of the reaction boundary and to describe the reaction mechanism. The arrangement of the zirconia and silica tablets in this method is shown in Fig. 1. The amount of ZrSiO_4 formed on the adjacent faces of the tablets was determined by chemical analysis [17].

RESULTS AND DISCUSSION

Kinetics and mechanism of ZrSiO_4 formation

DTA and TG/DTG curves of the three reaction mixtures used for the zircon preparation are shown in Fig. 2. From Fig. 2, it can be seen that there are no differences between the curves in the temperature range 20–700 °C. The mass of the samples changes slightly. The DTA curves exhibit a small but distinct endothermic effect corresponding to the α - to β -quartz modification transformation.

The endothermic effects in the DTA curves in the temperature range 640–760 °C correspond to the melting of the alkali components present in the reaction mixture (the melting temperature of the NaF–NaCl eutectic being 690 °C) [18]. On further heating, the melt phase attacks the starting oxides, particularly silica. In this chemical process, the silica is transformed

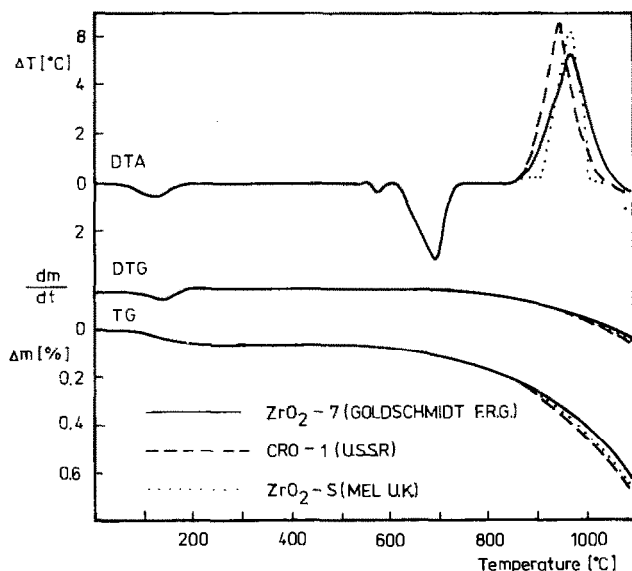
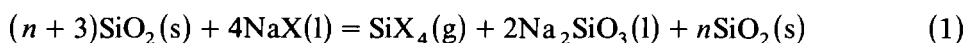


Fig. 2. DTA and TG/DTG results characterizing the thermal behaviour of the feed mixtures for the synthesis of zircon (ZrSiO_4) using different ZrO_2 specimens in the mixture with SiO_2 (heating rate 5 K min^{-1}) in air.

TABLE 1

Zirconia specimen notation	T_i onset (°C)	T_f end (°C)	ΔH (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	Conversion degree δ
ZrO ₂ -7 (F.R.G.)	880	1040	-18.2	80.1	0.92
CRO-1 (U.S.S.R.)	890	1060	-18.4	83.0	0.89
ZrO ₂ -S (U.K.)	905	1030	-17.9	86.0	0.93

into gaseous silicon tetrahalogenides SiCl₄ or SiF₄, and the melt of Na₂SiO₃. The decrease of the sample mass by 0.15% on the TG curves in the temperature range 700–880°C indicates the partial release of gaseous components before the formation of ZrSiO₄ takes place. The processes can be described by the following scheme

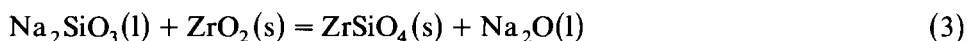
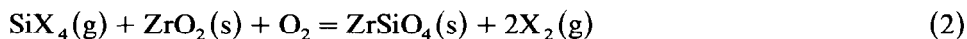


where X indicates F or Cl.

As indicated by the DTA curves in Fig. 2, the formation of ZrSiO₄ is accompanied by exothermic effects. The temperatures T_i and T_f of the onset and the end of this process differ for the three investigated feed mixtures. The characteristics of the ZrSiO₄ formation process, as evaluated from DTA curves in Fig. 2, and the results of the chemical analysis are summarized in Table 1.

As can be seen from Table 1, after heating the feed mixture up to 1100°C, 91 ± 2% of the zircon product is formed. A relatively low value of the activation energy E_a of the formation of zircon was found for the feed reaction mixture containing ZrO₂-7 (F.R.G.) zirconia. For this reaction mixture, the onset temperature T_i of the zircon formation was found to be 10–25°C lower than that for the onset temperature of other feed reaction mixtures investigated in this paper by DTA.

From the results of the Pt-labelled tablets [16], two reaction mechanisms can be suggested for the interaction of the feed reaction mixture to form the final product ZrSiO₄



Each of the two suggested reaction mechanisms is valid for another temperature range; reaction scheme (2) can be considered for the temperature range 750–900°C and reaction scheme (3) can be considered for the temperature interval above 900°C. In both suggested chemical reactions, the feed zirconia reacts with the gaseous or liquid silicium component, respectively. The kinetics of the reactions may differ for zirconia specimens of different reactivity.

Reactivity of zirconia estimated by emanation thermal analysis

Zirconia is a practically non-transportable component of the reaction mixture. Its reactivity is influenced by lattice defects and by the surface area of the sample. ETA [14] has proved a suitable method to investigate changes in the surface and in the defect state of solids, and has been applied here to estimate the reactivity of zirconia.

The ETA curves of the zirconia specimens investigated are given in Fig. 3. The effects on the curves in the range 50–150 °C correspond to the liberation of adsorbed water. The enhanced radon release rate \bar{E} and its subsequent decrease in the temperature range 270–500 °C, observed on the curves 1 and 2, correspond to the annealing of the surface defects of the powdered samples ZrO₂-7 and CRO-1, respectively. The samples have been characterized by relatively high surface areas ($s = 3.90$ and $3.31 \text{ m}^2 \text{ g}^{-1}$ respectively).

At temperatures above 800 °C, the thermal diffusion of radon in zirconia matrix is found to be possible (i.e. at 0.36 melting temperature (K)). It is obvious that in this temperature range the radon diffusion in ZrO₂ may be strongly affected by imperfections and defects of the matrix. The most intense release of the radon in this temperature range was observed with the ZrO₂-7 (F.R.G.) and CRO-1 (U.S.S.R.) samples. The slowing down of the

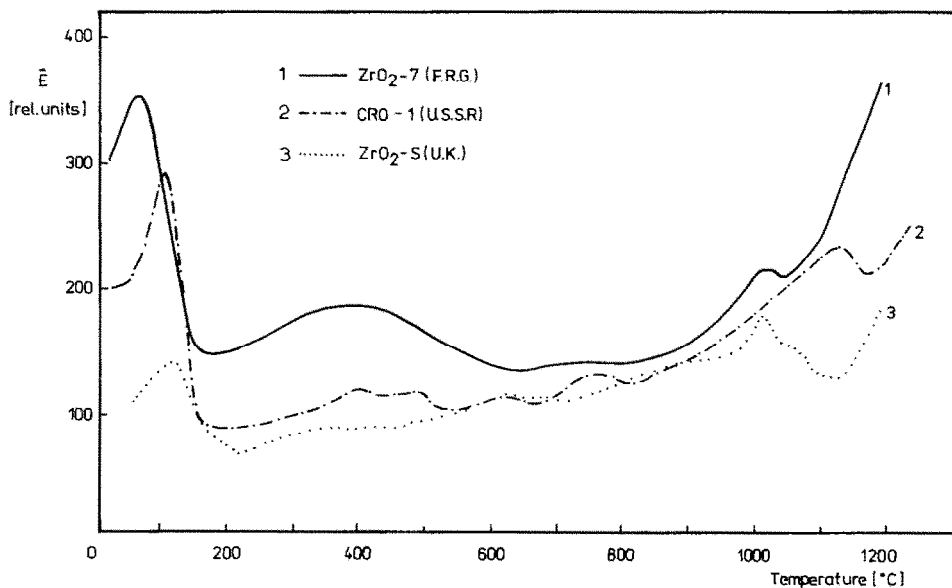


Fig. 3. ETA results of the three zirconia feed materials used for preparation of zircon (heating rate 5 K min^{-1}), in air.

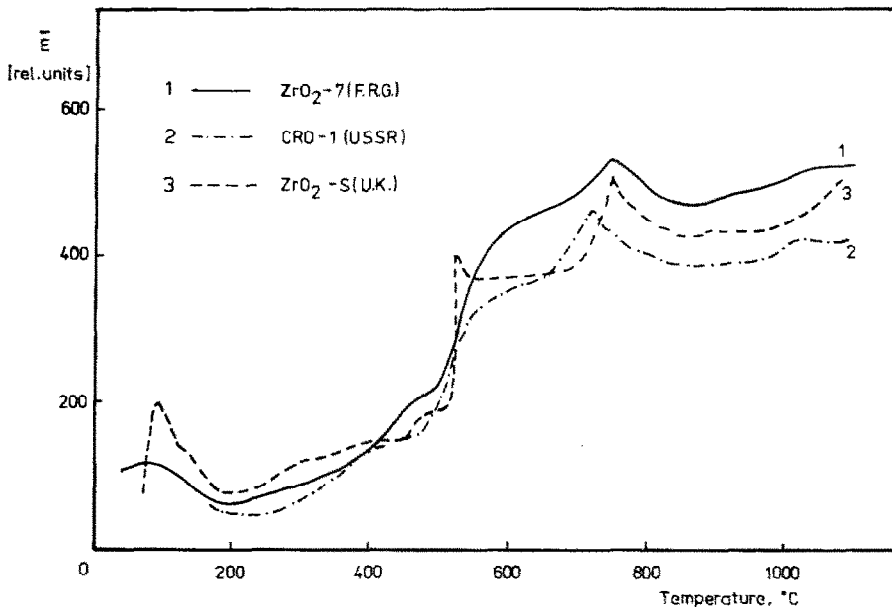


Fig. 4. ETA results characterizing the reactivity of the three zirconia samples used in the feed mixture for zircon preparation in air (heating rate 5 K min^{-1}).

radon release rate during heating above 1000°C corresponds to the sintering of the powdered samples.

From Fig. 3, the enhanced mobility of the surface and volume defects in ZrO_2 is to be expected in the temperature ranges $100\text{--}500^\circ\text{C}$ and $900\text{--}1000^\circ\text{C}$, respectively.

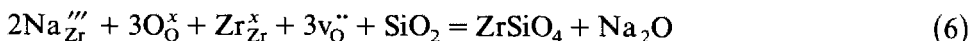
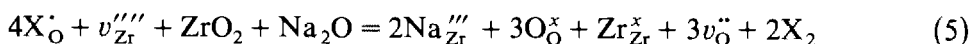
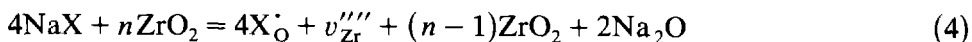
Figure 4 shows the ETA curves of the feed reaction mixtures containing different zirconia specimens, characterized in Table 1 and Fig. 2. In accordance with the ETA results in Fig. 3, the highest surface reactivity was observed with the mixture containing zirconia specimen $\text{ZrO}_2\text{-7}$ (F.R.G.), surface area $3.90 \text{ m}^2 \text{ g}^{-1}$, and the lowest surface reactivity was observed with the sample $\text{ZrO}_2\text{-S}$ (U.K.), surface area $0.70 \text{ m}^2 \text{ g}^{-1}$.

It should be noted that emanation thermal analysis is most sensitive to the processes taking place in the surface and the surface layers to a depth of within approximately 60 nm of where the radon atoms are implanted by the recoil energy of ^{228}Th and ^{224}Ra nuclides. The most intense radon release was observed with all the samples in the temperature range $500\text{--}550^\circ\text{C}$, corresponding to the interaction of the reaction mixture, enhanced possibly by the α - to β -quartz transition and by the presence of $\text{NaF}\text{--}\text{NaCl}$ admixtures. The slowing down of the radon release rate in the temperature range $600\text{--}760^\circ\text{C}$ may be caused by the appearance of the liquid phase.

The effects on the ETA curves in Fig. 4 in the temperature range $680\text{--}780^\circ\text{C}$ correspond, in accordance with the results of the Pt-labelled

tablet method [16], to the formation of $ZrSiO_4$ in the radon labelled layers of ZrO_2 . It can be seen from curve 3 in Fig. 4 that for the reaction mixture containing the zirconia specimen CRO-1 (U.S.S.R.) the interaction has already started at $680^\circ C$, while for the mixtures containing the other zirconia specimens the onset of the interaction is shifted to higher temperatures by $20-30^\circ C$. This is in agreement with the DTA results presented in Fig. 2, even though the DTA results reflect the stage of the bulk reaction.

The ETA results shown in Fig. 4 support the suggested mechanism for $ZrSiO_4$ formation according to the scheme given in eqn. (2). If the point defects in zirconia influence the reactivity of ZrO_2 in the reaction mixture at higher temperature, the following reaction scheme is suggested



CONCLUSION

The initial reaction of zirconia in the reaction mixture containing NaF-NaCl mineralizer was observed by ETA in the temperature range $680-780^\circ C$; the bulk reaction of $ZrSiO_4$ formation was indicated by exothermic effects in the DTA in the temperature range $880-1060^\circ C$. Of the three zirconia specimens tested, the specimen ZrO_2-7 (F.R.G.) was found to be the most active in surface mobility at $400-600^\circ C$ whereas the specimen CRO-1 (U.S.S.R.) was found to be the most reactive in the temperature range $750-900^\circ C$. The enhanced mobility in the surface layers of zirconia at $400-500^\circ C$ was observed by means of emanation thermal analysis with the samples ZrO_2-7 (F.R.G.) and CRO-1 (U.S.S.R.). We have suggested the use of a new type of mineralizer for the zircon preparation, enabling a lowering of the reaction temperature of $ZrSiO_4$ formation towards the temperature range $400-500^\circ C$. The results of the investigation of the new type of mineralizer, which will improve zircon pigments technology, will be reported in our next paper [19].

REFERENCES

- 1 F.T. Booth and G.N. Peel, *Trans. Brit. Ceram. Soc.*, 61 (1962) 359.
- 2 R.A. Eppler, *J. Am. Ceram. Soc.*, 53 (1970) 457.
- 3 R.A. Eppler, *Am. Ceram. Soc. Bull.*, 56 (1977) 213.
- 4 V.I. Matkovich and P.M. Corbett, *J. Am. Ceram. Soc.*, 44 (1961) 128.
- 5 A.S. Bystrikov and B.S. Cherepanov, *Russ. J. Inorg. Chem.*, 9 (1964) 654.
- 6 T. Demiray, D.K. Nath and F.A. Hummel, *J. Am. Ceram. Soc.*, 53 (1970) 1.

- 7 M. Trojan, *Sci. Papers, Inst. Chem. Technol. Pardubice*, 44 (1981) 255.
- 8 L. Cini and V. Pasalacqua, *Chim. Ind. (Milan)*, 45 (1963) 345.
- 9 T. Hibino, E. Miura and H. Sekyia, *Kogyo Kagaku Zasshi*, 70 (1967) 286.
- 10 M. Trojan and Z. Šolc, *Suppl. Proc. Conf. 8 ICTA, Bratislava, 1985*, p. 57.
- 11 V. Balek and J. Tölgyessy, *Emanation Thermal Analysis*, in G. Svehla (Ed), *Comprehensive Analytical Chemistry*, Vol. XIIC, Elsevier, Amsterdam, 1984, p. 304.
- 12 A. Blažek, *Termická analýza*, SNTL Praha, 1972.
- 13 H.E. Kissinger, *J. Res. Natl. Bur. Stand.*, 57 (1957) 217.
- 14 V. Balek, *Thermochim. Acta*, 22 (1978) 1.
- 15 G.O. Pilojan, *Vvedenije v Teoriju Termičeskovo Analiza*, Izd. Akad. Nauk, Moskow, 1964.
- 16 M. Trojan, *Dyes and Pigments*, 9 (1988) 221.
- 17 M. Trojan, *Czech. Patent* 233 691 (1984).
- 18 D. Penfold and A. Hellawell, *J. Am. Ceram. Soc.*, 48 (1965) 933.
- 19 M. Trojan and V. Balek, *Thermochim. Acta*, to be published.