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SIMULTANEOUS THERMAL ANALYSES FOR THERMAL DISSOCIATION STUDIES ON ZrO_2

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The behaviour of zirconium oxide ZrO_2 during its heating in the temperature range 300–2670 K under high-vacuum conditions and at different heating rates has been studied.

The experiments were performed with a Swiss made Universal Mettler thermoanalyser equipped with a super-high-temperature furnace SHT. Volatile products were analyzed simultaneously by means of a Balzers QMG-101 mass spectrometer.

An analysis of the TG, DTG, DTA and EGA curves recorded simultaneously has shown the complex character of the studied process. The elementary steps of the overall process were defined and taken into consideration. The mechanism of the thermal dissociation reaction of ZrO_2 as function of the heating rate was discussed too.

Keywords: kinetics, thermal dissociation, ZrO_2

Introduction

Due to experimental difficulties encountered when studying the thermal dissociation of high-melting oxides one observes scarcity of data on the mechanism and kinetics of these processes. The present work is an attempt at determining the thermal behaviour of ZrO_2 during its heating to 2673 K under high-vacuum conditions.

Zirconium dioxide, due to its high refractory properties is used as ceramics for production of tubes, crucibles, furnace linings and special glasses. ZrO_2 occurs at room temperature in monoclinic form, which, above 1270 K is transformed into tetragonal form. A very clear effect confirming this crystallographic transformation was obtained in the range 1373–1523 K by use of a Setaram thermoanalyser. The DTA curve shows an extremum at a temperature of 1426 K [1]. In that study 211.0 mg of ZrO_2 was heated in a graphite crucible at a rate of 20 deg/min in the temperature range 298–1723 K under helium flow.

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At temperatures above 2150 K tetragonal ZrO_2 transforms into cubic form. According to the authors of [1] the DTA peak appears at 2553 K.

By calculating from thermodynamic considerations the composition of the gas phase at high temperatures one can predict the dissociation mechanism. The procedure for the estimation of the gas composition over higher oxides of IVB group metals enabled the most probable mechanism of dissociation to be predicted [2]. In the dissociation of ZrO_2 the equilibrium pressure equal was assumed to be: $\lg p\,(ZrO_2) = -10.18$ at 2000 K. Given the dissociation reactions:

$$ZrO_2\,(s) = Zr\,(g) + O_2\,(g)$$

$$ZrO_2\,(s) = Zr\,(g) + 2O\,(g)$$

one gets:
$\lg p\,(O_2) = -16.09$, $\lg p\,(O) = 11.17$, $\lg p\,(Zr) = -11.47$ and the degree dissociation of ZrO_2 in the gaseous state is equal to 4.9%.

However, for the dissociation of ZrO_2 according to:

$$2ZrO_2\,(s) = 2ZrO\,(g) + O_2(g)$$

$$ZrO_2\,(s) = ZrO\,(g) + O_2\,(g)$$

$$ZrO\,(g) = Zr\,(g) + O\,(g)$$

one gets the gas phase composition as follows: 24.8% ZrO_2, 0.0% O_2, 37.6% O, 37.6% ZrO, 0.0% Zr. The degree of dissociation of gaseous ZrO_2 decomposing into monoxide and atomic oxygen is equal to 60% at a temperature of 2000 K. As it was shown, MeO_2 type oxides at high temperatures dissociate mainly into monoxides and oxygen atoms but not into metal and oxygen molecules. The degree of dissociation for dioxides in the gas phase exceeds 50%.

The aim of this study was to determine the mechanism and kinetics of reactions occurring during the heating of ZrO_2 in high vacuum by considering all existing data provided by thermal analyses. Such comparison can be made only when keeping the same experimental conditions. Therefore in the study reported below a method of simultaneous thermogravimetric analysis (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and mass spectrometry (EGA) was used.

Experimental

The experiments were carried out with a Universal Mettler Thermoanalyser equipped with a super-high-temperature furnace, SHT. For simultaneous analyses of gaseous products of thermal dissociation a quadrupole Balzers mass spectrometr QMG-101, built in the vacuum system of the thermoanalyser, was applied.

The measurements were performed in high-vacuum of $1.33\cdot10^{-6}$ kPa in the temperature range 298–2673 K by linear heating of the sample. Three rates of heating were applied: V_1 = 4 deg, V_2 = 6 deg and V_3 = 8 deg per minute. The measurement and regulation of the temperature were performed by means of thermoelements W/W 26 Re. 5 mg samples were heated in tungsten crucibles. Some preliminary tests showed that tungsten did not react with the heated sample up to 2673 K; there were no losses of the crucible weight. The mass spectra were recorded at a rate of 1 M/sec for the mass range 10–400 M/e and for the selected mass numbers. Chemically pure materials were used in the study.

Results

The curves of the simultaneous analyses obtained at a heating rate of 6 deg/min are presented in Figs 1 and 2. Up to 1713 K the DTA curve only shows an endothermal effect in the temperature range 1353–1473 K. The effect has been noted by few authors [1, 3] and taken as the phase transformation of ZrO_2 from monoclinic to tetragonal form. At temperatures over 1713 K one can observe in all the curves two distinct effects. In the temperature range 1713–2313 K (Fig. 1) the small effect is observed on all the curves except the EGA curve on which merely a small evolution of atomic oxygen is seen above 2123 K. The weight loss of the sample accompanied by that effect is about 9%. However, in the temperature range 2373–2673 K (Fig. 2) all the curves exhibit large effects. The temperatures of the onset, maximum and end of the effects are the sample for all the

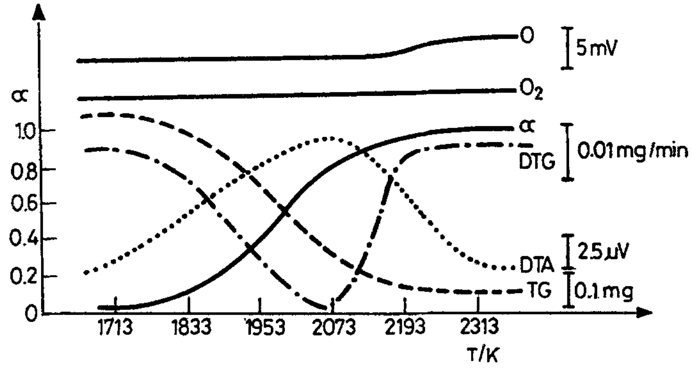

Fig. 1 Curves of the simultaneous analyses obtained for zirconium oxide at a heating rate of 6 deg/min in the temperature range 1713–2313 K

curves except the temperature of the evolution of molecular oxygen, the last being shifted by about 150°C towards higher temperatures. The weight loss of the sample was about 80%. At a temperature of 2370 K on the DTA curve, in contrast with the TG and DTG curves a single extremum is observed. It may indicate the tetragonal-cubic transformation of ZrO_2.

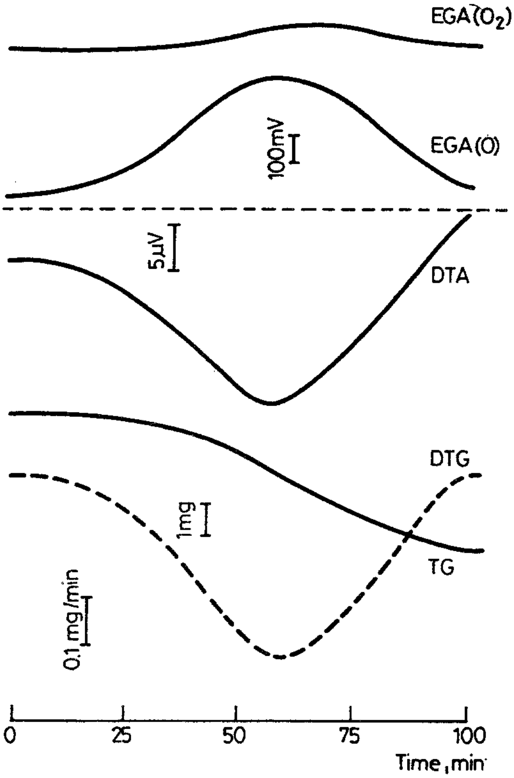

Fig. 2 Curves of the simultaneous analyses obtained for zirconium oxide at a heating rate of 6 deg/min in the temperature range 2373–2673 K

For the other rates of heating i.e. 4 deg/min and 8 deg/min the course of the curves is similar for all the analyses. It is to be noted that with the increase of the heating rate all effects are shifted towards higher temperatures. This is illustrated in Fig. 3 in which the kinetic curves of the degree of transformation α, at different temperatures are plotted for the three different heating rates. For the same degree of transformation the following sequence is observed: $T(V_1) < T(V_2) < T(V_3)$, likewise, the values of the kinetic coefficient calculated by Pilojan *et al.* [4] (their method was tested in the work [5]) increase with the heating rate. Table 1 gives results of the correlation in form of a straight line $y = \ln m - 2 \ln T$, where m – weight loss up to a given moment, as well as the calculated E values.

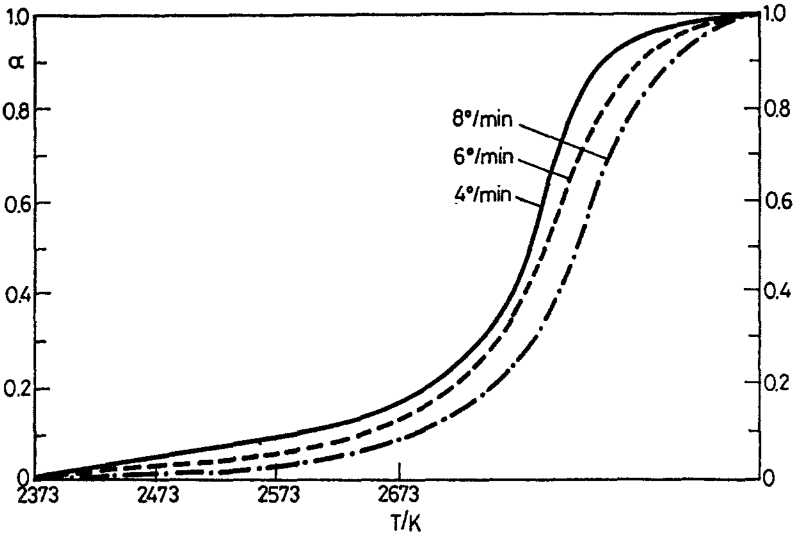

Fig. 3 Kinetic curves for ZrO_2 for the three rates of sample heating applied in the measurements

Table 1 Results of linear correlation and values of E for ZrO_2

	a	b	R (N = 7)	A_0	E/kJ
V_1	–14384.61	–0.66	0.997	–1.518	276.87
	S_a = 600.79	S_b = 0.25		±0.575	±16.58
V_2	–15260.07	–0.37	0.999	–0.851	293.71
	S_a = 388.37	S_b = 0.15		±0.345	±7.47
V_3	–18117.65	0.75	0.999	1.725	348.72
	S_a = 163.56	S_b = 0.06		±0.138	±3.15

Conclusions

The results of the studies reported above indicate the complex character of the processes occurring in the course of heating of ZrO_2 in high vacuum.

The first observed effect on the DTA curve corresponds to the polymorphic transformation of ZrO_2. The next effect observed between 1713 and 2313 K refers to the sublimation of a small fraction of ZrO_2 which is confirmed by the absence of oxygen formation. The atomic oxygen produced at the end of this effect comes from the partial dissociation of gaseous ZrO_2. The second effect observed on all the curves of simultaneous analyses is due to dissociation of ZrO_2, mainly to ZrO (g) and atomic oxygen. With a 'delay' of 150°C one can observe here that a decomposition reaction producing oxygen particles in small amounts occurs too. On the basis of the presented study the following mechanism of the process can be postulated for the first effect:

$$ZrO_2\ (s) = ZrO_2(g) = ZrO\ (g) + O\ (g)\ (1713\text{–}2313\ K)$$

while for the second one:

$$ZrO_2\ (s) = ZrO\ (g) + O\ (g)\ (\text{main reaction, } 2373\text{–}2670\ K)$$

$$2ZrO_2\ (s) = 2ZrO\ (g) + O_2(g)\ (\text{delayed parallel reactions})$$

$$ZrO_2(s) = Zr\ (g) + O_2\ (g)\ (\text{delayed parallel reactions})$$

The proposed mechanism of ZrO_2 dissociation is in agreement with results of thermodynamic calculations [2] which have shown that higher oxides of IVB group metals dissociate mainly to lower oxides and atomic oxygen.

The rate of the studied process depends distinctly on the heating rate which can be seen from either the results shown in Fig. 3 or the comparison of the kinetic coefficient E values listed in Table 1. The relatively high values of E suggest that this reaction takes place in the kinetic region. With the heating rate increase A substantial increase in the 'induction period' for all reactions taking place in the system is observed with increasing heating rate. It should be noted that the temperatures of the particular effects observed in all the curves of simultaneous analyses are in good agreement among themselves.

The method of Pilojan *et al.* [4] for the calculation of the kinetic coefficient E from the thermogravimetric curve, applied to the process under study, yields good results, as is confirmed by the high values of the correlation coefficients. Similar calculations made for the thermal decomposition of CeO_2 gave satisfactory results too. Actually this offers new possibilities for the application of the method discussed above originally referred to A (s) = B (s) + C (g) type reaction to the kinetic study of the reaction A (s) = B (g) + C (g) as well.

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Zusammenfassung — Im Temperaturintervall von 300 K bis 2670 K wurde im Hochvakuum und bei verschiedenen Aufheizgeschwindigkeiten das thermische Verhalten von Zirkoniumoxid ZrO_2 untersucht.

Die Experimente wurden mit Hilfe eines schweizer Universal Mettler Thermoanalysators, ausgerüstet mit einem SHT Super-Hochtemperatur-Ofen, ausgeführt. Flüchtige Produkte wurden simultan dazu mit einem Massenspektrometer QMG-101 der Balzers-Company analysiert.

Die Auswertung der durch aufgezeichneten TG-, DTG-, DTA- und EGA-Kurven zeigt den komplexen Charakter des untersuchten Prozesses. Die Elementarschritte der Gesamtreaktion wurden definiert und berücksichtigt. Weiterhin wurde der Mechanismus der Thermodissoziation von ZrO_2 auch in Abhängigkeit von der Aufheizgeschwindigkeit diskutiert.