

ISOTHERMIC DEPENDENCE OF ELECTRIC RESISTANCE OF TETRAGONAL ZIRCONIUM DIOXIDE

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The dependence of electric resistance of zirconium dioxide on time was measured within the region of the tetragonal modification. The measurement was carried out on two samples of non-stabilized ZrO₂ fired at 1700 °C and having different porosities. A mathematical relationship describing satisfactorily the isothermic processes has been derived.

INTRODUCTION

The properties and application possibilities of zirconium dioxide both pure and in mixtures with other substances, which either supply the required properties or prevent its modification transformations, are continuously the subject of extensive studies. The research is frequently aimed at its electric properties.

Some of the papers concerned with electric conductivity of non-stabilized zirconium dioxide revealed certain non-typical properties in the modification transformation range [1, 2, 3] and in the field of existence of the tetragonal modification [1]. It has been shown that in the range of the modification transformation from the monoclinic modification to the tetragonal one there takes place a considerable abrupt increase in electric conductivity, and vice versa during the back transformation. It was also observed that when a suitably long temperature lapse had not been provided within the region of the transformation, [3] the electric conductivity of the tetragonal modification depended on the thermal history of the specimen. The value determined at a certain temperature depends on whether the temperature has been achieved by heating the sample, or by cooling it down. It has further been shown that during gradual heating up the electric conductivity of an isothermally heated monoclinic sample of ZrO₂ increases with time. Since this phenomenon has not yet been studied in detail the present work has been aimed at determining the changes in electric conductivity of non-stabilized ZrO₂ samples in terms of time during isothermic heating up in the region of the tetragonal modification.

EXPERIMENTAL

The present paper is linked up to the results of an earlier study [1]. The experiments were carried out with two samples of non-stabilized zirconium dioxide, having the respective porosities of 18.3 % (sample No. 1) and 11.0 % (sample No. 2), both fired at 1700 °C. The resistance was measured using the Tesla BM 394 RLC bridge by the two-point method. The way of fixing the

sample and the other details have already been devised and reported on earlier [4, 5]. The temperature was kept constant by a chopper-bar thermostat with an accuracy of $\pm 3^\circ\text{C}$. The rate of heating was approximately 4°C per minute.

The isothermic dependences of electric resistivity in terms of time within the region of tetragonal modification are plotted in Fig. 1. The denser fine-grained sample was measured at 1294°C and at 1340°C , the less dense and coarse-grained one at 1300°C and at 1356°C . The values established show at first a very rapid decrease and approach a constant value asymptotically. A more significant change takes place with sample No. 2.

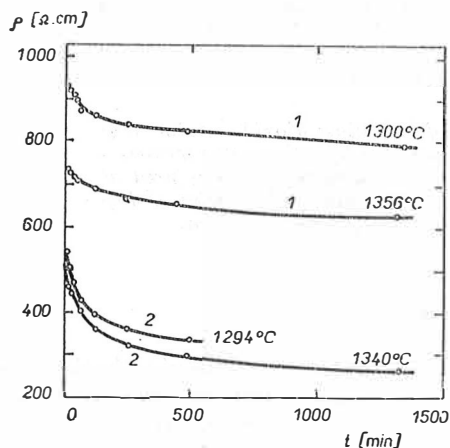


Fig. 1. Specific resistance vs. time.

The aim was to find a mathematical expression which would describe the relationships measured.

Rectification was carried out with the following differential equation

$$\frac{d\rho}{dt} = \frac{k'}{t + a}, \quad (1)$$

which gives after integration

$$\rho_t = k \log(t + a) + b, \quad (2)$$

where

t is time

ρ_t is specific resistance at time t

k' , k , a , b are constants.

Constant a was evaluated from the experimental data using the method described in [6], and its value was found to be close to unity.

After substituting for $a = 1$, which is advantageous for finding the initial resistance value, one obtains

$$\rho_t = k \log(t + 1) + b. \quad (3)$$

This expression further shows that at time $t = 0$

$$\rho_0 = b,$$

so that after substituting in (2) we obtain

$$\rho_t = k \log(t + 1) + \rho_0. \quad (4)$$

where ρ_0 is thus the resistivity at time $t = 0$.

Relation [4] has the advantage that when it holds one can determine the initial resistance ρ_0 , the value of which is difficult to establish by direct measurement due to unequalized temperature conditions when the chosen measuring temperature has been attained.

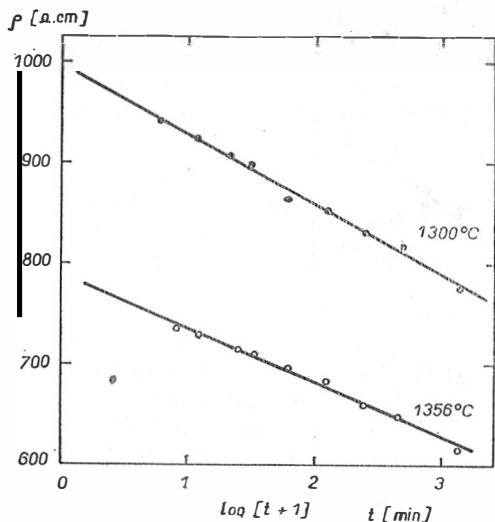


Fig. 2. Specific resistance vs. $\log(t+1)$ for sample No. 1.

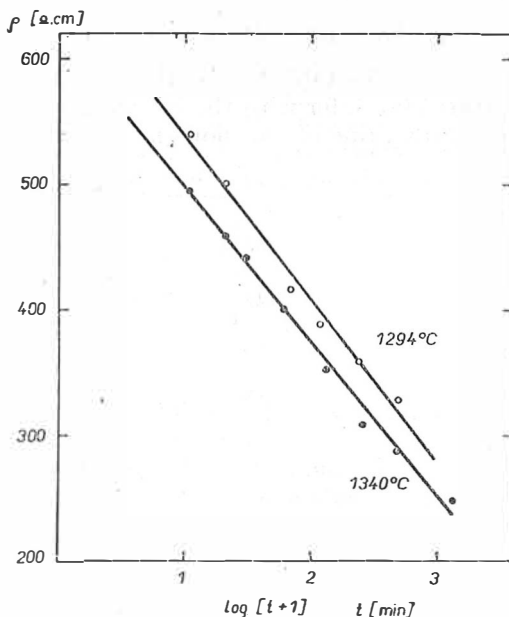


Fig. 3. Specific resistance vs. $\log(t+1)$ for sample No. 2.

For this reason, resistivity ρ_t in terms of $\log(t+1)$ was therefore plotted in the diagram for the individual isotherms. Figures 2 and 3 show that equation (4) describes well the isothermic relationships described above. The values of constants k and ρ_0 calculated by the least square method are listed in Tab. I.

Table I

Sample No.	Temperature °C	k ohm. cm	ρ_0 ohm. cm	$\frac{k}{\rho_0}$
1	1300	-68.043	995.8	-0.068
	1356	-53.407	787.9	-0.069
2	1294	-129.049	666.1	-0.194
	1340	-122.435	619.5	-0.197

The absolute slope values are higher with the denser sample. Equation (4) can further be divided by ρ_0 , thus obtaining

$$\frac{\Delta \rho_t}{\rho_0} = \frac{\rho_t - \rho_0}{\rho_0} = \frac{k}{\rho_0} \log(1+t). \quad (5)$$

When plotting into the diagram the relative change in specific resistance $\frac{\Delta \rho_t}{\rho_0}$ in terms of $\log(1+t)$ one obtains virtually identical straight lines for both temperatures, see Fig. 4. However, the linear dependences are different for the two different samples, which indicates that the values of ratios $\frac{k}{\rho_0}$ (see Tab. 1) established by the least square method, are independent of temperature and differ with the individual samples only. For the coarser sample the absolute value of the slope is roughly three times higher.

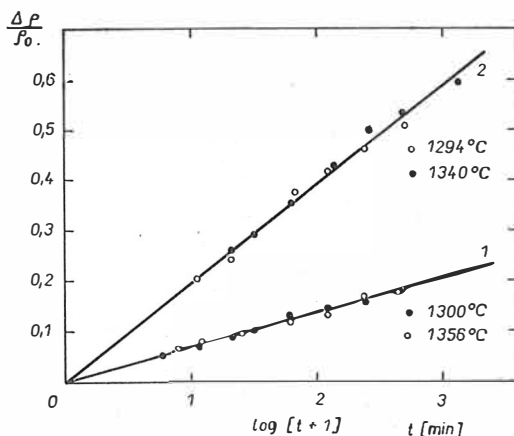


Fig. 4. Relative change in specific resistance $\Delta \rho / \rho_0$ vs. $\log(t+1)$.

The following exponential relations can be assumed to hold for the temperature dependence of the process rate constant and the specific resistance ρ_0 :

$$k = A_1 \exp\left(-\frac{E_1}{RT}\right), \quad (6)$$

$$\rho_0 = A_2 \exp\left(-\frac{E_2}{RT}\right). \quad (7)$$

By dividing relations (6) and (7) one obtains a picture of the temperature dependence of ratio $\frac{k}{\rho_0}$:

$$\frac{k}{\rho_0} = \frac{A_1 \exp\left(-\frac{E_1}{RT}\right)}{A_2 \exp\left(-\frac{E_2}{RT}\right)}. \quad (8)$$

If this ratio is independent of temperature it must necessarily hold that

$$E_1 = E_2,$$

so that

$$\frac{k}{\rho_0} = \frac{A_1}{A_2}. \quad (9)$$

DISCUSSION OF RESULTS

Equation (2) is not a quite usual one in kinetic relationships. It is listed in a survey of equations describing the clinker forming reactions published by Butt et al. [7, 8].

Grain and Garvie [9] studied the kinetics and transformation mechanism of the monoclinic ZrO_2 modification to the tetragonal one and vice versa. They succeeded in explaining satisfactorily this very complex type of transformation by means of the domain theory based on the Ubbelohde theory of gradual transformation. Within the framework of their study these authors also investigated the isothermic modification transformation of zirconium dioxide and found it to be controlled by the equation

$$\alpha = k_1 \ln(t + 1) + b_1, \quad (10)$$

where α is the share of the transformed monoclinic modification,

t is time,

k_1 and b_1 are constants.

The relation (10) has a form identical with the relationship established in the present study. One can therefore assume that the time dependence of the transformation of zirconium dioxide is controlled by the same relationship as the time dependence of the resistance of the tetragonal modification after concluded transformation.

However, when following the transformation of zirconium dioxide on a macroscale, i. e. for example by dilatometry, DTA or diffractometry, one finds that the transformation is usually concluded at 1200 °C [10]. Similarly, the greatest change in electric resistance usually takes place at about 1180 °C [1], [3] which obviously corresponds to the transformation of the modifications.

Grain and Garvie [9] further found that the value of the rate constant k_1 in equation (10) increases with decreasing size of the zirconium dioxide particles. The values of constant k , see (4), are higher with the denser sample prepared from ground zirconium dioxide and thus containing finer particles. The relation mentioned above is therefore also in agreement with the conclusions of the authors [9].

The arguments discussed above therefore allow to assume that at the temperatures employed in the present study, which are considerably higher than the transformation temperature region, the transformation is probably concluded and this results in the change in the electric resistance of the sample.

CONCLUSION

The time dependence of the electric resistivity of non-stabilized zirconium dioxide was measured in the region of its tetragonal modification. The relationship which describes satisfactorily the processes measured, has a form identical with that of the relation established for the modification transformation of zirconium dioxide. One can safely assume that the change in electric resistance of tetragonal zirconium dioxide indicates to a concluding transformation which, however, is no longer observable by macroscale methods such as dilatometry, diffractometry, DTA and the like.

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IZOTERMNÍ ZÁVISLOST ELEKTRICKÉHO ODPORU
TETRAGONÁLNÍHO KYSLIČNÍKU ZIRKONIČITÉHO

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Byla sledována časová závislost měrného elektrického odporu nestabilizovaného kyslíčnicku zirkoničitého v oblasti existence tetragonální modifikace. Měření bylo prováděno při konstantních teplotách dvoubodovou metodou na dvou různě hutných vzorcích vypálených na 1700 °C vždy při dvou teplotách. Vzorek byl zahříván rychlostí zhruba 4 °C/min přes oblast transformace až k zvoleným teplotám, při kterých bylo provedeno izotermní sledování.

Naměřenou izotermní závislost dobře popisuje matematický vztah:

$$\varrho_t = k \log(t + 1) + \varrho_0,$$

kde ϱ_t je měrný odpor v čase t ,
 ϱ_0 — měrný odpor na počátku ($t = 0$),
 k — rychlostní konstanta děje.

Dále bylo zjištěno, že poměr $\frac{k}{\varrho_0}$ je shodný pro obě proměřené teploty, avšak různý pro odlišnou hutnost, a tedy i jemnost použitých vzorků. Uvedený vztah je zcela analogický izotermní kinetické rovnici nalezené Grainem a Garviem pro přeměnu kyslíčnicku zirkoničitého z jednoklonné na tetragonální modifikaci. V soulase s jejich pracemi je i skutečnost, že rychlostní konstanta k je v absolutní hodnotě vyšší pro jemnější vzorek. Na základě této shody byla vyslovena domněnka, že ve sledované oblasti pravděpodobně dohání modifikační přeměna. Změny s tímto spojené jsou však pozorovatelné pouze v mikropohledu, tj. např. právě měřením změny elektrického odporu.

Obr. 1. Závislost měrného odporu na čase.

Obr. 2. Závislost měrného odporu na $\log(t + 1)$ pro vzorek č. 1.

Obr. 3. Závislost měrného odporu na $\log(t + 1)$ pro vzorek č. 2.

Obr. 4. Závislost relativní změny měrného odporu $\Delta\varrho/\varrho_0$ na $\log(t + 1)$.

ИЗОТЕРМИЧЕСКАЯ ЗАВИСИМОСТЬ ЭЛЕКТРИЧЕСКОГО
СОПРОТИВЛЕНИЯ ДВУОКСИ ЦИРКОНИЯ

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В работе исследуется временная зависимость удельного электрического сопротивления нестабилизированной двуокиси циркония в области существования тетрагональной модификации. Измерение проводилось с помощью двуконтактного метода при постоянных температурах на двух пробах с разной плотностью, обожженных до 1700 °С, всегда при двух температурах. Проба нагревалась скоростью около 4 °С/мин. в области трансформации до подобранных температур, при которых проводили изотермическое исследование.

Было установлено, что измеренной термической зависимости хорошо соответствует математическое соотношение:

$$\rho_t = k \log(t + 1) + \rho_0,$$

где ρ_t - удельное сопротивление во время t , ρ_0 - удельное сопротивление в начале ($t = 0$), k - константа скорости процесса.

Далее было установлено, что соотношение k/σ_0 совпадает для обеих температур, но отличается друг от друга в случае различной плотности, а следовательно и размера зерна примененных проб.

Приведенное отношение вполне аналогично изотермическому кинетическому уравнению, найденному Греном и Гарви для превращения двуокиси циркония из моноклинной модификации в тетрагональную. В хорошем соответствии с работами приведенных авторов имеется и тот факт, что константа скорости k по абсолютной величине выше для мелкозернистых проб. На основании этого совпадения выдвигается предположение, что в исследуемой области со всей правдоподобностью кончится процесс модификационного превращения, однако связанные с этим изменения можно наблюдать только в отделимости, т. е. например на основании измерения электрического сопротивления.

Рис. 1. Зависимость удельного сопротивления от времени.

Рис. 2. Зависимость удельного сопротивления от $\log(t + 1)$ для пробы № 1.

Рис. 3. Зависимость удельного сопротивления от $\log(t + 1)$ для пробы № 2.

Рис. 4. Зависимость относительного изменения удельного сопротивления $\Delta\rho/\rho_0$ от $\log(t + 1)$.