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THE EFFECT OF CERTAIN PROMOTERS ON TiO_2 CRYSTAL STRUCTURE TRANSFORMATION

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The effect of certain promoters on TiO_2 crystal structure transformation was studied by mean thermal and X-ray analyses. It was found that the addition of rutile nuclei and potassium, phosphorus, zinc, magnesium, and aluminium compounds to hydrated titanium dioxide before calcination process influences on the initial temperature and anatase transformation.

Keywords: crystal structure transformation, TiO_2

Introduction

Two crystallographic structures of TiO_2 (anatase and rutile) are obtained by the hydrated titanium dioxide calcination. This is one of the basic process in technology or titanium pigment production [1–10].

The polymorphic transition of thermodynamically unstable tetragonal anatase to stable tetragonal rutile phase is monotropic. This process leads to the total change of structure and physicochemical properties of TiO_2. At the temperature above 900°C the anatase obtained by the hydrolysis of titanium sulphates solutions is converted gradually into rutile. The degree of transformation depends on time and temperature of calcination, method of material preparation, particle size distribution, presence of impurities, etc.

The aim of the studies were investigations of additives like rutile nuclei, phosphorus, potassium, zinc, magnesium and aluminium compounds influence on the degree of anatase into rutile transition during calcination.

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Experimental

The starting material was the hydrated titanium dioxide $TiO_2 \cdot xH_2O \cdot ySO_3$ ($x = 7.694$, $y = 0.066$) obtained by the hydrolysis of the titanium sulphate solutions.

After the promoter addition the examined samples were placed into an electric furnace equipped with an electronic temperature controller and chromel-alumel thermocouple.

The samples were heated from a room temperature up to desired temperature level with the heating rate 10 deg·min^{-1} and remained at this temperature for 1–3 hours.

As the promoter additives rutile nuclei and solutions of KOH, H_3PO_4, $ZnSO_4$, $MgSO_4$ and Al_2SO_4 were used.

The thermal analysis was performed on a Derivatograph C (MOM Budapest) under the following conditions: static air atmosphere, heating rate 10 deg·min^{-1}, sample mass 100 mg, platinum crucible, Al_2O_3 as reference material.

X-ray powder diffraction patterns were performed on the Philips PW 1730 diffractometer with CuK_α radiation. The diffraction patterns were recorded automatically at room temperature in the angle range 10°–150°C.

Results and discussion

The results of the hydrated titanium dioxide thermal examination are illustrated in Figs 1 and 2.

The dehydration process occurs in the temperature range 20°–250°C (the first endothermic peak on the DTA curve).

The decomposition of sulphur compounds occurs in the temperature range 440°–800°C (the second plane endothermic endothermic peak on the DTA curve). The phase transformation of TiO_2 is almost invisible: the very small exothermic peaks appear at temperature about 1030° and 770°C on the DTA curves of the hydrated titanium dioxide samples without the rutile nuclei addition and with 5% of the rutile nuclei addition respectively.

The products of thermal treatment of the hydrated titanium dioxide were examined by the XRD method.

The hydrated titanium dioxide without the promoters addition dried at room temperature up to constant mass is amorphous, but the small peaks characteristic for the anatase structure are visible on the diffraction pattern. The increase of temperature up to 500°C does not cause distinctive changes of diffraction patterns (Table 1). Above the temperature 600°C the peaks characteristic for the anatase structure become larger. The new peaks characteristic for the rutile structure appear in the diffraction pattern of calcination at 900°C product. The quantitative phase analysis of this sample has shown the concentration of rutile phase 30.7%. The calcination products obtained at higher temperatures (1000° and 1100°C) contain above 99.5% rutile phase.

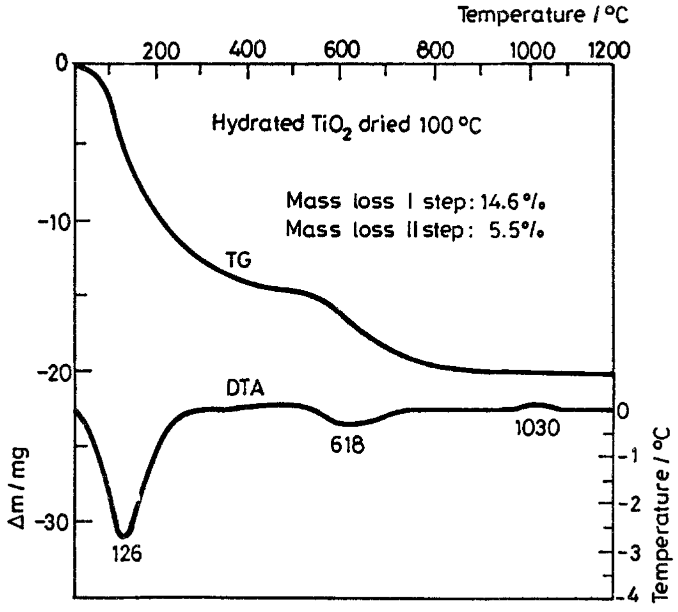

Fig. 1 TG and DTA curves of the hydrated titanuum dioxide

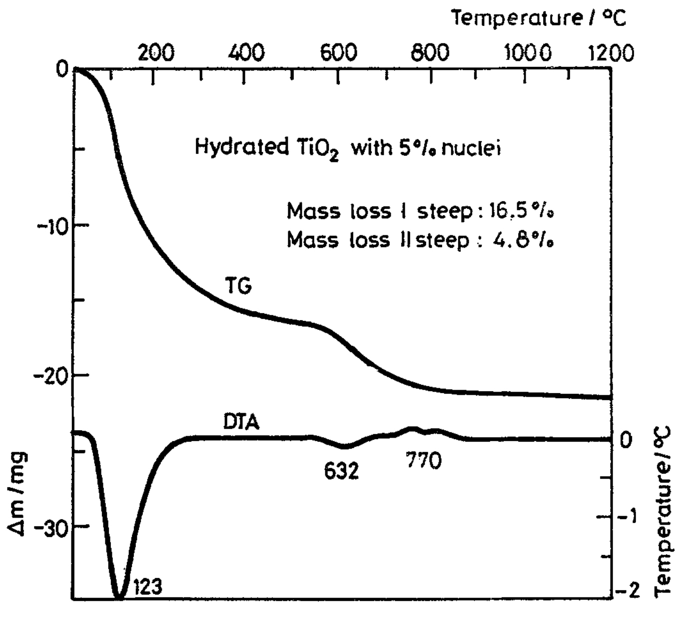

Fig. 2 TG and DTA curves of the hydrated titanuum dioxide with 5% rutile nuclei

As we can see the phase transformation of TiO_2 without the promoters proceeds between 900° and 1000°C.

The diffraction patterns of products of mixture of hydrated titanium dioxide with 5% rutile nuclei obtained at lower treatment temperatures (20°–500°C) are similar to the patterns discussed above. The anatase peaks intensity attains maximum at 700°C and the rutile phase concentration is 7.0% (Table 2). The calcination product obtained at 800° C contains 90.4% of rutile phase. The diffraction patterns of the calcination products obtained at higher temperatures does not contain anatase.

Table 1 X-ray powder data of the thermal treatment products of hydrated titanium dioxide without the promoters

Temperature / °C	Intensity	
	Anatase	Rutile
20	340	0
500	351	0
600	602	0
700	975	0
800	1482	0
900	689	254
1000	7	1541

Table 2 X-ray powder data of the thermal treatment products of hydrated titanium dioxide with 5% rutile nuclei

Temperature / °C	Intensity	
	Anatase	Rutile
20	160	8
500	514	27
600	771	40
700	1038	67
800	166	1433
900	0	1597
1000	0	1753

The phase transformation of TiO_2 with addition of 5% of rutile nuclei proceeds between 700° and 800°C.

The effect of different concentrations of rutile nuclei on the transition anatase-rutile during the calcination of hydrated titanium dioxide are shown in Table 3.

In Table 4 results of the influence of other promoters on the phase transition of TiO_2 are presented in the process of calcination.

Table 3 The effect of rutile nuclei on the transition anatase-rutile during the calcination (Conditions: 970°C, 1 h)

Rutile nuclei addition / %	Rutile concentration /%
0	69.1
2	96.2
4	98.3
6	98.9
8	99.5

Table 4 The effect of different promoters on the phase transition of TiO_2 (Conditions: 970°C, 1 h)

Addition / %	K_2O	P_2O_5	ZnO	MgO	Al_2O_3
0	69.1	69.1	69.1	69.1	69.1
0.05	92.0	78.2	93.3	96.5	99.4
0.1	94.4	83.8	99.8	99.8	99.8
0.2	76.6	71.3	99.8	99.8	99.4
0.5	46.5	60.9	99.8	99.6	99.0
1.0	1.3	1.1	99.8	99.3	98.6

The addition of KOH solution up to the 0.2% K_2O content causes the increase of the rutile concentration. The addition of K_2O in amounts higher than 0.2% causes decrease of rutile concentration. The addition of 1.0% K_2O inhibits the phase transition.

The influence of H_3PO_4 solution is very similar to KOH.

The addition of $ZnSO_4$, $MgSO_4$, and $Al_2(SO_4)_3$ to the hydrated titanium dioxide in the concentration range 0.05–1.0% of the corresponding oxides causes the increase of the rutile concentration.

Conclusions

During the calcination process of hydrated titanium dioxide the phase transformation of anatase to rutile takes place at temperature about 900°C. After introduction of 5% the rutile nuclei the temperature of transformation is decreased to about 770°C.

After addition of potassium hydroxide and phosphoric acid (the concentration 0.1% K_2O or P_2O_5) the transformation degree is increased but when the concentrations of additives were higher (0.2–1.0%) the process is inhibited. In the case of the concentration of K_2O or P_2O_5 equal to 1.0% the phase transition of anatase into rutile does not occur or proceeds very slowly.

The zinc sulphate, magnesium sulphate or aluminium sulphate addition (0.05–1.0% of the corresponding oxides) leads to the increase of extent of the transformation.

The results of these studies confirm that the introduction of small amounts of rutile nuclei and potassium, phosphorus, zinc, magnesium and aluminium compounds to hydrate titanium dioxide before calcination process can influence on the initial temperature and rate of anatase to rutile transformation.

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Zusammenfassung — Mittels Thermo- und Röntgendiffraktionsanalyse wurde der Einfluß gewisser Beschleuniger für Strukturumwandlungen in TiO_2-Kristallen untersucht. Man fand, daß ein Zusatz von Rutilkernen und Kalium-, Phosphor-, Zink-, Magnesium- und Aluminiumverbindungen zu hydratiertem Titanoxid die Anfangstemperatur und das Ausmaß der Anatas-Umwandlung beeinflussen.