

CHARACTERIZATION OF RUTILE AND ANATASE POWDERS BY THERMAL ANALYSIS

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Anatase and rutile powders prepared by various methods were characterized by thermoanalytical studies up to 1400 °C using a simultaneous TG-DTG-DTA apparatus. Preparation techniques were developed for the manufacture of amorphous titania, pure anatase, stabilized anatase and pure rutile.

Enthalpy effects originating from the crystallization of amorphous parts into the anatase modification and from the phase transition of anatase into rutile were investigated.

The latter phase transition was detected by means of heat flux DSC measurements. The transition enthalpy was determined.

Titanium dioxide exists in three structural modifications: rutile, brookite and anatase. The Ti^{4+} ion is surrounded by an irregular octahedron of oxide ions, but the number of edges shared by the octahedra increases from two in rutile to three in brookite, and to four in anatase. The three TiO_2 forms are natural minerals or can be prepared synthetically. Anatase and brookite are metastable and transform exothermally and irreversibly to rutile at higher temperatures.

The phase transition of anatase to rutile has been studied extensively. Literature data on the temperature of the phase transition range between 350 and 1175°. It has been reported that the transformation is affected by the method of preparation of the sample, by the presence of impurities or additives for the stabilization of the certain modification, and by the atmosphere present during the transformation [1–13].

The enthalpy of the phase transformation anatase–rutile is low. A survey of the literature reveals widespread disagreement (Table 1).

Balek and Emmerich reported that the phase transition is not investigable by DTA, because the exothermic effect is immeasurably low. Combined ETA-DTA-TG-DTG measurements are sensitive to it [18, 19].

The present investigations were carried out to characterize different anatase and rutile powders by means of thermoanalytical measurements up to 1400°. Thermal

Table 1 Literature values of the transition enthalpy

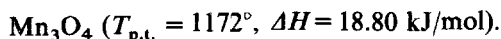
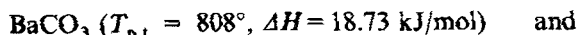
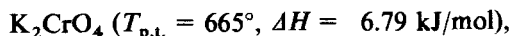
Ref.	Transition enthalpy,		Temperature, K
	kJ/mol	J/g	
[14]	-1.3	-16.3	915
[15]	-5.2±0.8	-65.1±10	
[16]	-5.2±0.8	-65.1±10	298
[16]	-6.6±0.8	-82.6±10	968
[17]	-3.3±0.8	-41.3±11	971

effects are to be expected from the crystallization of amorphous parts and/or from the phase transition.

Experimental

The following methods were applied for characterization:

Heat flux DSC up to 1400°, with the Netzsch STA 429 instrument on powders (25 mg), in a Pt crucible, at a heating rate of 20 deg min⁻¹, or on bulk samples (75 mg) at 5 and 20 deg min⁻¹. Calibration was performed with the recommended ICTA standard reference materials:



X-ray analysis with a horizontal goniometer, CuK_α radiation, at 22° ≤ 2θ ≤ 30°, 0.008 °/s, I = 1 · 10³ 1/s.

Details of the preparation and characteristics of the materials are given in Table 2.

Results and discussion

DTA curves obtained on commercial samples of rutile (USSR) and anatase (Merck 808) are presented in Fig. 1. For comparison those of prepared rutile and anatase (samples 1 and 2c) are also shown.

The rutile samples exhibit not thermal effect. For the anatase samples, the DTA curves do reveal an exothermic peak. This indicates the phase transformation of anatase into rutile. Merck anatase displays the highest transition temperature, due

Table 2 Preparation and X-ray diffraction characteristics materials

No.	Material, preparation/origin	Diffraction angle, 2 θ ^o	Peak height, mm	PWHH, mm
	Anatase (Merck 808), stabilized with sulphate and phosphate	25.3	252	2.5 (A)
	Rutile (USSR)	27.6	548	1 (R)
1	Thermal hydrolysis of H ₂ TiCl ₆ yields pure rutile	27.6	536	1 (R)
2	Titania gels, prepared by hydrolysis from			
	a) Ti(OR) ₄ (R = <i>i</i> -C ₃ H ₇) in water			
	dried at 110°	amorphous		
	calcined at 330°	25.5	78.5	9 (A)
	450°	25.4	123	6 (A)
	500°	25.55	152.5	5 (A)
	600°	25.5	186	4 (A)
	700°	25.5	209	2 (A)
		27.5	159	2 (R)
	b) Ti(OR) ₄ solution in ROH in water			
	dried at 110°	25.5	42	12 (A)
	calcined at 550°		109.5	6 (A)
	c) Ti(OR) ₄ solution in an equivalent amount of water in ROH			
	dried at 110°	amorphous		
	calcined at 550°	25.3	111	6.5 (A)
	600°	25.35	119	6 (A)
	yields amorphous TiO ₂ or anatase with amorphous parts			
3	From TiCl ₄ /H ₂ O mixture, containing 5 wt% H ₂ SO ₄ (with respect to TiO ₂), precipitation with ammonia leads to anatase			
	calcined at 550°	25.4	104.5	6.5 (A)
	680°	25.4	230	3 (A)
4	From TiOSO ₄ solution, precipitated by addition of ammonia, yielding pure anatase			
	calcined 3 h at 550°	25.45	142	6 (A)
	24 h at 550°	25.3	242	3 (A)

(A) = anatase; (R) = rutile; PWHH = peak-width at half-height.

to its high stabilization with sulphate and phosphate ions. The thermal effect of the bulk sample of Merck anatase occurs at lower temperature and is sharper than that of the powder sample, due to its higher mass and higher thermal conductivity. Anatase prepared by method 2c is not stabilized; it transforms into rutile at 930°.

The thermal behaviour of titania obtained by hydrolysis from Ti(OR)₄ (R = *i*-

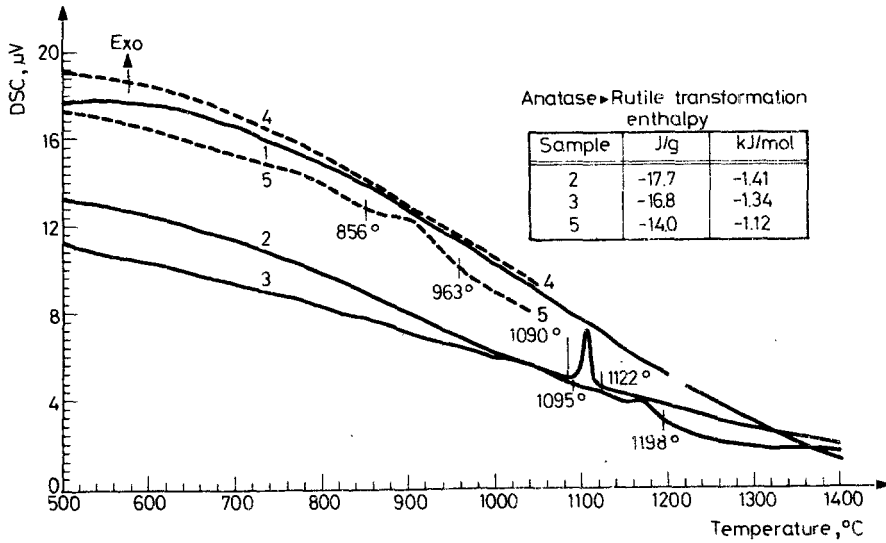


Fig. 1 DTA behaviour of pure standard rutile (1), and a highly stabilized anatase in powder (2), or bulk form (3) in comparison with own rutile (4) and own unstabilized anatase (5)

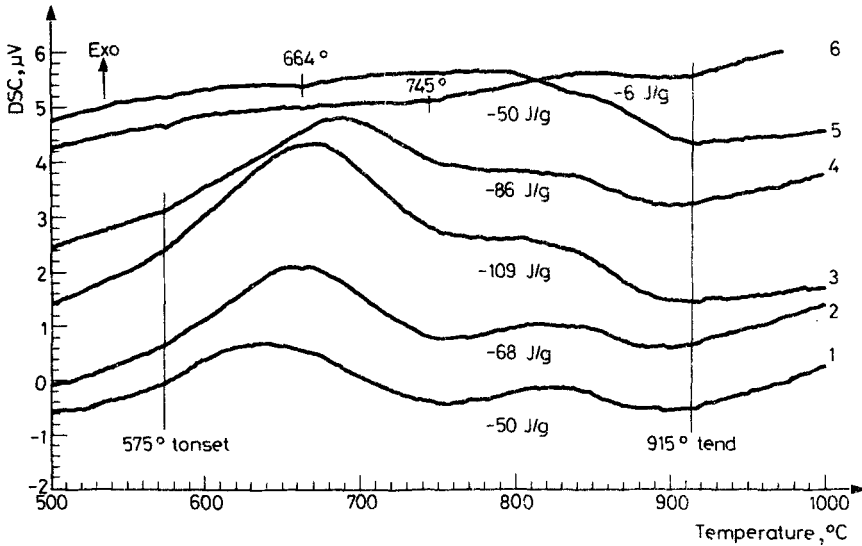


Fig. 2 Influence of drying and calcination temperature on the recrystallization of anatase, preparation 2 a, dried and calcinated at 110 °C (1), 300 °C (2), 450 °C (3), 500 °C (4), 600 °C (5) and 700 °C (6); enthalpies of exotherms given at each curve

C_3H_7) (sample 2a), dried and gradually calcined, is shown in Fig. 2. The hydrolysis of $Ti(OR)_4$ in pure water yields $TiO_{2-x-y}(OH)_{2-x-y}(OR)_{2y}$ gels. The product dried at 110° is amorphous. During calcination, processes of dehydration, oxidation of organic residues and crystallization of anatase take place up to 500° [20, 21]. The broad exothermic peak in the range 575 – $750/800^\circ$ is associated with recrystallization of the anatase modification. This exothermic effect was observed for the powders from all the preparation methods 2, 3 and 4 (Figs 2–4).

The recrystallization peak passes through a maximum on increase of the calcination temperature from 300 to 600° . The amorphous parts crystallize to a large extent into anatase at 300 – 450° . At the same time, grain growth takes place up to 600° . On increase of the calcination temperature, anatase begins to transform into rutile.

A comparison of the titania gels presented by hydrolysis from $Ti(OR)_4$ (samples 2a, b, c) is given in Fig. 3. The method of preparing the TiO_2 plays an important role in the transformation. Hydrolysis of $Ti(i-OC_3H_7)_4$ in aqueous isopropanol solution is the best way to form a product that yields anatase after dehydration, oxidation of organic residues and calcination. A very pure and well-crystallized anatase was obtained in preparation 2c. Calcination just above the onset temperature of the recrystallization peak yields pure anatase.

Figure 4 shows DTA curves of anatase powders precipitated from sulphate-containing solutions. Sulphate ions stabilize the anatase modification. From the

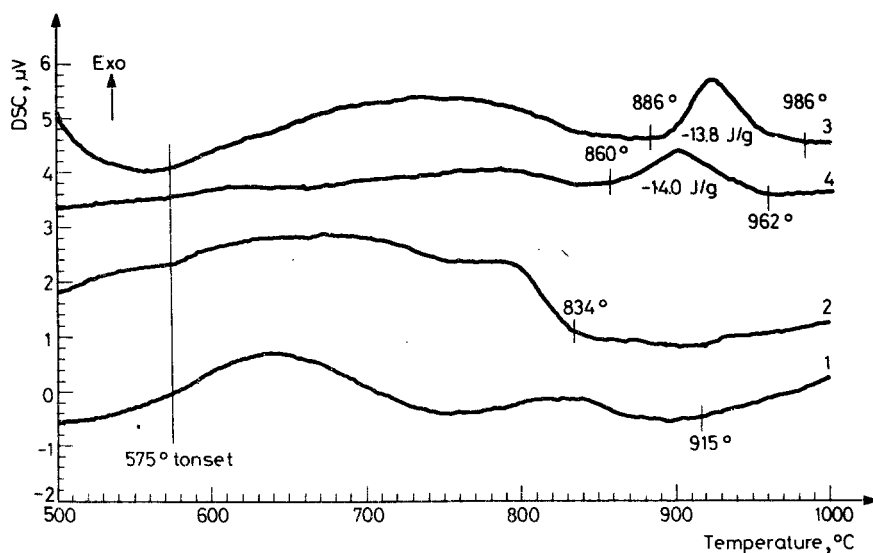


Fig. 3 Influence of preparation 2 a, b, c and calcination on the recrystallization of anatase. Preparation 2 a (1), 2 b (2), 2 c (3), 2 e and calcination at $600^\circ C$ (4)

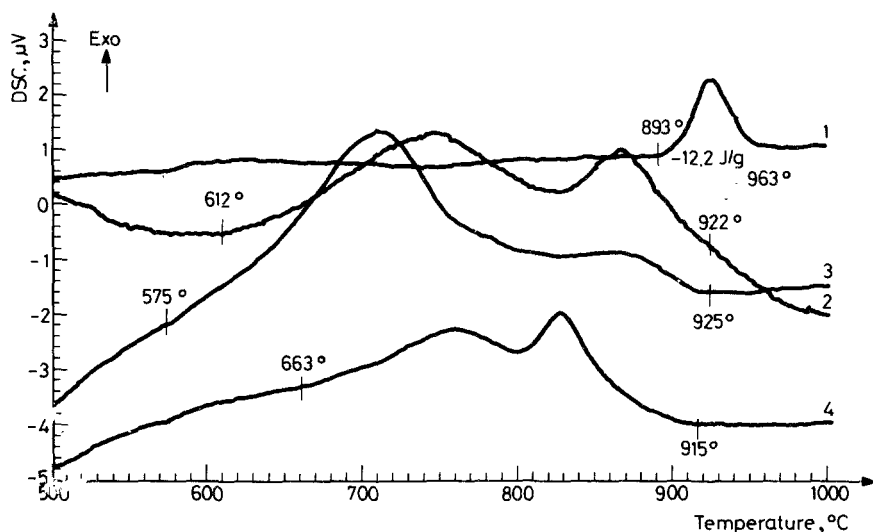


Fig. 4 Influence of the calcination temperature and calcination time on the recrystallization of anatase: preparation 3, annealed 680 °C, 3 h (1); preparation 3, annealed 550 °C, 3 h (2); preparation 4, annealed 550 °C, 3 h (3); preparation 4, annealed 550 °C, 24 h (4)

TiCl₄/H₂O mixture containing 5 wt% H₂SO₄ (with respect to TiO₂), precipitation with ammonia yields anatase even at 110°. Calcination at 550° and 680° completes the crystallization of the anatase modification. The precipitation from TiOSO₄ solutions always yields anatase. Nearly the same results are obtained by calcination just above the onset temperature of the recrystallization peak or by isothermal calcination for 24 h at 550° (Fig. 4, samples 3 and 4).

The exothermic peak after the recrystallization of anatase indicates the anatase-rutile transformation. The enthalpy values (12–18 J/g) correspond to the literature data [14].

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Zusammenfassung — Nach verschiedenen Methoden dargestellte Anatas- und Rutil-Pulver wurden mittels simultaner TG–DSC bis 1400 °C charakterisiert. Die Präparationsmethoden lieferten amorphes Titan(IV)-oxid, reinen Anatas, stabilisierten Anatas und reinen Rutil. Die Enthalpieeffekte infolge der Kristallisation amorphen Materials zu Anatas und der Phasenumwandlung von Anatas in Rutil wurden untersucht. Mittels Wärmefluss-DSC wurde letztere Umwandlung nachgewiesen und ihre Enthalpie bestimmt.

Резюме — Полученные различными методами порошкообразные анатаз и рутил были изучены совмещенным методом ТГ–ДТГ и ДТА до температуры 1400°. Разработаны методы получения аморфной окиси титана, чистого анатаза, стабилизированного анатаза и чистого рутила. Исследованы энтальпийные эффекты процесса кристаллизации аморфных участков на анатазе и фазового превращения анатаза на рутиле. Этот фазовый переход был также обнаружен методом ДСК теплового потока. Определена энтальпия этого перехода.