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X-Ray Diffraction Study of TiO_2 Thin Films on Mica

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Thin layers of polycrystalline TiO_2 were deposited on flaky muscovite and phlogopite particles. Deposition was performed in water slurry using aqueous $TiCl_4$ as titanium source. The effect of heat treatments on the structure of TiO_2 thin films was investigated at different layer thicknesses. On muscovite mica the films crystallized as anatase TiO_2. On phlogopite mica the increasing layer thickness favored partial rutile formation at higher calcination temperatures, although the films could not be converted to pure rutile. The preferred orientation of the TiO_2 films was evident. The most intense reflections were measured from (004) and (105) planes. The crystallite size of TiO_2 was strongly dependent on calcination temperature and TiO_2 layer thickness. It varied between 15 and 47 nm for films deposited on phlogopite, and 15 and 57 nm for films deposited on muscovite. © 1992 Academic Press, Inc.

1. Introduction

TiO_2–mica pigments consist of small mica platelets coated with TiO_2. Thin films of hydrous TiO_2 are deposited from acidic Ti(IV) solutions on the mica flakes slurried in water. Hydrous films are converted to crystalline TiO_2 by calcination. The color of the pigments is controlled by the thickness (about 40–150 nm) of the TiO_2 layer because the difference in the refractive indexes of the mica substrate and the TiO_2 coating gives rise to optical interference.

The patent literature for synthetizing these pigments is numerous (*1*) but there are no reports describing the structural properties of these pigments. The aim of this study was to investigate the effects of different heat treatments on the crystal structure of TiO_2 thin films deposited on mica flakes. Results were also compared to unsupported TiO_2.

2. Experimental

The micas used as substrates were phlogopite and muscovite. The phlogopite was from Siilinjärvi ore in Finland. Structural, chemical, and physical properties of Siilinjärvi phlogopite have been published earlier by Puustinen (*2, 3*). Muscovite mica was of Indian origin. The shape of the mica particles in both samples used as substrates for TiO_2 deposition were flakes. The diameter of the particles ranged from 5 to 50 μm and the thickness was below 1 μm. The chemical composition of both micas is given in Table I.

Titanium tetrachloride was of technical purity. Before use it was diluted with water so that the titanium(IV) concentration was 2.1 mol dm^{-3}. Sodium hydroxide used was also of technical purity.

The deposition of TiO_2 was performed with following technique. Fifty grams of mica was slurried with 500 grams of water.

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TABLE I

CHEMICAL COMPOSITION OF PHLOGOPITE AND MUSCOVITE MICAS USED AS SUBSTRATES

	SiO_2 (%)	MgO (%)	Al_2O_3 (%)	K_2O (%)	Fe (%)	Na_2O (%)
Phlogopite	47.0	24.5	10.6	10.4	6.0	0.06
Muscovite	47.9	0.5	34.2	10.4	1.4	0.52

The batch was then heated to 70°C and pH was adjusted to 2.2 with dilute hydrochloric acid. Then aqueous titanium tetrachloride solution was introduced to the agitated slurry at a constant speed of 0.5 ml min^{-1}. The pH of the slurry was kept constant with simultaneous addition of aqueous sodium hydroxide solution. After the deposition step the solids were separated and washed with ion-exchanged water and dried for 16 hr at 120°C. The coating thicknesses varied from 20 to 200 nm. After drying, the resulting TiO_2-mica composite powders were calcined in air at different temperatures. The samples supported by phlogopite and the unsupported TiO_2 were put into hot oven and kept there 1.0 hr; the samples supported by muscovite were put into a cold oven that was heated to calcination temperature in 30 min, where they were kept for 1.5 hr. In some cases, flowing O_2 was used as calcination atmosphere.

The X-ray diffraction patterns were recorded with a Philips PW 1840 diffractometer using Ni-filtered Cu $K\alpha$ radiation. The 2θ values were scanned from 20° to 70°. The instrumental parameters used were: voltage 40 kV, tube current 40 mA, time constant 2 sec, receiving slit 0.2 mm, step width 0.01 degrees, and time per step 5 sec. The patterns were first smoothed, and then integrated areas of the peaks, peak positions, and widths at half maximum intensity were determined by standard procedures.

The mean crystallite sizes of thin TiO_2 films were determined from the broadening of the peaks, according to Debye–Scherrer equation, after corrections for $K\alpha$ doublet and instrumental broadening based on the Warren equation (*4, 5*). The average crystallite size was determined as the geometric mean of the crystallite sizes calculated from (101), (004), and (105) reflections.

Powdered samples for the diffraction analysis were spread with spatula onto the sample holder. This technique allowed particles to orient their basal planes parallel (*6*). The repeatability of the sample preparation and measurement was investigated and it could be shown that the intensity of the diffraction peaks varied by ±15% around the mean intensity.

The approximate TiO_2 film thicknesses were determined from interference colors which became visible during deposition (*1*).

3. Results and Discussion

3.1. Crystal Structure of TiO_2

Unsupported TiO_2. TiO_2 without substrate was precipitated according to the method described in Section 2. Initially the precipitate was crystallized as anatase. The transformation from anatase to rutile took place between 750 and 800°C.

The anatase–rutile transformation temperature reportedly varies between 610 and 1100°C, depending on the calcination time, precipitation method, raw materials and the impurities present (*7–15*). Wilska showed that the transition occurred at 800°C when TiO_2 was prepared by hydrolyzing 10% $Ti(SO_4)_2$ or $TiCl_4$ solutions with NH_4OH at room temperature. When sodium hydroxide was used, however only traces of anatase were visible at 500°C (*14*). Nishimoto *et al.* reported that a range of phase transition temperatures for TiO_2 (when prepared from titanium tetra-2-propoxide) was 600–650°C and 750–800°C from titanium sulphate (*9*). The observed temperature range for the phase transition from anatase to rutile was in good agreement with results obtained by

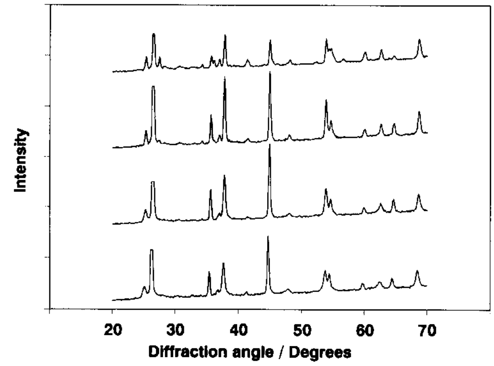

FIG. 1. XRD patterns of 80-nm thick TiO_2 films on phlogopite after calcination at 650 (bottom), 750, 850, and 950°C (top).

other investigators. Differences detected could be explained by use of different raw materials and different precipitation methods.

TiO_2 on mica. Weak diffraction patterns of the TiO_2 anatase modification were recorded from the dried TiO_2 films supported by phlogopite as well as muscovite. TiO_2 was well crystallized already at 600°C. In the thin TiO_2 films supported by phlogopite anatase dominated up to 850°C, whereas only traces of rutile were visible. TiO_2 was partially converted to rutile at 950°C. The effect of calcination temperature on the XRD patterns of an 80-nm thick TiO_2 film on phlogopite is shown in Fig. 1.

The amount of rutile increased with increasing TiO_2 layer thickness. This can be seen in Fig. 2, which shows the XRD patterns of samples with layer thicknesses of 80 and 140 nm calcined at 950°C for 1 h. There was a remarkable amount of rutile in the sample calcined at 950°C. A value over 70% could be given as a crude estimate. The balance between the two polymorphs of TiO_2 on phlogopite changed essentially when the TiO_2 layer thickness increased to 200 nm. Rutile content became remarkable (~60%) already when samples were calcined at 850°C.

The change in crystal structure from anatase to rutile could be hindered by controlling the heating rate and atmosphere during calcination. When the temperature was raised by 10°C min^{-1} from room temperature to 850°C in flowing O_2, the TiO_2 layer was found to remain anatase. This phenomenon could be detected even in the thickest TiO_2 films (200 nm) grown in this study. The anatase–rutile transformation is known to be dependent on the calcination atmosphere, but the results of this investigation differed from the observations made with unsupported TiO_2. According to Iida and Ozaki (*16*) the transformation proceeds faster when the partial pressure of O_2 is decreased. However, the transformation proceeds faster in flowing air than in static air. The difference was attributed to the faster evaporation of water in flowing air than in static air. Results of Suzuki and Kotera revealed the same trend (*17*). The difference between present results and earlier investigations may be attributed to the retarding effect of phlogopite substrate on the phase transition.

The effect of heat treatment of TiO_2 on muscovite differs from that on TiO_2 on phlogopite. The anatase modification was more stable in films deposited on muscovite. The anatase structure remained intact at

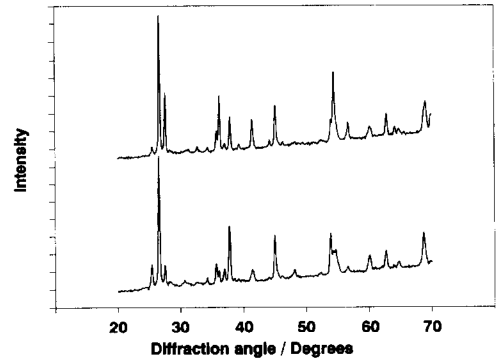

FIG. 2. XRD patterns of 80- (bottom) and 140-nm (top) thick TiO_2 films on phlogopite. Calcination temperature 950°C.

least to 1000°C. The calcination method did not have any influence on the balance between TiO_2 polymorphs. At 1000°C there were no evidence of rutile in the diffraction patterns.

Thus the anatase polymorph of TiO_2 deposited on phlogopite or muscovite was more stable toward phase change than the powdered TiO_2 obtained with the same precipitation method. This implies that micas stabilized the anatase form considerably. Phase transition temperature above 900°C is high when compared to results obtained by other investigators for thin supported TiO_2 films. Takahashi and Matsuoka e.g., reported a value as low as 650°C for TiO_2 films prepared on glass plates from $Ti(O\text{-}i\text{-}Pr)_4^-$ diethanolamine-H_2O-*i*-PrOH system (*18*). Also lower values were reported by Fukushima and Yamada, because they detected only the rutile structure for films deposited on sapphire, Si(100) and alumina by the ionised cluster beam (ICB) method after annealing in O_2 at 600°C (*19*). Chang *et al.* deposited thin TiO_2 films by MOCVD on Si(111), and sapphire (0001), and (1120) (*20*). The films on Si were polycrystalline anatase at the temperature range from 400 to 800°C. On sapphire(0001) the films consisted of epitaxial anatase up to 800°C, but on sapphire(1120) the films were rutile at 800°C. From these observations it is obvious that the crystal structure of supported thin TiO_2 films is affected at least by the substrate and preparation method.

In the present work the difference in phase transition temperatures between thin TiO_2 films deposited on phlogopite and muscovite substrates was obviously not caused by the structural differences between the substrates, because both of these layer silicates belong to the true mica group and hence they are structurally quite similar (*6*). The more probable explanation is the effects of the impurity ions mentioned earlier. By the addition of suitable additives the anatase to rutile transformation temperature can be lowered or increased. Known transformation accelerators are, for example, Fe_2O_3 (*8, 16*), CuO (*8, 16*), LiF (*8*), NiO (*16*), and MnO_2 (*8, 16*), whereas sulphate and phosphate ions (*11*), K_2O (*11*), and Al^{3+} or Al_3O_2 (*21, 22*) act as inhibitors. The role of Na_2O is not well known because it was reported to be an accelerator and also an inhibitor (*11, 16*).

The chemical composition of muscovite is somewhat different than that of phlogopite. The concentrations of several possible accelerators and inhibitors, viz., Fe_2O_3, Al^{3+}/Al_2O_3, and Na_2O, differ. The amount of iron in phlogopite is four times than that in muscovite and the amount of Al_2O_3 is only one third of that in muscovite, as indicated in Table I. Both factors lead to the conclusion that TiO_2 on phlogopite should transform from anatase to rutile at lower temperature if the accelerators or inhibitors can move from the mica substrate into the TiO_2 layer during calcination. This kind of process could explain the observed differences between TiO_2 films deposited on muscovite and phlogopite.

The incorporation of impurity ions is quite probable because Bach and Schröder reported that sodium ions can diffuse from glass substrate through overlaying thin TiO_2 films during heat treatment (*23*). Diffusion was detected already below 600°C. It is also known that Cr, Fe, Co and Ni, when introduced as nitrates or acetates in alcoholic solution on the surface of TiO_2 rutile single crystals, can diffuse into the rutile lattice upon heating (*24*).

3.2. Preferred Orientation of TiO_2 on Mica

The orientation of thin TiO_2 anatase films on phlogopite and muscovite was studied as a function of the TiO_2 layer thickness. The relative intensities were calculated against TiO_2 (004) reflection. The intensities are presented in Tables II and III. The measured relative diffraction intensities differed remarkably from those reported in standard

TABLE II

THE RELATIVE XRD INTENSITIES OF TiO_2 THIN FILMS DEPOSITED ON PHLOGOPITE AND CALCINED FOR 1 hr AT 850°C

Thickness of TiO_2 layer (nm)	Miller index						
	(101)	(103)	(004)	(200)	(105)	(211)	(204)
10	411	180	100	192	61	394	267
20	214	70	100	99	186	113	184
40	44	23	100	32	88	10	56
80	21	12	100	11	71	9	24
140	24	8	100	8	67	3	24
TiO_2 powder	100	9	22	33	21	19	13

diffraction patterns for randomly oriented TiO_2 powder (*25*). This was a clear indication of preferred orientation of the TiO_2 crystallites.

The relative diffraction intensities changed continuously when the layer thickness of TiO_2 was increased. Intensities of the (101) and (200) planes were the strongest at the beginning of the growth. However, the intensity of the (004) plane increased steadily and it was the most intense when the layer thickness approached 40 nm. The intensities of other diffraction peaks were simultaneously suppressed. The increase in relative intensity of the (004) plane was already clearly visible on dried samples. This could be thought as an indication of an oriented overgrowth of nuclei which had their (004) planes parallel to surface of mica. A similar kind of behavior was reported for TiO_2 films deposited by the CVD technique from isopropyl titanate on glass (*26*). In that case the overgrowth mechanism lead to growth of rutile crystallites on anatase crystallites.

Orientation of rutile TiO_2 films has been observed when they were prepared by the RICB method on quartz, alumina, Si(100), and sapphire (*19*). The most intense reflections were measured from the (110), (110), (110) and (200), and (301) and (002) planes, respectively. For TiO_2 films deposited by dip-coating method on glass plates orientation for anatase was reported to be (101) and for rutile (110) (*18*). It can be concluded from these observations that the orientation direction of thin TiO_2 films depends at least on the substrate itself, crystal orientation of the substrate, and the deposition method.

3.3. Crystallite Size of TiO_2 on Mica

The effect of calcination temperature on the mean crystallite size of anatase crystallites in TiO_2 films was determined at different film thicknesses in the temperature range from 600 to 1000°C. For comparison the mean crystallite size of unsupported anatase TiO_2 was determined at 650, 700, and 750°C.

From results presented in Table IV, it is evident that the size of TiO_2 crystallites on both micas was the same after thermal treatment at 600 and 650°C and was not dependent on TiO_2 layer thickness. It is also clear that the crystallites of unsupported TiO_2 were larger than those deposited on mica. During calcination the mean crystallite size of TiO_2 on mica was increased when the TiO_2 layer thickness and calcination temperature were increased. Below 850°C the crystallite size was increased only slightly when the layer thickness was increased. At 850°C or above the crystallite size was strongly

TABLE III

THE RELATIVE XRD INTENSITIES OF TiO_2 THIN FILMS DEPOSITED ON MUSCOVITE AND CALCINED FOR 1.5 hr AT 850°C

Thickness of TiO_2 layer (nm)	Miller index					
	(101)	(103)	(004)	(200)	(105)	(204)
20	246	57	100	214	96	130
40	61	25	100	44	83	50
80	22	10	100	21	75	27
100	23	16	100	14	67	20
140	21	12	100	6	67	20
TiO_2 powder	100	9	22	33	21	13

TABLE IV

THE MEAN CRYSTALLITE SIZES (nm) OF TiO_2 FILMS SUPPORTED BY PHLOGOPITE AND MUSCOVITE MICAS

Calcination temperature (°C)	Film thickness (nm) 20	40	80	140
	Phlogopite			
650	15	17	18	18
750	14	20	21	20
850	16	26	29	35
950	18	33	36	47
	Muscovite			
600	16	16	15	22
850	18	28	33	37
1000	27	35	44	57
	Unsupported TiO_2			
650	22			
700	23			
750	26			

dependent on both factors. An abrupt increase in crystallite size was observed between layer thicknesses of 20 and 40 nm, when the calcination temperature was 850°C or above. This was an indication that crystallite growth was suppressed by the thickness of TiO_2 layer when the layer thickness was 20 nm. When the TiO_2 layer was 40 nm or thicker the crystallites could grow larger and the growth was dominated by the calcination temperature and TiO_2 film thickness.

The crystallite size was doubled for TiO_2 deposited on phlogopite and tripled for TiO_2 deposited on muscovite in the temperature range studied. The results were in accordance with the observations of Sullivan and Cole (*12*) for unsupported TiO_2 obtained from industrial titanium sulphate solutions. According to their results the crystallite size was 10 nm at 600°C and 35–110 nm at 900°C. The differences at higher temperatures were caused by the modifications in the preparation method. Similar results were obtained also by MacKenzie (*27*) and Yoganarasimhan (*28*).

4. Conclusions

Thin TiO_2 layers were deposited on flaky phlogopite and muscovite substrates from acidic $TiCl_4$ solutions. All TiO_2 films deposited on both substrates were primarily polycrystalline anatase. At temperatures over 850°C films on phlogopite began to transform to rutile, although the films could not be converted to pure rutile in the temperature range studied. The micas stabilized the anatase polymorph of TiO_2 since the anatase–rutile transformation took place in unsupported TiO_2 already between 750–800°C.

The crystallite size was affected by the calcination temperature and layer thickness of TiO_2 film.

The differences between crystal structure and crystallite size of the films supported by phlogopite and muscovite may have been caused by the different chemical composition of the substrates. Al^{3+}, Fe^{3+}, and Na^+ ions could have been diffused to films during calcination and affected the crystal structure transformation and growth of crystallites. This must be confirmed by further investigations.

The orientation of TiO_2 film calcined at 850°C increased when the layer thickness was increased but epitaxial relationship was not achieved. The crystallites oriented mainly to the (004) direction.

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