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The Effect of Calcination on the Surface Composition and Structure of Titanium Dioxide Coated Mica Particles

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Thin layers of polycrystalline TiO_2 were deposited on flaky muscovite and phlogopite particles. Deposition was performed in a water slurry using aqueous $TiCl_4$ as the titanium source. The effects of heat treatments on the surface composition of thin TiO_2 films were studied by XPS technique. The surface composition was strongly dependent on the calcination temperature. The substrate components diffused through the film and as a consequence the outermost surface was a mixture of oxides of titanium, silicon, aluminum, and sodium. Surface composition was not affected by calcination after a certain induction period. The diffusing cations are believed to have an effect on the anatase-to-rutile transformation which was observed in the TiO_2–phlogopite system but not in the TiO_2–muscovite system.

1. Introduction

TiO_2–mica pigments are small mica platelets coated with a thin layer of TiO_2. They are prepared by depositing hydrous TiO_2 from Ti(IV) solutions onto the mica flakes. After the deposition step the flakes are calcined in order to increase their refractive index and light stability. The difference in refractive indices between mica and TiO_2 gives rise to optical interference and hence the pigments have different colours depending on the layer thickness of the TiO_2 coating.

In a previous study (*1*) it was shown that the type of the mica has an influence on the phase transition temperature of TiO_2 from anatase to rutile. Powder XRD measurements revealed that the coating on muscovite mica remained in the anatase structure through the whole calcination temperature range studied, which extended up to 1000°C. On phlogopite mica TiO_2 began to transform from anatase to rutile at 850°C. At 950°C 50% of the coating was already rutile. In the literature this transformation temperature is reported to vary between 610 to 1100°C for unsupported TiO_2 depending upon the method of synthesis, the atmosphere, and the presence of foreign ions (*2–10*).

The aim of this study was to investigate whether annealing transfers impurity ions from the mica substrate to the thin overlaying TiO_2 films. Then the differences in crystallization behavior of thin TiO_2 films deposited on chemically different mica substrates could possibly be explained in this way.

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2. Experimental

2.1. Deposition of the TiO_2 Coating

The micas used as substrates were muscovite and phlogopite. Muscovite was of Indian origin whereas phlogopite was from Siilinjärvi ore in Finland. Structural, chemical and physical properties of Siilinjärvi phlogopite have been published earlier by Puustinen (*11, 12*). The shapes of mica particles used were platelike. The diameter of particles ranged from 5 to 50 μm and the thickness was less than 1 μm.

The titanium source was technically pure $TiCl_4$. Before use it was diluted with water so that titanium(IV) concentration was 2.1 mol dm^{-3}. The sodium hydroxide used was also of technical purity.

A quantity of 50 g of mica was slurried with 500 g of water. The batch was then heated to 70°C and the pH was adjusted to 2.2 with dilute hydrochloric acid. Then aqueous $TiCl_4$ solution was introduced to the agitated slurry at a constant speed of 0.5 ml min^{-1} and hydrous titanium dioxide was deposited on mica flakes. The pH of the slurry was kept constant by the simultaneous addition of aqueous sodium hydroxide solution. After the deposition step the solids were separated and washed with deionized water and dried for 16 hr at 110°C. After drying the resulting TiO_2 coated mica powders were calcined at different temperatures in air in order to crystallize the coating.

Thicknesses of the TiO_2 films were estimated by means of both the interference colour of the reflected light and the quantities of $TiCl_4$ solution used. The coating thicknesses varied from 10 to 200 nm. Figure 1 reveals that the TiO_2 coating is polycrystalline with a smooth surface except for some tiny cracks. The widths of these cracks increased with increasing calcination temperature or with increasing coating thickness. However, the widths of the cracks in the pigments studied were so small that the contribution of the uncovered substrate to the surface composition is negligible. The complete results of the powder XRD measurements are presented in Ref. (*1*).

2.2. XPS Measurements

Samples for XPS measurements were prepared by fixing the coated mica platelets onto the molybdenium sample holder with Leak Sealing Compound (Vacuum Generators Ltd) diluted with acetone. When a drop of this solution was dried on molybdenum plate for a minute, platelets were gently pressed to achieve a complete coverage of the molybdenum surface over an area of about 1 cm^2. After a drying period of an hour loosely held platelets were shaken off the sample. Finally the sample was blown with hot air. This might lead to the contamination of platelet surfaces with elements like carbon, hydrogen, and oxygen in the form of hydrocarbons, carbon oxides, and water, but it was necessary to avoid the pressure rise due to the attachment of loosely held platelets to valves of the vacuum system.

XPS measurements were carried out with a PHI Small Spot ESCA 5400 electron spectrometer in the constant analyzer energy mode. The XPS spectra were excited by nonmonochromatized Mg$K\alpha$-radiation. The area of the analyzed sample surface was approximately 1 mm^2. The survey spectra of samples covered binding energies 0–1100 eV. Samples were also depth profiled by argon ion sputtering using a PHI 04-300 ion gun with 3.0 kV acceleration voltage and 25 mA current. The profiling speed was approximated to be roughly 1 nm/min by means of calibration measurements using a SiO_2/Si–system.

Sample preparation might lead to the contamination of surfaces increasing especially their carbon, hydrogen and oxygen content. Because the main interest was to study the behavior of the cations of mica the major emphasis was given to following calcination

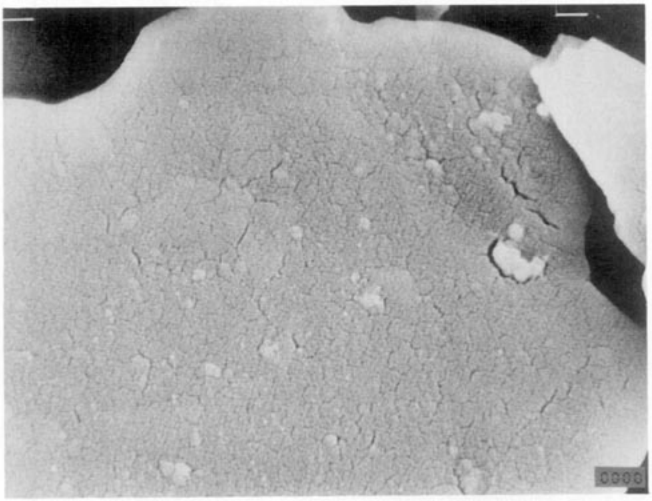

FIG. 1. SEM picture (10,000 ×) of muscovite platelets coated with a 100 nm thick TiO_2 film (calcined at 850°C).

induced changes in the cation fractions of the surfaces.

3. Results and Discussion

3.1. Micas

The effects of the heat treatment on the substrate surface compositions were investigated by comparing surface compositions of dried (110°C) and calcined (850°C) micas (Table I). It can be seen that the calcination effects are small except those concerning sodium. At the surfaces of muscovite platelets the sodium concentration increases by a factor of 4 during the calcination. However, the situation is the reverse at the phlogopite surfaces, where the sodium content decreases from 0.4% to below the detection limit of XPS. The most probable explanation for this discrepancy is contamination of the uncalcined phlogopite sample.

3.2. TiO_2 on Muscovite

Platelets which had about an 80 nm thick TiO_2 coating were calcined at 850°C for different times and their surface compositions were evaluated from survey XPS spectra. Figure 2 depicts cation fractions as a function of calcination time. After calcination a remarkable amount of cations from the mica can be found on the TiO_2 surface. The TiO_2 film is thick enough (80 nm) to guarantee that photoelectrons emitted from the substrate cannot escape through the film without scat-

TABLE I

MICA SURFACE COMPOSITIONS BEFORE AND AFTER CALCINATION

	Muscovite		Phlogopite	
	110°C	850°C	110°C	850°C
O	67.6	66.6	59.1	53.6
Si	15.7	15.6	14.7	18.1
Al	12.9	12.9	9.7	12.0
Mg	0	0	9.3	9.1
K	3.0	2.6	3.3	3.5
Na	0.6	2.2	0.4	0
Fe	0	0	1.8	1.9
F	0.3	0.1	1.1	1.5
Ca	0	0	0.4	0.3
Ag	0	0	0.1	0

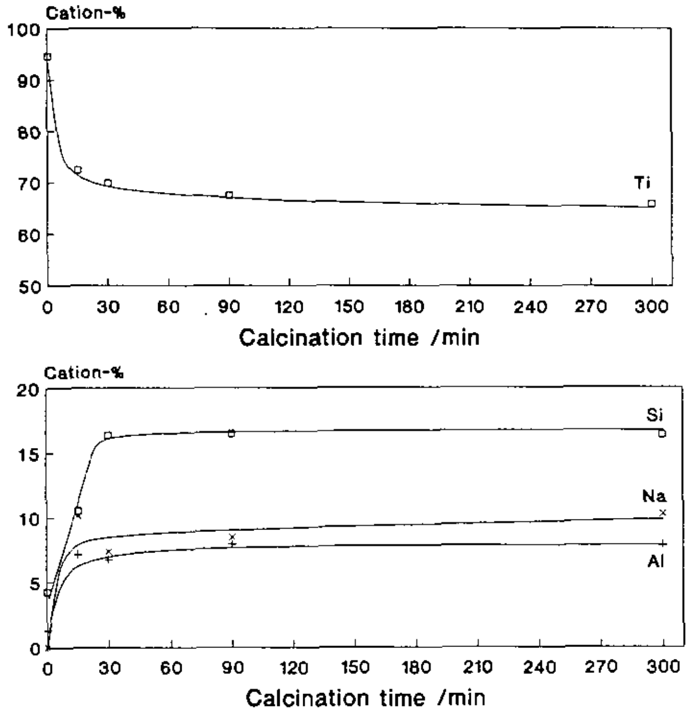

FIG. 2. Cation contents at the surface of an 80 nm thick TiO_2 film on muscovite as a function of calcination time at 850°C.

tering inelastically. Furthermore, because cations exist on the surface of TiO_2 in a different ratio than on the mica surface it is reasonable to conclude that the observed increase is caused by the diffusion through the TiO_2 film and not by the tiny cracks of the film observed in SEM pictures. It can be seen that the composition of the surface is stable when the calcination time exceeds 30 min. This can be explained either by the saturation of the surface or by the limited amount of diffusing cations available from the thin mica platelets. It is worthwhile to notice that chloride from the titanium source was not detected in any sample.

Bach and Schröder have reported a similar kind of diffusion of sodium ions in TiO_2 films deposited on glass plates (*13*). They observed that the diffusion of sodium ions also had an effect on the crystal structure of the TiO_2 coating. It should be noted that Na^+ and/or Na_2O are known to inhibit the anatase–rutile transformation in unsupported TiO_2 (*6*, *14*). The aluminum ion is also known to inhibit this transformation (*15*, *16*).

The calcination temperature had a significant effect on the stabilized surface composition (Fig. 3). When the T ≤ 650°C only the sodium content has increased compared to the dried (110°C) and uncalcined sample. At the higher temperatures amounts of other mica cations increase with increasing temperature. An interesting feature is that the sodium content of the sample calcined at 1000°C is only about a half of its content in the sample calcined at 850°C. This is probably due to the slow sublimation of Na_2O at 1000°C. In 80 nm thick films the potassium content exceeds the XPS detection limit

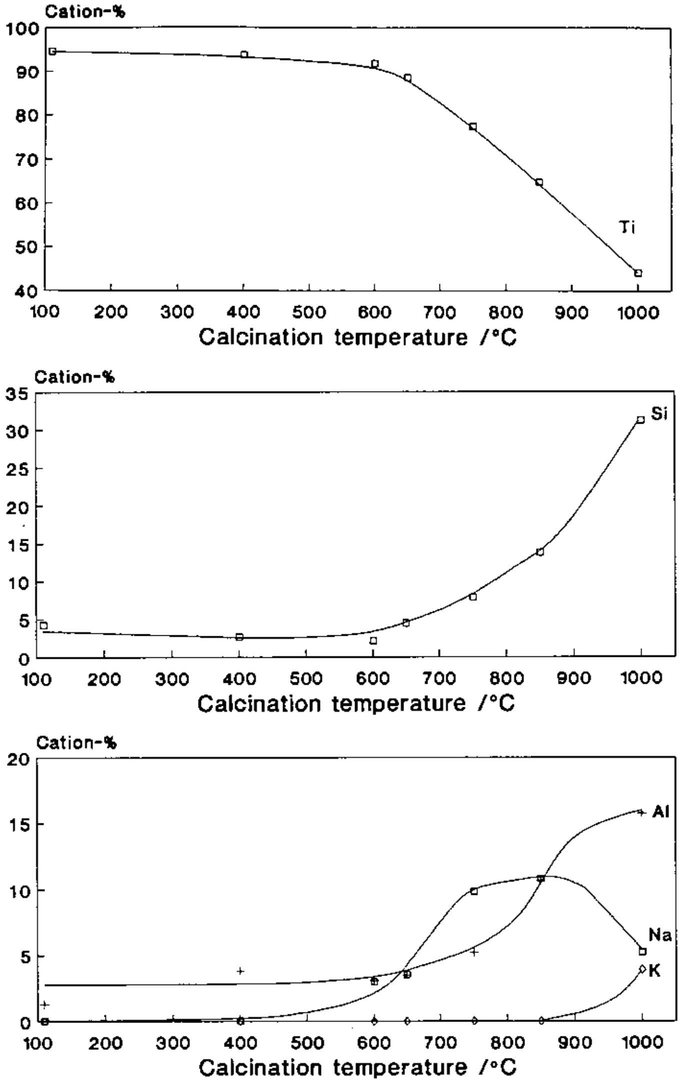

FIG. 3. Surface cation fractions of an 80 nm thick TiO_2 film on muscovite as a function of calcination temperature.

only when the calcination temperature reaches 1000°C. In thinner coatings (40 nm) potassium is observed at the surface already in samples calcined at 850°C. The temperature dependence of surface composition can be explained either in terms of the temperature dependence of the saturation concentration of the surface or in terms of different amounts of mica cations available for diffusion at different temperatures as a result of temperature dependent structural changes of mica. These structural changes leading to partial decomposition of mica can be seen in X-ray diffraction patterns.

Depth profiling measurements show that the silicon and aluminum contents increase

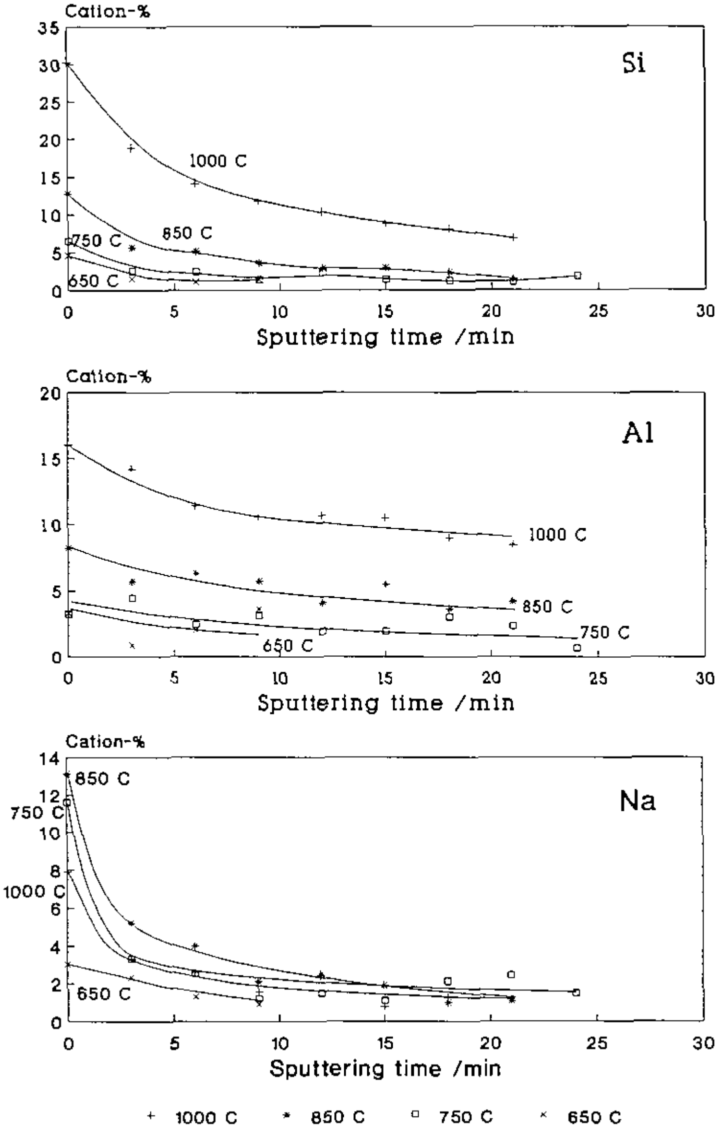

FIG. 4. Depth profiles of impurity cations in an 80 nm thick TiO_2 film at different calcination temperatures.

over the entire profiled depth with increasing temperature (Fig. 4). Sharp profiles of silicon show that it is accumulated at the surfaces of the films. Profiles of aluminum are much smoother, which can be attributed to the better solubility of aluminum into TiO_2 compared with other cations. Sodium differs from the other cations because in the samples calcined at 1000°C the sodium contents are smaller than in samples calcined at 750 and 850°C due to the partial depletion of the surface region because of the assumed sublimation of Na_2O. However, the shape of the sodium profile near the surface implies that sodium is accumulated at the surface of TiO_2 film also in samples calcined at 1000°C. Probably this accumulation has happened during the cooling period when the temperature is high enough for diffusion but too low for sublimation of Na_2O.

When the depth profiles are compared to those evaluated theoretically, assuming that the diffusion through a thin film has a grain boundary diffusion mechanism and that diffusing components are accumulated at the surface of the film (*17*), it can be seen that measured depth profiles of mica cations are very much alike. So we can qualitatively deduce that the diffusion process has a grain boundary mechanism.

The thickness of the TiO_2 film had very little effect on the surface compositions or depth profiles (Fig. 5). This is presumably due to the surface saturation controlled diffusing processes.

It is a well known fact that the cooling rate has an effect on surface composition because of segregation equilibria (*18*). To study the effects of the cooling rate for this particular case we cooled our samples in two different ways. The faster way was to take samples from the furnace (850°C) straight to room temperature. The slower way was to let samples cool down in the furnace at the same speed as the furnace. Silicon and aluminum contents and profiles did not show any marked cooling rate dependence. However, the sodium content over the entire profiled region was noticeably larger in the slowly cooled sample compared with the more quickly cooled sample (Fig. 6).

3.3. TiO_2 on Phlogopite

The TiO_2–phlogopite system was studied for comparison to the TiO_2–muscovite system. The behaviour of the surface concentrations and depth profiles of TiO_2 films on the phlogopite platelets were similar to those of muscovite substrate. The magnitudes of surface concentrations differed from films on muscovite substrates but this is simply because of different mica compositions. As a most extreme example the sodium content exceeded the detection limit of XPS in the TiO_2–phlogopite samples just when the calcination temperature was over 850°C (1.2 cation %). In TiO_2–muscovite samples at the same temperature the sodium content was 11 cation-%. This is undoubtedly due to the small sodium content of phlogopite, which is only about 10% of the sodium content of muscovite. Also, the aluminum content of the surface of the TiO_2–phlogopite system (5 cation-% at 850°C) was only half of its value in the TiO_2–muscovite system (11 cation-% at 850°C).

According to these results the observed anatase to rutile transformation of the TiO_2–phlogopite system, which was absent in the TiO_2–muscovite system, can be connected with the smaller transformation inhibitor (Na, Al) contents of the TiO_2–phlogopite system. Iron is known to accelerate this transformation (*3, 14*). The iron content of the phlogopite mica is tenfold its content in the muscovite. However, it was not observed in XPS measurements.

Because the deposition process is the same for both samples the different sodium contents of TiO_2 film surfaces are also clear evidence that the detected sodium is really diffused through the TiO_2 film from mica instead of being codeposited from sodium hydroxide solution. Our latest experiments have confirmed this observation (*19*).

As a consequence of its higher content in phlogopite magnesium was detected from samples calcined over 850°C as distinct from samples with a muscovite substrate. This fact can be of use when the type of mica coated is analyzed.

3.4. The Effect of the Washing of the Calcined Sample

Films deposited on muscovite, 40 nm thick, were washed with hot water after

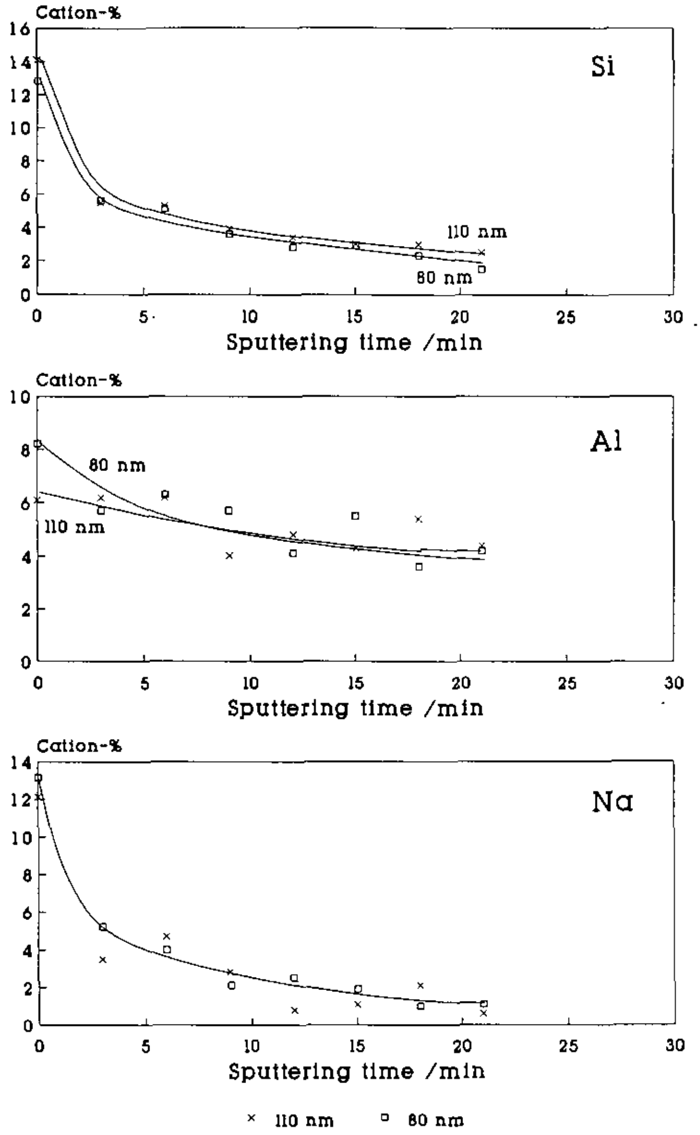

FIG. 5. Depth profiles of impurity cations in samples with different coating thicknesses calcined at 850°C for 90 min.

calcination at 850°C to study how tightly diffused cations were bonded at the surface. The XPS measurements showed that potassium content was reduced from 2 cation-% to below the detection limit of XPS during the washing procedure. Also the sodium content was markedly reduced from 12 to 2 cation-%. The ratios Si/Ti and Al/Ti did not change in washing.

3.5. The Effect of Substrate Precalcination

In the previous samples mica was not calcined before TiO_2 deposition. We conducted

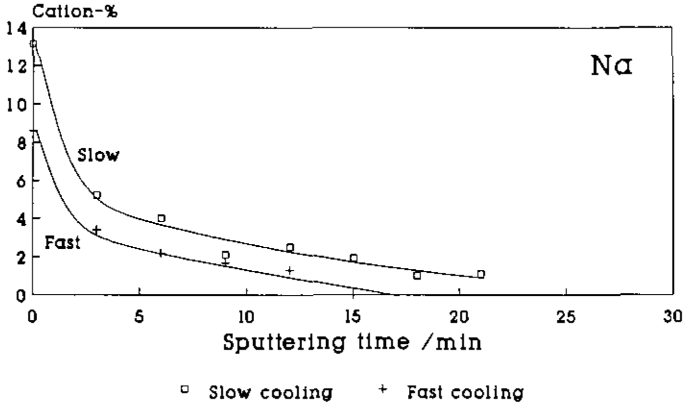

FIG. 6. The effect of the cooling rate on the sodium profiles in the sample with an 80 nm thick TiO_2 coating.

a experiment where muscovite was calcined before coating and compared the XPS results for this sample with a sample which had a coating of equal thickness on uncalcined muscovite. Both samples were calcined after deposition at 850°C for 60 min. The result was that sodium content was noticeably smaller in the sample with precalcined substrate (8 cation-%) than in the sample with nonprecalcined substrate (12 cation-%). This is probably due to the liberation of sodium during the first calcination after which sodium is accumulated at the surface of mica (Table I). During the deposition step this accumulated sodium can be easily dissolved into the slurry and as a consequence the coated precalcined mica has a smaller sodium content than coated uncalcined mica. Also the potassium content is smaller in the sample with the precalcined substrate but the difference (2.1 and 1.6 cation-%) is not very remarkable, particularly when the accuracy of XPS is taken in account. When all the surface atoms, i.e., also carbon and oxygen, are considered the corresponding potassium contents are only about 0.3–0.4 atomic-%. For potassium the accuracy of XPS in these concentration levels is around 0.05–0.1 atomic-%.

The silicon content also depends on whether the substrate is calcined or not before coating. The sample with precalcined substrate has a larger silicon content at its surface (19 cation-%) than the nonprecalcined sample (13 cation-%). This is probably due to the partial decomposition of mica during the first calcination (cf. 3.2) which enables the silicon to move more freely during the next calcination period. Aluminum concentration was not dependent on the pretreatment of the mica substrate.

4. Conclusions

We coated mica platelets with TiO_2 and investigated, by means of XPS, what influences the calcination conditions have on the surface compositions of TiO_2 films. Our results showed that cations from the mica diffuse through the film to its surface. The calcination temperature has a strong effect on the composition of the surface. By means of depth profiling measurements it can be qualitatively deduced that the diffusion has a grain boundary mechanism. Depth profiles also reveal that cations accumulate at the surface of the TiO_2 film. The different surface compositions of TiO_2 coatings can be used to distinguish the muscovite and phlogopite substrates.

The observed differences in chemical compositions and amounts of diffusing impurity cations, especially sodium and aluminum, in TiO_2 films may have a contribution to the different crystallization behaviour of films on muscovite and phlogopite substrates.

The next thing to study are the influences of cation diffusion on the pigment properties. To do this we will prepare pigments without diffusion process. We assume that this is possible with a chemical vapor deposition (CVD) technique.

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