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RAMAN AND X-RAY DIFFRACTION DATA ON ANATASE IN FIRED KAOLINS

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Abstract—The Raman spectra of many kaolins are dominated by bands from ancillary anatase. Fired samples of a commercial anatase-bearing kaolin from the Jari River deposit in Brazil showed significant variations of Raman spectra as a function of the firing temperature. The spectra showed the full range of anatase bands up to a firing temperature of 900ºC. From 950ºC the background increased significantly, leading to an unfavorable signal/noise ratio that allowed observation of only the most intense (E_g) band at ~144 cm^{-1}. X-ray diffraction (XRD), however, confirmed that this band, which persists up to 1200ºC, results from anatase. Two factors may be responsible for the high thermal stability of anatase in this sample: its relatively large particle size of ~120 nm and possible reactions with Si and Al that become liberated during kaolinite breakdown. When evaluated with circumspection, Raman and XRD data on anatase can serve as 'thermometers' to elucidate the thermal history of fired anatase-bearing kaolins and other anatase-bearing clays.

Key Words—Anatase, Firing, Kaolinite, Raman Spectroscopy, X-ray Diffraction.

INTRODUCTION

Kaolins contain Ti in amounts that range from zero to several wt.%. While part of this Ti can be bound in the kaolinite structure, anatase (TiO_2) is a common ancillary constituent of almost all Ti-containing kaolins. Anatase can be readily identified by Raman spectroscopy, the intensity of the E_g band at ~144 cm^{-1} allowing the unequivocal identification of this mineral at concentrations in kaolins as low as 0.02% (Murad, 1997).

Anatase is not the thermodynamically stable polymorph of TiO_2, and numerous studies have addressed the thermal transformation of anatase to rutile. Early work by Dachille *et al.* (1968) indicated pure anatase to convert to rutile in the absence of water and at a pressure of 1 atm at ~610ºC. However, various effects including pressure, water content, foreign element substitution, selected accompanying minerals, and particle size can lead to variations of the temperature of this transformation (*e.g.* Heald *et al.*, 1972; Lottici *et al.*, 1993; Gribb and Banfield, 1997). Thus Zhang and Banfield (1999) noted a range of published values for the anatase-to-rutile transformation between 390 and 1090ºC (the lowest temperatures having been observed for nanosize samples). Such variations led Lindsley (1991) to suggest that "... most (perhaps all) published 'phase boundaries' between rutile and anatase ... reflect kinetics rather than equilibrium". The bulk of published values for the anatase-to-rutile transformation must therefore be considered as valid only under the specified conditions and for the specific sample(s) under survey.

The breakdown of anatase upon heating suggests that the presence or absence of this mineral could be a useful indicator of the thermal history of ceramics produced from anatase-containing kaolins or other anatase-containing clays. To test the possibility of such a dependence, a pilot study using Raman spectroscopy and XRD was carried out on an anatase-bearing but otherwise pure commercial kaolin after firing to temperatures between 100 and 1250ºC.

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EXPERIMENTAL

Materials

The sample used for this study was the kaolin 'Amazon 88' from the Jari River deposit in the State of Amapá, Brazil. The sample consists of a disordered kaolinite ('Hinckley index' ≈0.30) with a relatively high TiO_2 content of ~1.4% (Murray and Partridge, 1982). X-ray diffraction on samples spiked with anatase indicates an anatase content of ~0.8%. Aliquots of this sample were fired in air for 48 h in steps of 50ºC from 100 to 1350ºC, and the firing products were characterized by a variety of methods including XRD, infrared (IR) spectroscopy and Mössbauer spectroscopy at room temperature and 4.2 K (Murad and Wagner, 1991). Both XRD and Mössbauer spectroscopy revealed the transformation of kaolinite to metakaolin between 400 and 450ºC, the breakdown of metakaolin between 900 and 950ºC, and the subsequent formation of high-temperature phases.

Methods

Fourier-transform Raman spectra were taken on a Nicolet Magna 550 FT-IR spectrometer equipped with a Raman accessory. Excitation was achieved with a Nd:YVO_4 laser operated at 0.20 W; a filter placed between the laser and the sample to reduce thermal emission decreased the intensity of the incident radiation by a factor of ~7. The samples were packed into NMR glass tubes and 3 to 5 runs of 1000 scans each were taken

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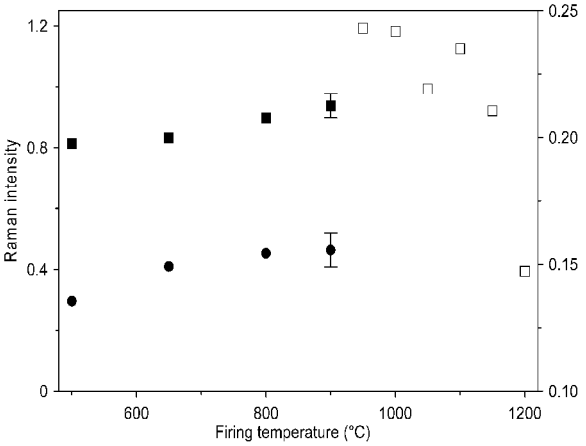


Figure 1. Intensities of the Raman E_g bands at ~144 (squares and left *y* axis) and 639 cm^{-1} (closed circles and right *y* axis) in the Amazon kaolin as a function of the firing temperature. The closed squares outline the field in which other anatase bands were also observed, whereas no other bands could be discerned at higher temperatures (open squares). Error bars shown for the sample fired at 900ºC indicate the standard deviations for the two anatase bands.

at different positions of the tubes. Instrumental settings included a 180º reflective sampling configuration, a CaF_2 beamsplitter and an InGaAs detector operated at room temperature. The resolution was 4 cm^{-1}. Raman band positions are given as shifts relative to the wavelength of the exciting radiation (1064 nm ≡ 9394 cm^{-1}). Positions and intensities of the anatase Raman E_g bands at ~144 and 639 cm^{-1} were determined in the wavenumber ranges 120–170 and 580–700 cm^{-1}, respectively, using the Galactic PeakSolve™ program.

X-ray diffraction was performed using CuKα radiation on a Bruker D8 instrument equipped with a sample spinner and a diffracted-beam graphite monochromator. Powder specimens produced by sedimentation of the samples on a silicon slide were step-scanned in 2θ steps for 30 s per 0.02º step. To determine the intensities and widths of the anatase 101 peaks, additional scans were carried out in the 2θ range from 23 to 28º for 60 s per 0.01º step. Peak parameters were determined by fitting the XRD data with a Voigt function using a program described by Stanjek and Friedrich (1986). Estimates of the anatase particle sizes were obtained by applying the Scherrer formula to data that been stripped of the $K\alpha_2$ component and corrected for instrumental broadening using the NIST standard reference silicon powder #640.

RESULTS AND DISCUSSION

The Raman spectrum of the Amazon kaolin is dominated by anatase bands, with an E_g band at ~144 cm^{-1} that is particularly prominent (Murad, 1997; Murad and Köster, 1999). Figure 1 shows the intensities of this band and the E_g band at 639 cm^{-1} as a function of the firing temperature. Both bands show moderate increases in intensity after firing between 500 and 900ºC. These changes can be attributed to minor changes in the matrix, *e.g.* in color, that have previously been described for this sample (Murad and Wagner, 1991). Between 900 and 950ºC the spectra show a steep rise in background intensity and an abrupt increase in intensity of the anatase E_g band at 144 cm^{-1} (Figure 1), whereas the other anatase bands 'disappear' in the unfavorably high background (Figure 2). Above 1100ºC, the band at 144 cm^{-1} also begins to decrease in intensity, and is absent in the sample fired at 1250ºC. The band positions indicate no change in energy between 900 and 950ºC and vary by <1 cm^{-1} in the total temperature range covered.

X-ray diffraction of the fired kaolinite shows a distinct anatase 101 peak at 3.50 Å (Figure 3) up to a firing temperature of 1200ºC. The peak widths indicate that anatase occurs in relatively large particles ~120 nm in size (Figure 4). In agreement with the Raman data, however, the intensity of this peak decreases noticeably above 1100ºC, and it can no longer be observed at 1250ºC (Figure 4). A minor peak at ~27.5º2θ (3.24 Å) that can be tentatively attributed to rutile was first observed at 1050ºC (Figure 3) but had also disappeared at 1250ºC.

X-ray diffraction and Mössbauer spectroscopy have shown kaolinite in the Amazon kaolin to break down between 900 and 950ºC, leading to the formation of new phases (Murad and Wagner, 1991). The temperature to which anatase persists in this sample, however, is significantly higher. One reason for this thermal stability of anatase in this kaolin may lie in its relatively large particle size. Additives of silica and alumina, moreover, have been shown to significantly retard the anatase-to-rutile transformation (Yang and Ferreira, 1998). These components would become available as kaolinite breaks down, thereby causing the anatase-to-rutile transformation to shift to higher temperatures.

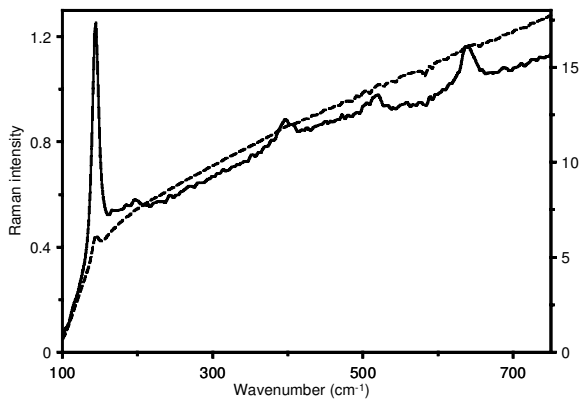


Figure 2. Raman spectra of the Amazon kaolin fired at 900ºC (solid line) and 950ºC (broken line) showing the anatase bands at 398, 515 and 639 cm^{-1} at 900ºC and the unfavorable signal/background ratio at 950ºC. The left and right *y* axes refer to the samples fired at 900 and 950ºC, respectively.

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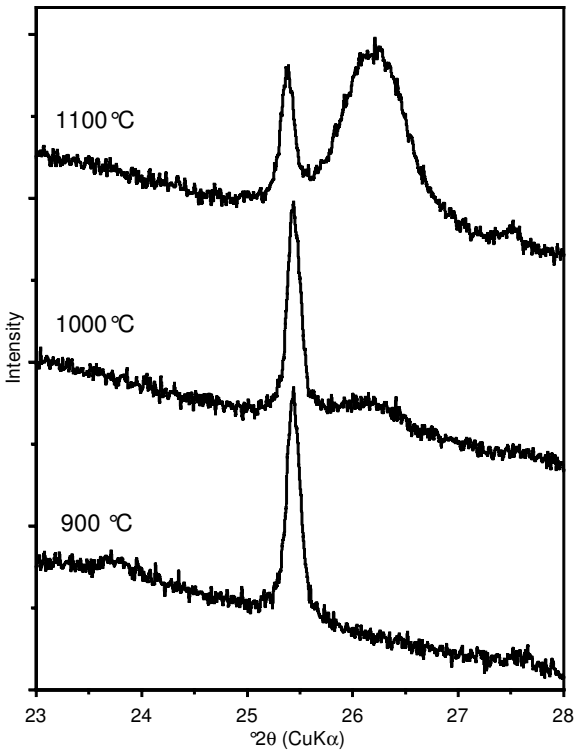


Figure 3. XRD patterns of the Amazon kaolin fired at (from bottom to top) 900, 1000 and 1100ºC. Note the prominent anatase 101 peak at ~25.4º2θ (3.50 Å) and the gradual appearance of the (still unresolved) mullite 120 and 210 peaks at ~26.2º2θ. The *y* axis scale divisions correspond to 5 counts per second.

The total TiO_2 content of the Amazon kaolin (1.4%) is in excess of the anatase content (~0.8%), and this excess Ti will be released from the kaolinite structure as this mineral breaks down. The fact that no rutile Raman bands were observed may be due to the enhanced fluorescence above 900ºC, but although XRD tentatively indicates that rutile was formed at the expense of anatase from 1050ºC onwards, it appears all that Ti released from kaolinite and anatase eventually becomes incorporated in high-temperature silicate phases such as mullite above 1200ºC.

CONCLUSIONS

Raman spectra of the Amazon kaolin show distinct variations in the course of firing: an abrupt increase in intensity of the E_g band at ~144 cm^{-1} between 900 and 950ºC, followed by a decline of this band above 1100ºC and its disappearance between 1200 and 1250ºC. The strongest XRD peak of anatase can also be observed up to 1200ºC. This study thus indicates that Raman spectroscopy, a technique that requires minimal sample preparation whilst providing rapid results, can generally be used to elucidate the thermal history of fired kaolins and other clays, although it may be necessary to determine possibly 'characteristic' temperatures of anatase transformation for the material under survey. A distinct advantage when using Raman spectroscopy is the sensitivity of this method towards anatase, allowing the detection of this mineral at significantly lower concentrations than by XRD.

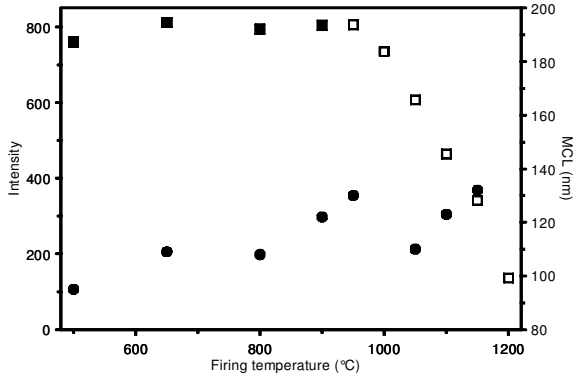


Figure 4. Intensities of the anatase 110 XRD peak at ~25.4º2θ (3.50 Å) in the Amazon kaolin (squares and left *y* axis) and mean coherence lengths, which are taken as a measure of particle size (circles and right *y* axis), as a function of the firing temperature. The closed symbols outline the field in which anatase Raman bands, besides that at ~144, were also observed.

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