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Properties Related Phase Evolution in Multilayer Silicate Ceramics

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Abstract. The use of ceramic processes inducing a microstructural organization at the grain scale favors the improvement of strength and toughness. With layered structures, it is possible to design the microstructural characteristics of materials, leading to increased threshold strength. Layered structures can be arranged to control the local residual stresses causing elastic mismatches between dissimilar materials and crack deflection at interfaces. In this way, multilayer composites from kaolinite and alumina or mullite fibers were shaped by tape casting and staked by thermo-compression, or by centrifugation. During sintering, they show at strong anisotropic behavior, which is in correlation with different activation energy for sintering. Mullite growth is also anisotropic, inducing the formation of an organized micro composite microstructure.

The mechanical and elastic properties are correlated with the organization degree of mullite crystals, due to the formation of an interconnected mullite network in the microstructure. It is also shown that variations of mechanical and elastic properties are correlated with the texture index obtained by Quantitative Texture Analysis from X-ray data. The anisotropy of the elastic properties is evidenced by different values of Young's modulus in directions parallel and perpendicular to the casting direction. Beside, the crack growth resistance is governed by discontinuities along layer boundaries and fiber interfaces.

Introduction

Ceramic materials with organized microstructure can be obtained from powder with anisotropic grains, using tape casting or centrifugation shaping processes. Tape casting [1,2] is a forming method that gives laminated green tapes for the manufacture of substrates and multilayer structures [3,4]. Centrifugation also gives oriented powder compacts from suspensions of various anisotropic grains as phyllosilicates [5]. Compacted thick layers up to 4 mm are obtained from the accelerated settling of suspensions.

During sintering of green powder compacts, oriented grains induce specific recrystallization processes [6]. It leads to ceramics with improved properties, such as mechanical properties, since morphology, orientation degree and connectivity of crystals in microstructures are determinant in macroscopic properties.

In silicate ceramics from clay minerals, we reported that mullite crystallization occurs in preferential crystallographic directions of the initial muscovite [7,8]. The 3D interlocking mullite network within the glassy matrix favors the increase of mechanical properties [9-11], and the control of the starting composition, as well as the optimization of the different processing parameters are very important [12].

The objective of this study is to obtain silicate ceramics having an organized microstructure with mullite, to improve mechanical properties. Materials were shaped by aqueous tape casting of concentrated suspensions composed of kaolin and muscovite powders. Centrifugation of aqueous suspensions was also used to compare results. Shaping and sintering processes were optimized to favor the formation of a 3D network of mullite within microstructures. Mechanical properties at microscopic and macroscopic scales were characterized and correlated with microstructural characteristics [13] and mullite orientation degree.

Table 1: Processing parameters used for shaping samples by centrifugation or tape casting. C series samples are from centrifugation (previous study [5]) and TC sample is from tape casting. The texture indexes by QTA are also reported.

Sample	Kaolin Vol%	Mica Vol%	Centrifugation high mm	Dispersant wt%	PVA wt%	PEG wt%	Stacking mode	Heating rate °C/min	Overall Texture Index m.r.d.²
C 1	25	-	9.8	-	-	-	-	5	1.14
C 2	25	-	11.2	-	-	-	-	15	1.17
C 3	25	-	11.2	-	-	-	-	5	1.22
C 4	22.5	2.5	11.2	-	-	-	-	5	1.77
C 5	22.5	2.5	11.2	-	-	-	-	15	1.68
C 6	20	5	11.2	-	-	-	-	5	1.34
TC 7	38	3.8	-	0.27	5	5	90°	5	1.77

Experimental

The tape cast slurries were prepared in three main stages : - aqueous suspensions were prepared by grinding kaolin (Denain-Anzin-Minéraux) in a planetary mill with the addition of a dispersant (Dolaflux); - a binder (PVA 22000) and a plasticizer (PEG 300) were mixed with the suspension; - muscovite mica (Micromica, 10 wt%) was ball milled with the suspension during 1h at 100 rpm in quantity of 5% wt.

Tape casting was performed with a non-continuous laboratory equipment, controlling the thickness of green tapes (500 µm). Cylindrical samples were cut from the dried green tapes and stacked (8 individual layers) at T=60°C and p=50 bars. After a debinding stage, (800°C, 1.5°Cmn^{-1}), sintering was at the maximum temperature of 1400°C during 2 hours.

Centrifugation was performed with an aqueous suspension of the same kaolin, as in ref [5]. Suspensions were prepared by grinding kaolin particles in water with a dispersant (Dolaflux, 0.2wt %) in a planetary mill. It results in disc-shaped samples (diam. 36 mm, height 1-5 mm).

Elastic properties of sintered ceramics were measured by nanoindentation (NanoXP^{TM}, MTS Instruments) with a Berkovich tip, in a continuous stiffness measurement mode (CSM) [14,15], and at a penetration depth of 2000 nm. Measurements were carried out in directions parallel and perpendicular to the tape casting directions (r and z respectively). At the macroscopic scale, Young's moduli were obtained by ultrasonic echography operated in immersion, in the r and z directions. Fracture strengths were obtained by biaxial disc flexure in a piston on ring assembly.

To quantify crystal orientation, Quantitative Texture Analysis (QTA) was performed using a 4-circle diffractometer allowing the acquisition of the whole diffraction pattern up to 80° 2θ, for each tilt angle χ and azimuth angle φ of the samples orientation. Diagrams were acquired for many sample orientations (using a 5°x5° measuring grid in (χ,φ), up to χ=55°). The whole data set was analyzed using the Whole-Powder-Pattern Rietveld analysis within the combined analysis formalism [16], and the orientation distribution functions were refined using the E-WIMV approach [17]. Pole figures were plotted using an equal area projection on the disc plane, with their center being the r direction. Intensities are normalized into distribution densities using multiple of a random distribution (m.r.d.) units. The overall texture strength is evaluated through the texture index [16]. The normalization of the pole figures into m.r.d. values is operated during the orientation distribution (ODF) refinement of crystallites during the E-WIMV step. The ODF and profile refinement reliabilities are estimated using conventional reliability factors [18].

Results

Data reported in table 1 present the range of processing parameters used for shaping samples which have a significant influence in the microstructural characteristics. The Rietveld analyses of XRD patterns firstly reveal that the only crystalline phase is (3:2) mullite, which coexists with an amorphous phase. Considering that the amorphous phase is similar to an alkaline silico-aluminate, Rietveld fits were obtained with good reliability factors, and the refined cell parameters are a = 7.553 Å, b = 7.686 Å, c = 2.886 Å, that are similar to literature data [19,20].

Quantitative Texture Analysis (QTA) from XRD patterns of the same sample gives pole figures of Fig. 1, for {001}, {020} and {200} mullite orientations, the former direction being in plane with the tape surface. The overall texture index and the fraction of texture components are determined from inverse pole figures of Fig. 2, which are plotted for the main sample directions, r (ND), x (RD) and y (TD). The overall texture index of this material is 1.77 m.r.d.^{2}, and this value can be compared in Table 1 with texture indexes from different samples obtained either by tape casting or centrifugation. The main processing parameters are also reported in Table 1, to show how the processing parameters change the texture index.

With TC7 sample of Table 1 obtained by tape casting, Fig. 3a-b presents the Young's modulus measured in directions parallel (E_r) and perpendicular (E_z) to the casting plane, when the muscovite

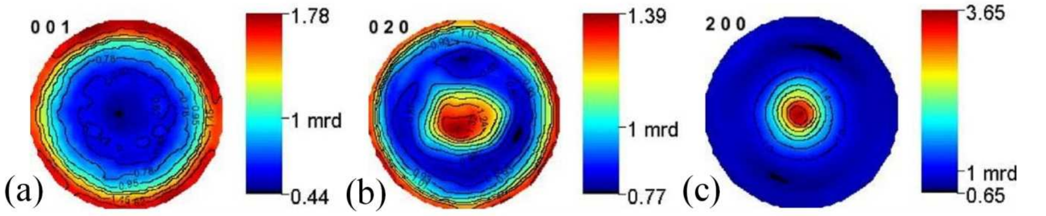

Fig. 1: Pole figures of mullite axes for a kaolinite-muscovite material (sample TC7 of Table 1). (a): {001}; (b): {200}; (c): {020}.

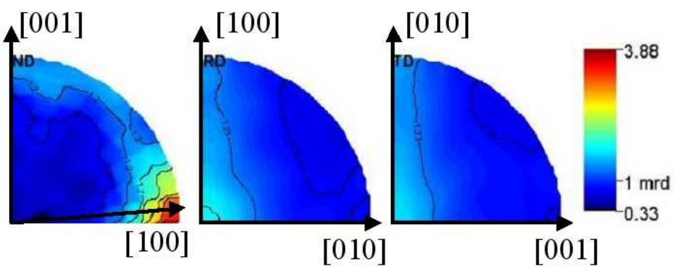

Fig. 2: Inverse pole figures for the main sample directions of sample TC7 of Table 1. r (ND), x (RD) and y (TD).

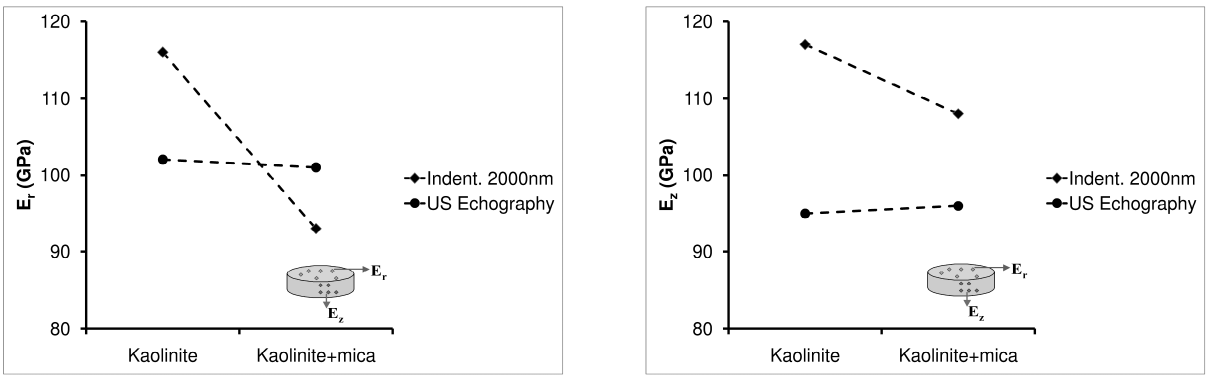

Fig. 3: Sample TC7 from tape casting. Influence of muscovite addition (5 wt%) on the Young's modulus. (a, left): r-axis (E_r); (b, right): z-axis (E_z). Measurements techniques are indentation at 2000 nm depths, and US echography.

quantity changes. With US echography, the addition of muscovite induces a slight variation of both E_r and E_z, but the decrease of the anisotropy of elastic properties ($E_r - E_z$). At a more local scale when indentation is used, values of E_r and E_z are significantly decreased, but the anisotropy of elastic properties is increased. With samples from centrifugation process, the variations of E_r and E_z are very similar.

From data in Table 1, the Texture Index can be correlated with the Young's Modulus in *r* and *z* directions from samples obtained either by centrifugation and tape casting, see Fig. 4. With samples from centrifugation, the general trend is an increase of the elastic properties with the Texture Index. It can be supposed a similar trend with tape casted samples, but the lack of supplementary data implies complementary experiments.

In a similar way, the flexural strength of samples obtained either by centrifugation and tape casting are presented in Fig. 5 as a function of the Texture Index. In the case of centrifugation, the strength increases with the texture index, but a plateau is observed above about 1.4 m.r.d². As for the elastic properties, one data from tape casting evidences a very higher value and an increasing trend with the texture index can be supposed.

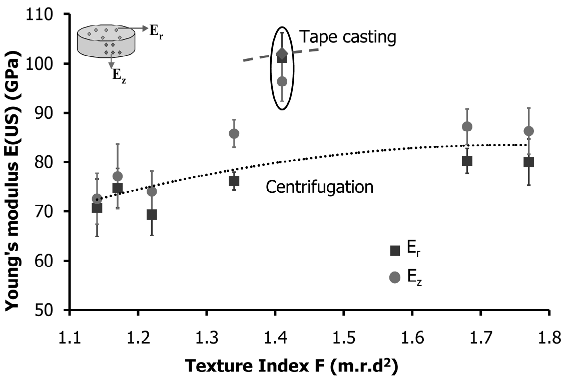

Fig. 4: Correlation of Young's modulus by US echography with the Texture Index from QTA. Data are from samples obtained either by centrifugation and tape casting.

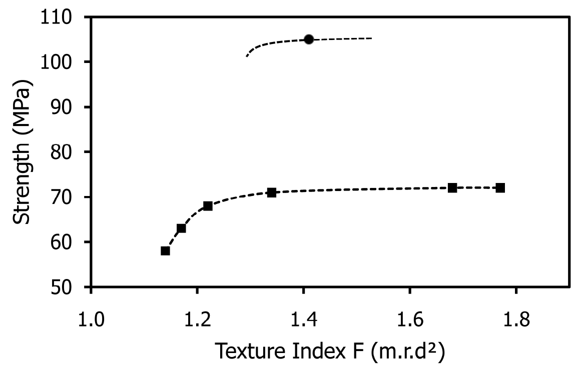

Fig. 5: Correlation of the flexural strength with the Texture Index from QTA. Data are from samples obtained either by centrifugation and tape casting.

Discussion

Quantitative Texture Analysis of a representative material (sample TC 7 of Table 1), for {001}, {020} and {200} directions of mullite are given in poles figures of Fig. 1a-c. The {001} pole figures of Fig. 1a evidence that *c*-axe is aligned parallel to the sample plane, that is the casting direction. It forms a planar texture where the maximum orientation density is located at the periphery of the {001} pole figures and reaches 1.78 m.r.d. The orientation density is uniformly distributed at the periphery of the figure, indicating that the tape casting process leads to a quasi-uniformly oriented mullite in-plane of layers. The minimum value of the {001} pole figure indicates that only 44Vol% of the material is not oriented within the planar texture.

Since other crystallographic directions are supposed to be randomly distributed from *c*-axis, a broad maximum should be observed in the center of any {hk0} pole figure. Accordingly, the center of {020} and {200} figure (Fig. 1b-c) has maximum of 1.39 m.r.d. and 3.65 m.r.d. respectively. But for {020} pole figure (Fig. 1b) a supplementary orientation density is located at the periphery that indicates the coexistence of a planar component. This observation is coherent with the existence of a second texture component shown in Fig. 1c, that is a <200> preferential orientation. This component is predominant in the material with a 3.65 m.r.d orientation density.

Orientations are also observed in inverse pole figures calculated from the ODF function for the 3 directions (Fig. 2). A slight accentuation occurs in RD and TD directions of samples, for <001> and <010> orientations, which evidence a planar texture. A more accentuated texture index is also observed in ND figure, in the <100> direction, which further indicates a <100> fiber-like texture. It confirms that mullite *a*-axe is parallel to the casting plane. The minimal value of the ODF indicates that 33vol% of material are not in the main orientation direction. The maximum OD texture index is 3.88 m.r.d.^{2}, revealing a relatively high texture strength.

In Fig. 3a-b, the characterization of elastic properties evidences that the addition of muscovite improves the orientation degree of mullite. Whatever the studied shaping parameters, the difference (E_r-E_z) is dependent in the measurement technique, since it strongly increases when indentation is used, but do not varies with E_{US} measurement. A first explanation comes from the measurement scale, since indentation at 2000nm depth is a micro-scale characterization (indent diagonals of about 6-8 µm), while ultrasonic echography gives information at the macroscopic scale (mm scale). Such indent size allows measuring the Young's modulus over a few tens of needles and it is greater than the size of local flaws. It averages local measurements, but it remains sensitive to mullite orientation at low scale, that ensures the significance of measurements.

Fig. 4 shows the correlation of Young's modulus by US echography with the Texture Index from QTA. Considering that data are from centrifugation, a simple correlation between Young's modules E_{US} along *r* and *z*-axis and the texture index can be found whatever the qualitative regression method. It evidences that a first increase is followed by a plateau value above a texture index of 1.5 m.r.d^2. With a sample obtained by tape casting having a higher Young modulus, a similar variation against the texture index should be supposed (Fig. 4).

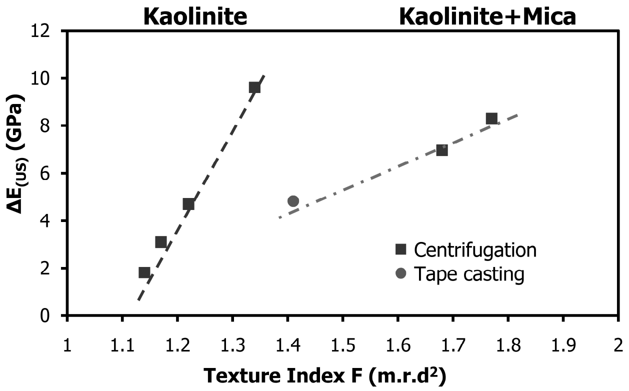

Fig. 6: Correlation between the anisotropy of the Young Modulus ΔE_{US} and the Texture Index, as a function of sample compositions.

The change of fracture strength is also dependent in the texture index and in the shaping process (Fig. 5). As for the elastic properties, the strength is firstly increased when the texture index increases and attains a plateau value at about 1.4 m.r.d^2. One's again, it is verified that the orientation degree of mullite is an important factor in mechanical properties. The influence of the shaping process is also illustrated since the sample from casting presents a higher strength. In that case, the leading role of the shaping process can be also supposed in Fig. 5.

From our results, the texture index is related to the mullite orientation degree in plane of samples. It induces anisotropic elastic and mechanical properties, the former ones being measured by ultrasonic echography, as in Fig. 3a-b. Correspondingly, in Fig. 6 we obtain two specific linear relations between the anisotropy of the Young's modulus ΔE_{US} and the texture index. Both relations are interestingly linear and depend on the material composition. It further evidences the organization degree in microstructures, when the addition of muscovite increases the texture index by promoting the preferred orientation of mullite. This representation of ΔE_{US} according to the texture index shows that much more than the shaping method, it's mainly the processing parameters that are essential in the formation of organized microstructures.

Conclusion

The study of the processing and characterization of micro-composite materials with mullite from kaolinite and muscovite mica reveals the preferential orientations of mullite in sintered materials. Both the Young's modulus and the biaxial flexure strength of sintered materials are changed by the processing parameters, whatever the shaping method, centrifugation or tape casting. Microstructural characteristics were obtained by both the orientation degree by QTA and by SEM observations. The Young's modulus and the biaxial flexure strength present an increasing trend with the texture index and a plateau value above 1.5 m.r.d^2. The correlation between the orientation degrees, calculated from the texture index from QTA, and the anisotropy of elastic properties evidence interestingly linear relations, which depends in the material composition.

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