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Structural and morphological characterization of mullitic substrates obtained by dry-pressing

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In our previous work [1] a study has been described on the possibility of producing ceramic substrates for low-cost solar cells by means of the simple and cheap technology of moulding by dry-pressing. In the present paper, we shall deal with the structural and morphological properties of the above substrates. The study, which has been made by means of X-ray diffraction and scanning electron microscopy, resulted in some useful information, which can be used for fully understanding the reasons for the macroscopic properties of the substrates, and thus for examining the possibility of modifying and improving them.

1. Introduction

In previous work [1], we described the preparation of mullitic ceramic substrates to be used for low-cost polycrystalline silicon solar cells by means of the simple technique of moulding by dry-pressing.

Evaluation of the thermal and mechanical properties revealed that these substrates were quite able to withstand the thermal shock produced by immersion in molten silicon and subsequent extraction at speeds of 1 to 25 cm min^{-1}. It was also easy to reach perfect agreement between the thermal expansion coefficients of the substrate and the silicon from ambient temperature to 800° C, without having to rely on the addition of other mineralogical phases to the original mix, which was composed of commercial kaolins with about half the powder pre-calcined at temperatures between 1200 and 1350° C.

Extremely interesting is the characterization of these ceramic substrates from the structural (above all, by means of X-ray diffraction) and morphological (by means of scanning electron microscopy) points of view, with the aim of fully understanding the reasons for their macroscopic properties, and of being able to examine the possibility of modifying and improving them.

2. Experimental details

2.1. Sample preparation

Commercial Kamig-P 50 kaolin was used as the basic raw material for the preparation of the ceramic substrates. Since kaolinite clays are normally very fine and powdery, the all too frequent inconvenience of flaking during dry-pressing forming operations was avoided by granulating the product beforehand, using an aqueous solution with 0.5 to 1.0% of carboxymethyl-cellulose (CMC). This solution was sprayed in the form of finely subdivided drops onto the original powder, which was then passed through sieves having 16 to 36 meshes cm^{-2} so as to leave adequately solid granules with maximum diameters of 1.5 to 2.5 mm. After homogenization of the humidity in the granulated mass, pressing took place in a laboratory hydraulic press with a power of some 300 kg cm^{-2}. Once the thin rectangular plates (measuring 90 mm × 50 mm × 1 mm approximately) had been formed, they had to be endowed

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with a certain mechanical resistance that would enable them to be worked without risk of breakage before the final high temperature firing, which makes them quite unsuitable for any conventional treatment.

The problem was solved by preliminary firing at a temperature of 1200° C, which turned out to be the best compromise between resistance and workability of the plates. At this point, a series of cross-slots (for applying electrical contacts from the back of the finished solar cells) was made in the plates, as were the holes that would be used for suspending them in the molten silicon. For this purpose, a special sliding face-plate frame was used, together with a diamond wheel (20 mm in diameter and 0.8 mm thick) mounted on a small electric drill. After shaping, the plates were subjected to final firing in a laboratory intermittent electric furnace (resistances in Super-kantal) at 1600° C. The plates were placed on refractory bases made 80% of Al_2O_3 covered with Al_2O_3 powder to avoid sticking. A few hours at 1600° C showed more uniform results compared to samples that had been kept at that temperature for only a few minutes.

Various mixes were prepared and examined, with variation of:

1. firing temperature of the chamotte (pre-calcined Kamig P-50 kaolin);
2. particle size of the chamotte;
3. type of additive to the material when raw;
4. proportion of additive to the material when raw;
5. pre-firing temperature of the formed, unperforated plate;
6. final firing temperature of the perforated plate;
7. duration of exposure to temperature.

2.2. Sample characterization

The reader is referred back to the previous work [1] for thermal and mechanical characterization techniques; here, we shall deal only with the structural and morphological ones.

2.2.1. X-ray diffraction

Details were recorded of the X-ray diffraction spectra by means of a Rigaku-Denki (model SG-7) powder diffractometer with Bragg–Brentano geometry and fitted with a scintillation counter detector and graph paper recorder. The radiation used was Cu$K\alpha$ ($\lambda = 0.15418$ nm).

Subsequently, a semi-quantiative system was devised for evaluating the respective percentages of silicatic vitreous phase and mullitic crystalline phase present in the various samples. Furthermore, crystallinity was estimated, both from the resolution of the doublet of close diffraction lines (1 2 0) and (2 1 0) [2] and from the average sizes of the crystallites, measured with the conventional Scherrer method on the line (1 1 0) [3]. The resolution R of the doublet (1 2 0)–(2 1 0) of the mullite had been calculated as a ratio between the mean intensity of the maxima of the two lines and that corresponding to the minimum between the two, account, obviously, being taken of the background. Clearly, for the nonresolved doublet, R has a value of 1.

It should be noted that for samples with an absolutely random distribution of crystallite orientations, the two lines in question have practically equal intensities [2]. Once the kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) between 450 and 600° C has lost crystallization water, reducing itself to the so-called metakaolinite ($Al_2O_3 \cdot 2SiO_2$), when the temperature is raised around the 1100 to 1200° C the following reaction takes place:

$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 \quad (1)$$

according to which, that is to say, an essentially bi-phase system is formed, consisting of crystalline mullite and a silica-rich vitreous phase. In this reaction, the mullite formed is 63.9% of the weight, whereas the vitreous silica is the remaining 36.1%.

In the X-ray diffraction spectra the peaks of the crystalline mullite stand out clearly, especially the intense doublet (1 2 0)–(2 1 0). However, also the maximum broadened by the vitreous silica (which, with the Cu$K\alpha$ radiation, has its highest point around = 11.5°) can be easily identified in comparison to the flat background encountered when there is no vitreous phase.

Considering the ratio between the mean intensity, corrected for the background, of the mullite doublet $I_{(1\,2\,0)} + I_{(2\,1\,0)}/2$ and that of the vitreous silica hump in samples heat treated at such temperatures as to lead to the disappearance of any silica crystalline phase (and hence suitable for interpretation as bi-phase systems with a good approximation), a mean value (20 ± 2) was obtained on about ten different samples, which can be considered representative of the above ratio between the diffracted intensities, when the proportions in weight of mullite and silicatic glass are within the ratio $p(\mathrm{M})/p(\mathrm{V}) = 0.639/0.361 = 1.77$.

Extrapolating in the case of $p(\mathrm{M})/p(\mathrm{V}) = 1$ (50%–50% composition in weight), one obtains:

$$\frac{I_{\max(\mathrm{M})}}{I_{\max(\mathrm{V})}}:1 = 20:1.77 \quad \text{and} \quad \frac{I_{\max(\mathrm{M})}}{I_{\max(\mathrm{V})}} \simeq 11.3$$

Moving to a semi-quantitative scale, the ratio observed for any sample being known, one proceeds by means of the proportion:

$$\frac{I_{\max(\mathrm{M})}}{I_{\max(\mathrm{V})}}:x = 11.3:1 \quad \text{and} \quad x = 0.0885\frac{I_{\max(\mathrm{M})}}{I_{\max(\mathrm{V})}}$$

from which one has: $p(\mathrm{V}) = 1/x + 1$ and, of course, $p(\mathrm{M}) = 1 - p(\mathrm{V})$. These estimates are obviously affected by a minimum unreliability factor of 10%, but they are nonetheless indicative and useful for following the effect of heat treatment and distinguishing between samples in which the crystalline phase prevails over the vitreous one and vice versa.

It is also useful to recall that care was taken in the above evaluations to check that the intensities of the peaks in consideration were not affected by preferential orientations. The usual corrections for the $K\alpha_1$–$K\alpha_2$ doublet and for instrumental broadening on our diffractometric apparatus were applied to the measured broadening of the (1 1 0) peak, that were used for evaluating the average sizes of the crystallites.

2.2.2. Scanning electron microscopy

With their surfaces made conductive by the sputtering deposition of thin carbon or gold films, the samples were examined under a scanning electron microscope (SEM) (model Cambridge Stereoscan 150 MK 2). Certain samples were observed as they are, while others were observed after chemical etching in hydrofluoric acid at 49% for 1.5 min to remove the silicatic vitreous phase and reveal the characteristics of the mullite crystals that had formed.

3. Results and discussion

Table I shows the results of the X-ray diffractometric characterization of the main samples we prepared for dry-pressing and, for the sake of comparison, those pertaining to a typical roll-compaction product made by Coors Porcelain Co. (USA) [4] and yet another obtained by casting on belt with "doctor blade shaping" by the IRTEC–CNR Institute (Italy) [5]. We observe first of all, that the resolution of the mullite doublet (1 2 0)–(2 1 0) and the average size of the crystallites evaluated with the Scherrer method from the half-maximum broadening of the peak (1 1 0) are in a proportional linear relation up to about $D_{110} = 150$ nm; while the resolution of large crystallites remains practically constant, their dimensions grow beyond 500 nm, which can be taken as the highest experimental limit within which the Scherrer method is applicable [6], even when use is made of high-collimation systems that involve small experimental broadenings.

It is immediately evident that there is no correlation between these two parameters that define the mullite's "degree of crystallinity" and the proportions in weight in the bulk between mullite and silicatic vitreous phase. The latter, on the other hand, are in relation with the mechanical properties of the finished products that we measured in our previous paper [1]. When the pre-calcination temperature of the chamotte (added in proportion of around 50%) is in the 1200 to 1350° C range (where one obtains the best results in terms of thermal and mechanical properties), the proportions in weight of mullite and vitreous phase are rather close to the "theoretical" proportion ($p(\mathrm{M})/p(\mathrm{V}) = 1.77$).

With chamotte annealing temperatures lower than 1200° C, the result is a considerable excess of vitreous phase, with a $p(\mathrm{M})/p(\mathrm{V})$ ratio that can even drop below 0.5. With temperatures higher than 1350° C, one notices the opposite tendency ($p(\mathrm{M})/p(\mathrm{V})$ up to 3.0), but the average sizes of the mullite crystals remain decidedly low, indicating bad crystallization of the mix, that is by no means homogeneous enough. As for the average sizes of the crystallites (which must not be confused with the grains, for it is recognized that a grain can be formed of several disoriented crystallites), one clearly observes a distinct maximum with chamotte annealing temperatures of 1200–1250° C (see Fig. 1) and sharp drops with both lower and, even more so, with higher temperatures.

With the addition of 50% chamotte annealed at temperatures above 1250° C, average sizes are even smaller compared with products obtained from raw kaolin alone.

The addition of alumina hydrate to the raw mix produces rather pronounced increases in the proportion of mullite ($p(\mathrm{M})/p(\mathrm{V})$ up to 7.0),

TABLE I Structural properties as evaluated by X-ray diffraction of ceramic mullitic substrates obtained by dry-pressing

Mix	Resolution of the (1 2 0)–(2 1 0) mullite doublet, R	Crystallite dimensions from the (1 1 0) mullite peak, D (nm)	Weight ratio $p(M)/p(V)$	$p(M)$ (%)	$p(V)$ (%)
Kaolin (alone) when raw	2.37	110	1.77	63.9	36.1
Kaolin with 30% fine chamotte (1300° C)	3.37	285	1.77	63.9	36.1
Kaolin with 30% coarse chamotte (1300° C)	2.58	180	1.77	63.9	36.1
Kaolin with 40% chamotte (1300° C)	2.35	110	2.80	73.7	26.3
Kaolin with 50% chamotte (1300° C)	2.10	96	3.00	75.0	25.0
Kaolin with 60% chamotte (1300° C)	2.00	85	3.20	76.2	23.8
Kaolin with 50% chamotte (1100° C)	1.76	280	0.44	30.3	69.7
Kaolin with 50% chamotte (1200° C)	3.09	> 500	1.77	63.9	36.1
Kaolin with 50% chamotte (1250° C)	2.67	> 500	1.37	57.7	42.3
Kaolin with 50% chamotte (1350° C)	1.23	51	1.77	63.9	36.1
Kaolin with 50% chamotte (1500° C)	1.21	41	1.77	63.9	36.1
Kaolin with 20% $Al_2O_3 \cdot nH_2O$	2.56	285	6.75	87.1	12.9
Kaolin with 30% chamotte (1300° C) and 20% $Al_2O_3 \cdot nH_2O$	2.85	350	5.17	83.8	16.2
Kaolin with 40% chamotte (1200° C) and 10% anhydrous Al_2O_3	1.75	81	1.16	53.6	46.4
Coors Porcelain sample (roll-compaction)	2.80	400	1.34	57.3	42.7
IRTEC–CNR sample (casting on belt)	2.99	> 500	2.50	71.4	28.6

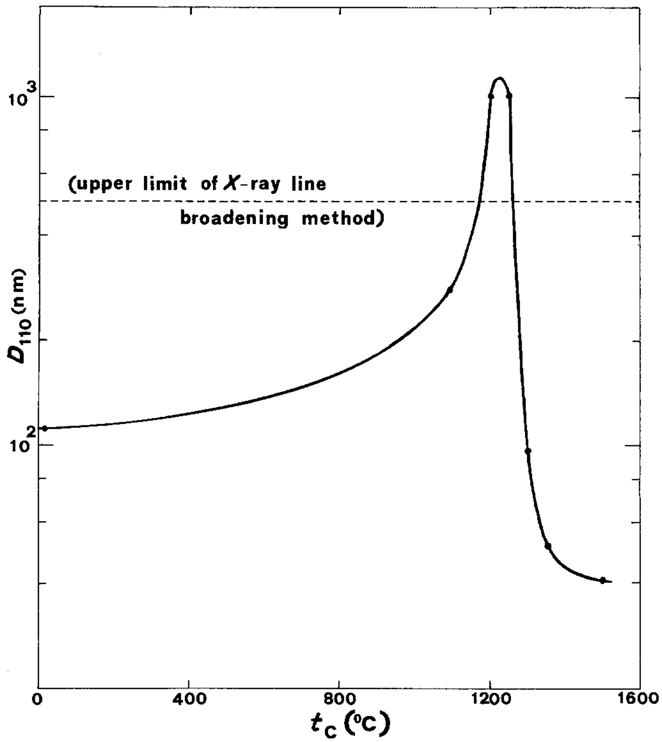

Figure 1 Average sizes of the mullite crystallites (as determined by the Scherrer method from the (110) peak broadening) as a function of the chamotte annealing temperature. All the samples have a chamotte percentage of 50% and a final firing temperature of 1600° C. For the values greater than 500 nm, the smallest dimension of the needle-shaped crystallites (as observed by SEM) has been used.

whereas mixes containing anhydrous alumina produce the opposite effect (p(M)/p(V) close to 1.0). Furthermore, crystallite sizes in this second case remain markedly lower than in the first. This behaviour can be attributed to the higher reactivity to high temperatures of alumina hydrate as opposed to corundum.

Fig. 2 shows the SEM pictures of our substrates annealed at 1600° C and containing 50% of chamotte calcined at 1200° C, in (a) without treatment, and in (b) after removal of the superficial silicatic vitreous phase by chemical etching for 1.5 min in hydrofluoric acid at 49%.

The Coors product shows less developed mullite crystallites and a proportion of vitreous phase decidedly higher than the "ideal" value (also revealed by the SEM pictures in Fig. 2c. The IRTEC–CNR product, on the other hand, shows the opposite tendency, that is to say, there is a greater proportion of mullite than is deduced from the simplified reaction 1 (see Fig. 2d).

It should be noted that the best samples we prepared by dry-pressing have a bending tensile strength σ_F from 60 to 70 MN m^{-2} and a polycrystalline elastic (or Young's) modulus E from 80 to 90 GN m^{-2} [1].

In comparison, the Coors Porcelain products have a $\sigma_F = 95$ to 100 MN m^{-2} and $E = 115$ to 125 GN m^{-2}.

The σ_F/E ratio, which, provided there is a substrate thermal expansion coefficient in fair agreement with that of silicon up to 800° C, is proportional to thermal shock resistance, turns out to be around 0.76×10^{-3} for our samples, 0.54×10^{-3} for the American products made by roll-compaction and around 1.0×10^{-3} for those obtained by casting on belt.

It seems therefore that the substrates obtained by the simple and cheap method of dry-pressing do have a markedly lower bending tensile strength compared to ones produced with more sophisticated technologies, but they make up for this "defect" of lower resistance to thermal shock with their lower rigidity (decidedly lower Young's modulus).

From the morphological point of view, it may be added, one can see from Figs. 2a and b that our samples show a well developed three-dimensional network of needle-shaped mullite crystals, with the interstices "cemented" by the silicatic vitreous phase.

Since it is recognized that both E and σ_F clearly depend on the porosity of the sample (the latter in particular), for they both decrease in proportion to the increase in porosity [7] (porosity levels needed to halve these values compared to pore-free values are normally around 30% for E and 10% for σ_F), it emerges that, apart from the proportions of

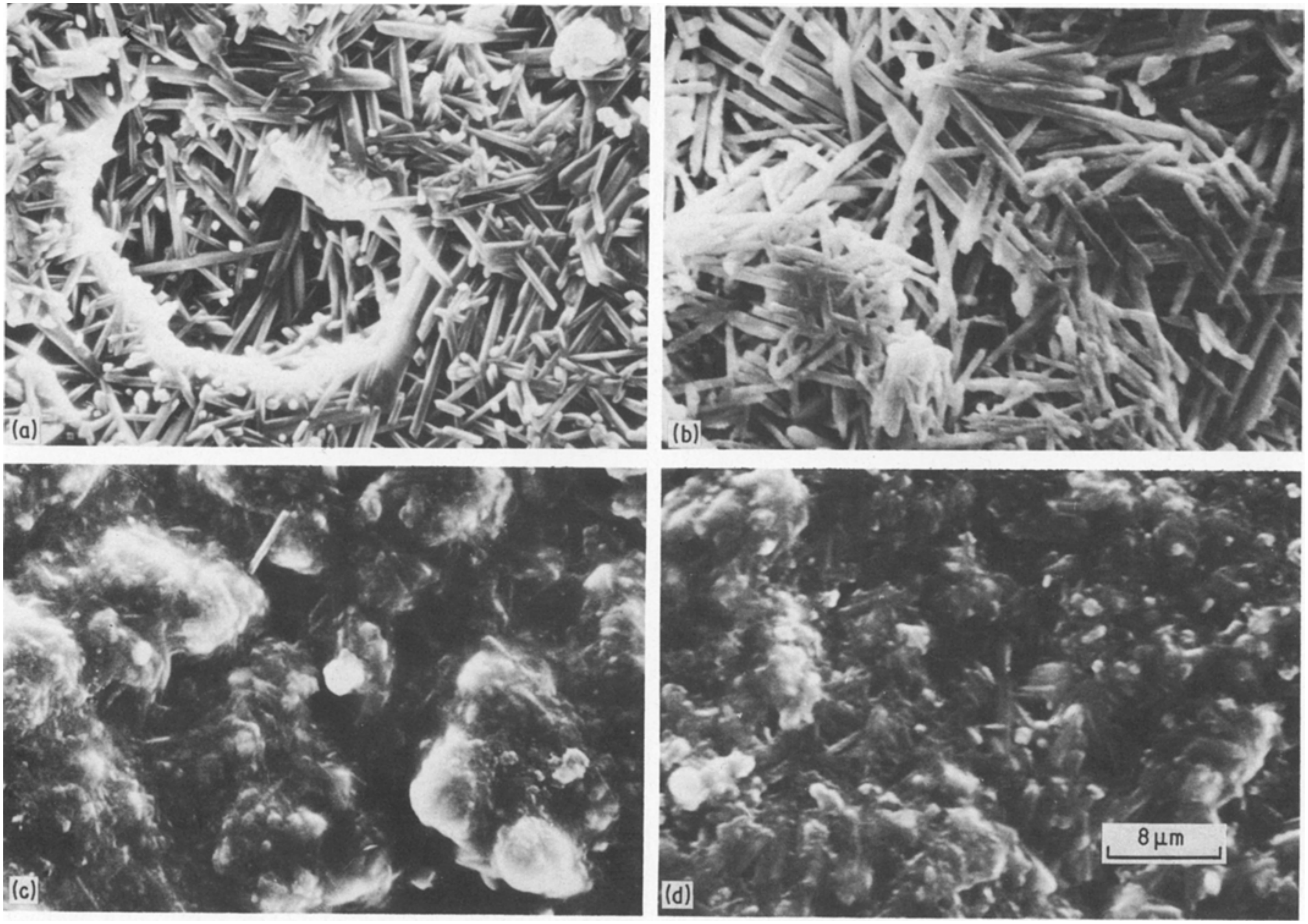

Figure 2 Some mullitic substrates after metallization with a gold thin film, as observed by SEM. (a) Our sample obtained by dry-pressing (50% chamotte at 1200° C); (b) the same after etching with 49% HF for 1.5 min; (c) Coors Porcelain sample obtained by roll-compaction; (d) IRTEC–CNR sample obtained by casting on belt and "doctor blade shaping".

mullite and silicatic vitreous phase (for mullite $E = 138\,\mathrm{GN\,m^{-2}}$ and $\sigma_F = 170\,\mathrm{MN\,m^{-2}}$, while for vitreous silica $E = 72\,\mathrm{GN\,m^{-2}}$ and $\sigma_F = \mathrm{MN\,m^{-2}}$), porosity itself is the third determining parameter as regards mechanical properties.

Another property that strongly influences σ_F is the average size of the grains, to which σ_F is in inverse proportion. Bearing in mind the two compositional parameters (proportion of mullite and vitreous phase) and the two morphological ones (porosity and average sizes of the grains), the different mechanical properties encountered in substrates obtained by different moulding methodologies are fully justified.

In any case, it is obvious that, even using a simple, low-cost preparation technique such as dry-pressing, it is possible to obtain finished products with mechanical and thermal characteristics that compare well with those typical of more sophisticated and more expensive forming techniques. It is well worth adding that the dry-pressing forming technique is fairly suitable for the transition from the laboratory scale to industrial-scale production and thus offers a valid alternative to the other methods of manufacturing ceramic substrates for polycrystalline silicon to be used in the photovoltaic applications.

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