



Effect of binder's size and chemistry on pure aluminium-oxide vacuum formed ceramic fibre boards

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ARTICLE INFO

Handling Editor: Dr P Colombo

Keywords:

Refractory fibre board
Aluminium oxide fibre
Ceramic vacuum-forming

ABSTRACT

Pure aluminium oxide vacuum-formed fibreboards were obtained from new generation of alumina fibres synthesized by the sol-gel method. The effect of the chemical composition and the particle size of the binder on the vacuum-formed boards was examined. High-temperature testing took place at 1500 °C for 24 h. The mechanical properties (both modulus and compressive strength) are better with Boehmite than with aluminium hydroxide. Decreasing the size of the binder particles enhances these mechanical properties. Field emission scanning electron microscopy was used to study the micro-scale morphology. Well-developed crystals can be found in both the fibres and binders, regardless of the binder system used, after the prolonged high-temperature treatment. The smaller binder particles cause decreased crystal size. The most stable α -aluminium oxide phase was identified by XRD in all systems.

1. Introduction

High-temperature insulation materials are mostly used in industrial applications such as metal, ceramics and glass production, chemical and petrochemical industries and power generation. Refractory fibre furnace linings in these industries are essential for minimizing energy consumption and greenhouse gas emissions.

Insulation materials can be characterized by a heat transfer coefficient of less than or equal to 0.2 W/mK [1]. Ceramic fibre materials possess high thermal insulation properties due to their high porosity (greater than 45%) [2]. Conventional refractory bricks that have good heat resistance, but poor thermal insulation, are now being replaced by high-performance insulators, i. e. alumina fibre and wool [3]. Refractory fibre materials can be produced using wet forming process [4], gelation of slurry [5], or vacuum-forming [6] methods.

Alumina-based continuous fibres can be used as refractory insulators up to 1600 °C and are synthesized by sol-gel processes [7,8]. Compared to other refractory fibre insulation materials alumina fibre products exhibit better thermal insulation at higher temperatures: alkaline earth silicate fibres can only be used up to 1200 °C [9]. Using polycrystalline alumina fibres thermal insulation at 1800 °C can theoretically be achieved [10].

To control the nucleation and growth of the alumina grains and the porosity of the product silica precursors or α -alumina seeds can be added to the fibre precursors. The presence of silica, however, leads to reduced Young moduli, creep strength lowered application temperature [11].

Commercially available α -alumina fibres include FP by Du Pont, Almax by Mitsui Mining, and Nextel 610 by 3 M [11].

Moulded bodies can be produced in one step using vacuum-forming, which makes the process cost-effective. The slurry applied for vacuum-forming processes consists of ceramic fibre, suitable binders, and water ([12]. During the vacuum-forming method cut fibres are suspended in a slurry containing inorganic (e. g. Boehmite) or organic (e. g. starch) binders [13]. The suspension is then conveyed into a moulding form where it is compacted by the force exerted by the vacuum. Vacuum is used to remove water and trap the solid ceramic fibre in the mould. After demoulding and drying a ceramic fibre moulded body is produced [14]. The driving force for the removal of liquid through the permeable mould can be increased up to five times by applying vacuum [15].

The rheology of the used suspension depends on the fibre and binder concentrations and the pH of the slurry. Viscosity must be adjusted to achieve good vacuum-pressure infiltration [16]. Significant process variables affecting product mass are vacuum forming time and oven temperature [17]. The process can also be called vacuum casting [18].

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<https://doi.org/10.1016/j.oceram.2024.100553>

Received 27 November 2023; Received in revised form 19 January 2024; Accepted 6 February 2024

Available online 7 February 2024

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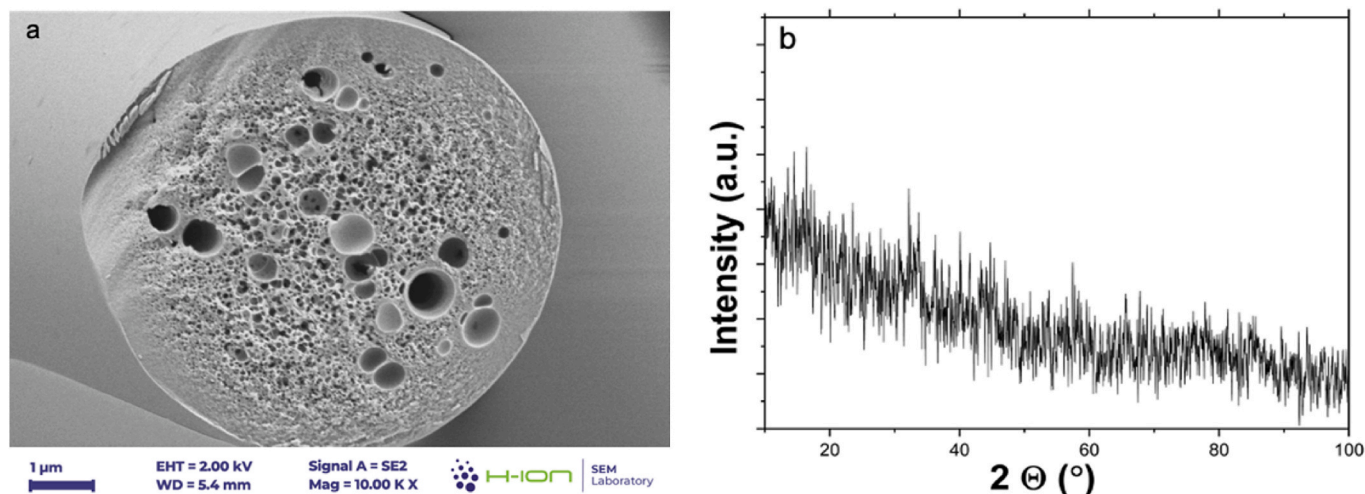


Fig. 1. SEM micrograph and X-ray diffractogram of used aluminium-oxide fibres.

To prevent tangling of fibre and to guarantee homogeneous distribution flocculants may be used. It is crucial to use flocculants in the required quantity and quality to prevent inorganic residue in the final product after thermal treatment [19].

To maximize heat resistance, addition of non-aluminium based binders should be avoided. It has been reported that Boehmite (AlOOH) or nano-scale aluminium hydroxide in addition to aluminium chlorohydrate could be used as binders in our slurries. Aluminium chlorohydrate is a chemical bonding agent, it is used to form strong chemical bonds between the castable constituents [20]. The binder composition forms a gel thus preventing migration during the forming and drying process.

2. Experimental

2.1. Synthesis

The sample preparations were based on the recipe of [21], binder materials were varied from sample to sample. Pure alumina fibres were synthesised by sol gel process. The used method described previously [7, 22]. The fibres have a Gaussian distribution with a diameter ranging between 3 and 10 μm . The used fibres are porous, the pore size varied between 5 and 500 nm (Fig. 1). Most of the pores are below 100 nm. The porosity determined from the SEM is 50–60%. At the end of sol-gel process 500 $^{\circ}\text{C}$ was used to convert sol-based fibres to ceramics. At that temperature, crystallization does not take place, thus fibres are amorphous (Fig. 1). The as prepared fibres were chopped before use. The gap between the choppers' blades was 10 mm; therefore, the estimated length of the fibres is also 10 mm (see Fig. 2).

Firstly, chopped alumina fibres were dispersed in water with

continuous stir by turbo stirrer at 1500 rpm, then binder was added in small portions. 4 different binders were used: i) pseudospherical Boehmite (B) with particle size 90–130 μm (Dequachim) and aluminium hydroxide with 3 different particle size: ii) large-size 90 μm (OH90, Merck), iii) medium-size 6.5 μm (OH6, VWR) and iv) a small-size 6–18 nm (OH01, nanografi) respectively.

Poly Aluminium Chloride (PAC) was used additionally as a flocculant. pH was adjusted by concentrated hydrochloric and sulphuric acids. The concentrations were kept 0.15 g/ml to fibre, 0.27 g/ml to PAC solution, 0.01 g/ml to hydrochloric acid and 0.005 g/ml to sulphuric acid, respectively. The whole suspension was stirred for another 15 min then separated into 6 even batches. The small portions then were poured into 3D printed moulds with 50 mm by 25 mm cross section. The bottom of the mould was made from 100 μm mesh. Vacuum pump (Vacuubrand MZ 2C NT) with 7 mbar end vacuum was applied for remove the liquid between the fibres. The filtrate was collected for further examination. The vacuum-formed samples were dried at 80 $^{\circ}\text{C}$ for 1 h and then dechlorinated at 260 $^{\circ}\text{C}$ for 12 h in a convection drying cabinet (POL-ECO SLW 32 smart). After 260 $^{\circ}\text{C}$ treatment samples are ready for characterization. Figure 2 shows the schematics of the whole preparation process.

2.2. Characterization methods

Dimensions of the pre- and post-heated samples were measured by digital calliper type Mitutoyo 500-181-30. Weights were measured by Mettler Toledo ME4002 digital scale. Average density was calculated from the measured weight and dimensions of the samples. Mechanical properties were tested United Test WDW-100Y-SW universal testing machine. The deformation speed was 1 mm/min. Parameters were set

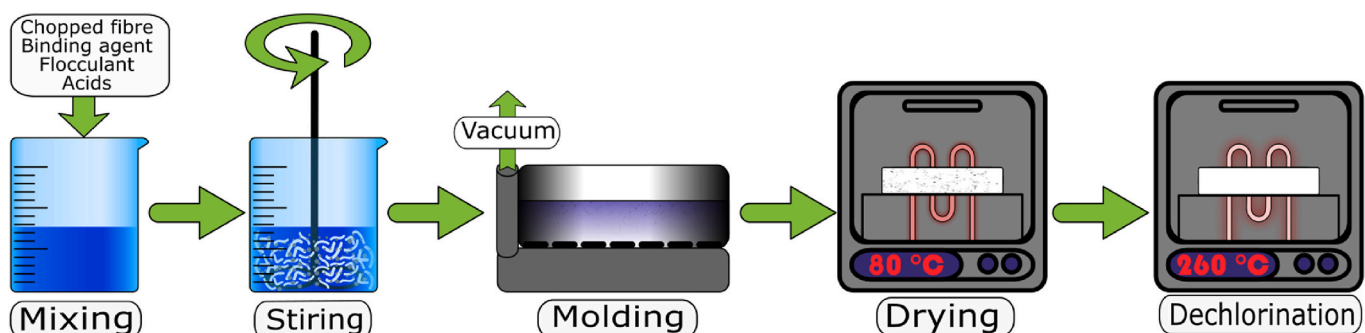


Fig. 2. Schematics of the sample preparation.

Table 1
Density, shrinkage and weight loss data.

Sample	Green ρ	Brown ρ	$\Delta\rho$	Δx	Δy	Δz	Δm
	kg/m ³	kg/m ³	%	%	%	%	%
B	298 ± 19	426 ± 10	45.8 ± 13.3	14.8 ± 1.9	15.1 ± 3.0	18.1 ± 2.2	13.9 ± 1.7
OH90	227 ± 19	303 ± 28	34.0 ± 3.3	14.1 ± 0.1	14.7 ± 1.4	14.8 ± 0.5	16.3 ± 0.6
OH6	206 ± 9	282 ± 14	39.5 ± 0.7	14.5 ± 1.0	14.9 ± 0.5	15.9 ± 1.6	14.7 ± 0.7
OH01	227 ± 6	313 ± 7	36.1 ± 2.9	15.0 ± 0.4	14.8 ± 0.4	15.1 ± 2.1	16.4 ± 0.6

*Green ρ and Brown ρ are the density before and after the heat treatment. $\Delta\rho$ is the density change. Δx , Δy , Δz is the change in length, wide and hight, respectively. Δm is the weight loss during the heat treatment.

based on ISO 10059–1:1992. Compressive strength was defined as $\sigma = \frac{F}{A}$ where σ is the strength, F is the applied load and A is the area of the examined sample. Young modulus was defined the slope of the line fitted at the beginning of the stress-strain curve.

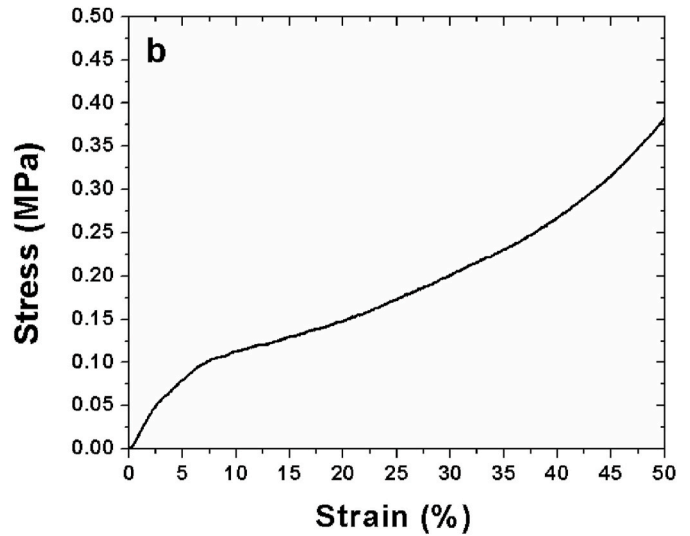
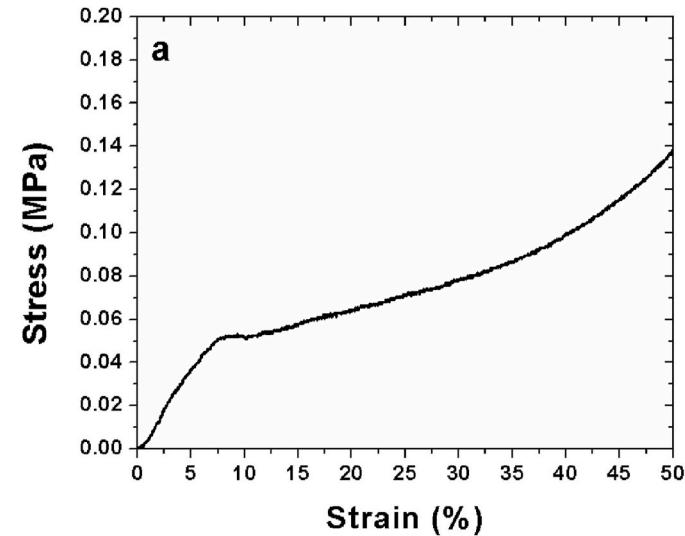


Fig. 3. Two types of stress-strain curves: with (a) and without (b) of local maximum.

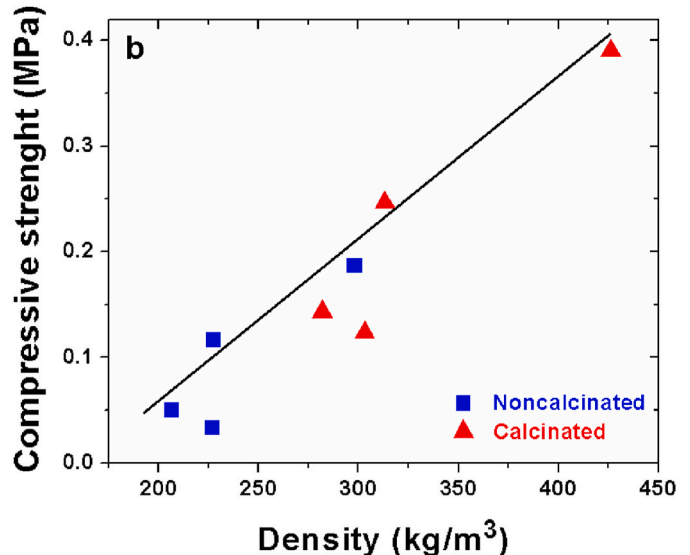
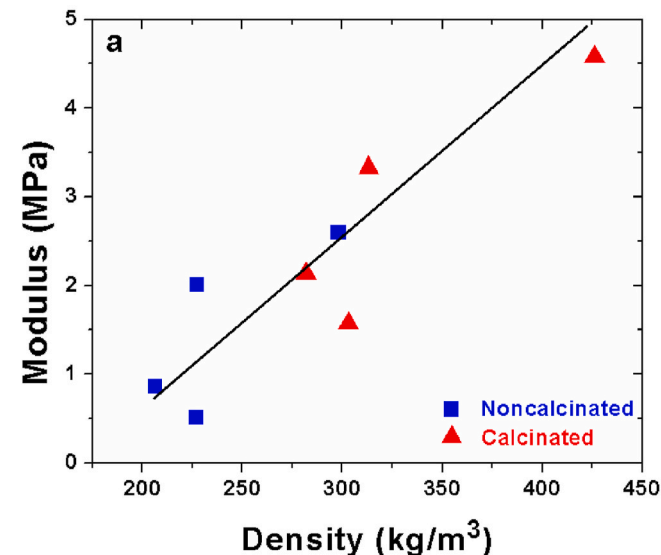


Fig. 4. Modulus (a) and compressive strength (b) vs density (lines for guide for eyes).

Shrinkage was tested by a 24 h, 1500 °C heat treatment in a Denkal 1550 furnace. Heat up ramp was 750 °C/h and after the heat treatment finished, natural cooldown was allowed. Dimensions and weight were measured before and after the heat treatment, then shrinkage and weight loss were calculated.

Crystal phases were identified by powder X-Ray Diffraction (XRD). The XRD patterns were obtained in the range $2\theta = 10\text{--}100^\circ$ with Bruker D8 advanced X-ray apparatus using Co K α radiation.

Scanning electron micrographs were taken by a Zeiss Sigma 300 Field Emission Scanning Electron Microscope (FESEM). All magnification compared to Polaroid 545 reference. Micrographs was evaluated by ImageJ version 2.0.0. Size of fibres and crystals was manually measured after calibration.

3. Results and discussion

Following the vacuum-forming, the samples became shape-retaining with a rough surface. The drying and dechlorinating process conserves the appearance of samples. The samples can be prepared reproducibly, with a height variation of 4–6%. The difference between samples

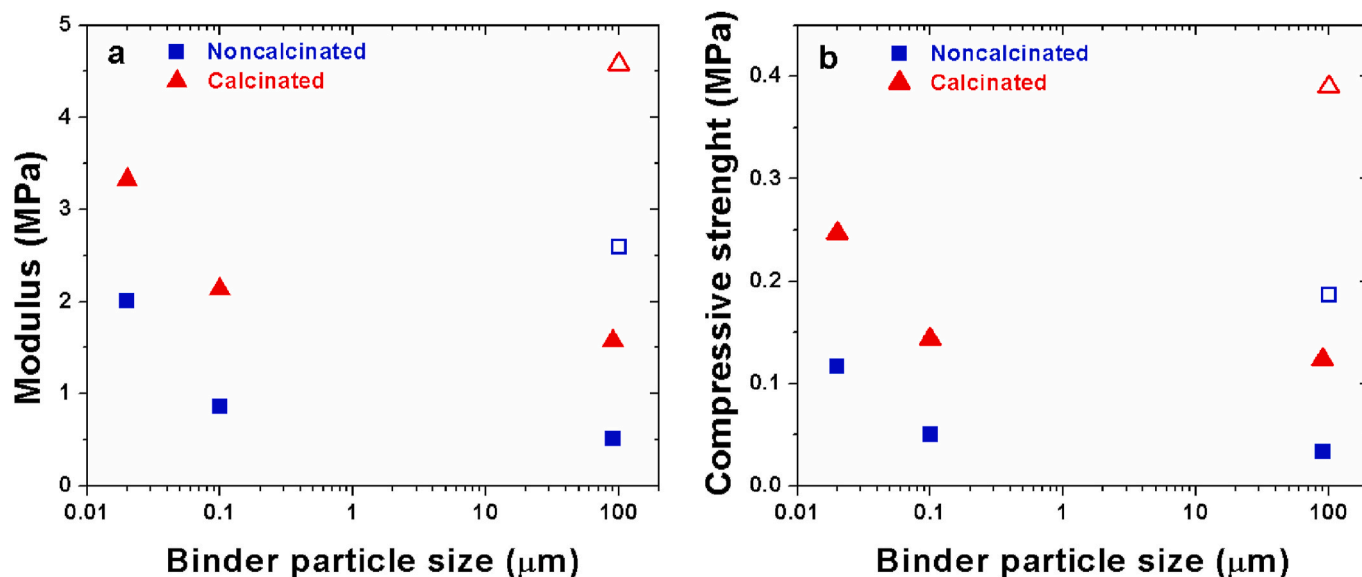


Fig. 5. Modulus (a) and compressive strength (b) vs binder particle size. Hollow markers represent samples with Boehmite.

prepared with different binding agents is substantially greater than the variation observed among parallel samples. The recipe defined the density of samples. The obtained densities do not correspond proportionally to the particle size of the applied binding agent.

After the high temperature heat treatment shrinkage and weight loss were determined. After being removed from the furnace following a 24-h heat treatment, all samples were intact, no cracks were observed. There were no signs of disintegration or dust from sample.

However, on samples that have a rectangular shape, isotropic shrinkage can be observed. All dimensions became approx. 15% shorter, measured differences are insignificant (Table 1). Although there are significant weight losses were detected, the densities of the samples are greatly increased due to the high temperature heat treatment.

In terms of application, mechanical properties have a great significance. Our fibrous composite materials have pseudo elastic behaviour due to their unique loosely connected net-like structure. In this work two types of curves were observed: i) strictly monotonically increasing pseudo elastic curve (typically samples before heat treatment) and ii) pseudo elastic curve with local maximum (typically samples after heat treatment). In case of latter, compressive strength values were determined as the local maximum value. Even in cases where the curve strictly monotonically increases, an inflection point can be observed in Fig. 3. The compressive strength values were approximated by numerically determining the inflection points.

Both modulus and compressive strength depend on density (Fig. 4). The denser samples are stronger and have higher modulus. Both values increased by the heat treatment. The modulus and compressive strength values of the calcined samples are approximately twice as high as those of the green samples.

Regardless of the sample condition (calcined or green), the values are directly proportional to the density.

The modulus and compressive strength of the samples varies between 0.5–4.5 Mpa and 0.04–0.4 Mpa, respectively and presented in Fig. 4. This latter is comparative to the typical value of commercial high alumina content (>97%) fibre boards (between 0.1 and 1 Mpa [23–25]).

It was found that the mechanical properties have a strong dependence on the applied binder system as can be seen in (Fig. 5). Comparing the samples with different chemical composition, Boehmite containing samples perform better as the highest modulus and compressive strength values were obtained with these samples. When comparing the three aluminium-hydroxide containing systems, the trends consistently align. Reducing the particle size significantly improve both the modulus and

compressive strength. This phenomenon is already known in case of bulk ceramics [26,27]. It has also been reported, that mechanical properties are more sensitive to the density than grain size of ceramics [26]. Samples prepared with Boehmite have higher density, probably that suppresses the size effect.

The micro-scaled morphology was examined by FESEM (Fig. 6). Inhomogeneities along the cross-section scanning were found in every samples. On the side closer to the filtering surface, a greater quantity of binding agent was observed between the fibres compared to a larger distance from the surface. This phenomenon probably arises from the laboratory scale dead-end filtration-like sample preparation. This effect was not observed our previous works with inhouse pilot vacuum-forming system, however, the recipe was not exactly the same. In the case of Boehmite containing samples, coagulant with almost exclusively smooth surface can be seen between fibres. Only a few (2–3 pieces) Boehmite particles were identified in the examined cross-section with approx. 60 mm² area. Based on our calculation as described in the supplementary section, the average particle density should be 6.7 particles/mm².

During the filtration, the applied mesh size was 100 μm. Apart from the filtering effect of the fibres, this could allow a significant portion of smaller size Boehmite to pass through, possibly causing the weight reduction. In order to investigate this weight loss, the sample preparation filtrate was collected. Several drops of filtrate were prepared onto a mica, dried and examined by FESEM. The remaining filtrates were then vacuum dried and solid contents were calculated. The solid content of the filtrate was 9.4%, 7.0%, 9.3% and 9.8% in case of B100, OH90, OH6 and OH01 samples, respectively. The values are similar, the OH90 samples contain a bit more binder mixture, then others.

The FESEM observations were similar to those with the prepared samples: in the case of aluminium hydroxide containing samples, many embedded particles are present within the flocculant, while in case of Boehmite containing sample very few particles are found. The conditions present in the filtrate are not conducive to the dissolution of Boehmite [28]. This was experimentally confirmed by mixing Boehmite, hydrochloric- and sulphuric acid in water and properly stirring it. After even 24 h there was no sign of dissolution of the particles. It could be possible that during synthesis process, the Boehmite particles accumulate at the bottom of the composite board and detach from the surface while sample was prepared to FESEM. Lack of Boehmite particles may contribute to the higher density of the samples. Since there are very few particles among the fibres, they can be positioned closer together,

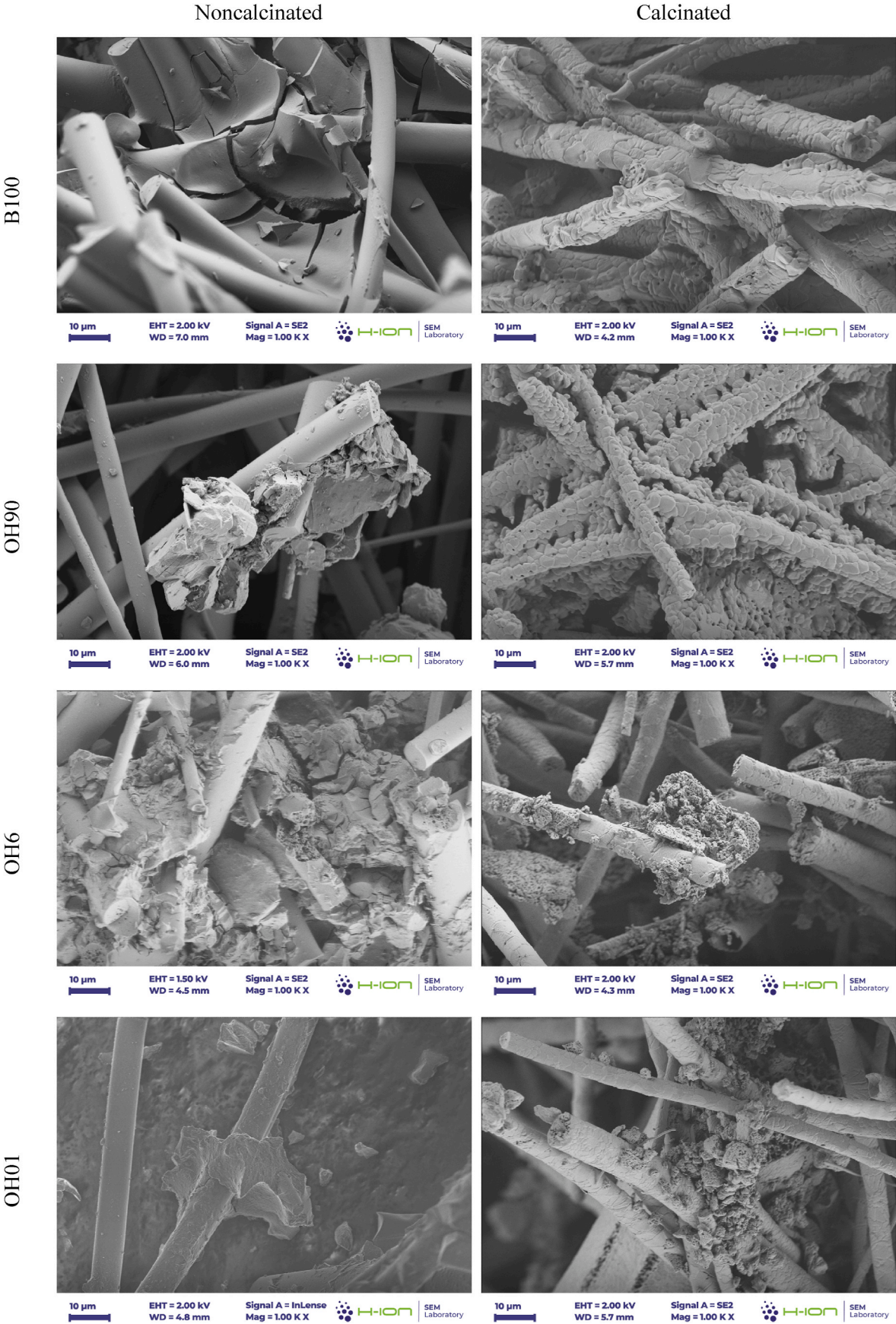


Fig. 6. FESEM micrographs of noncalcinated and calcinated samples.

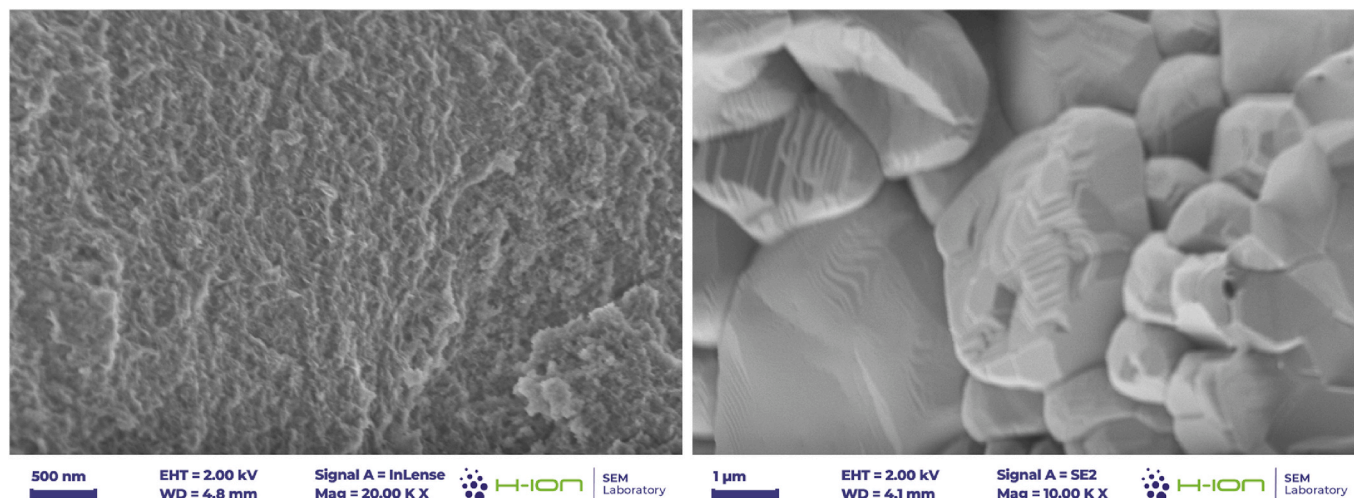


Fig. 7. Detailed FESEM micrographs of noncalcinated and calcinated samples.

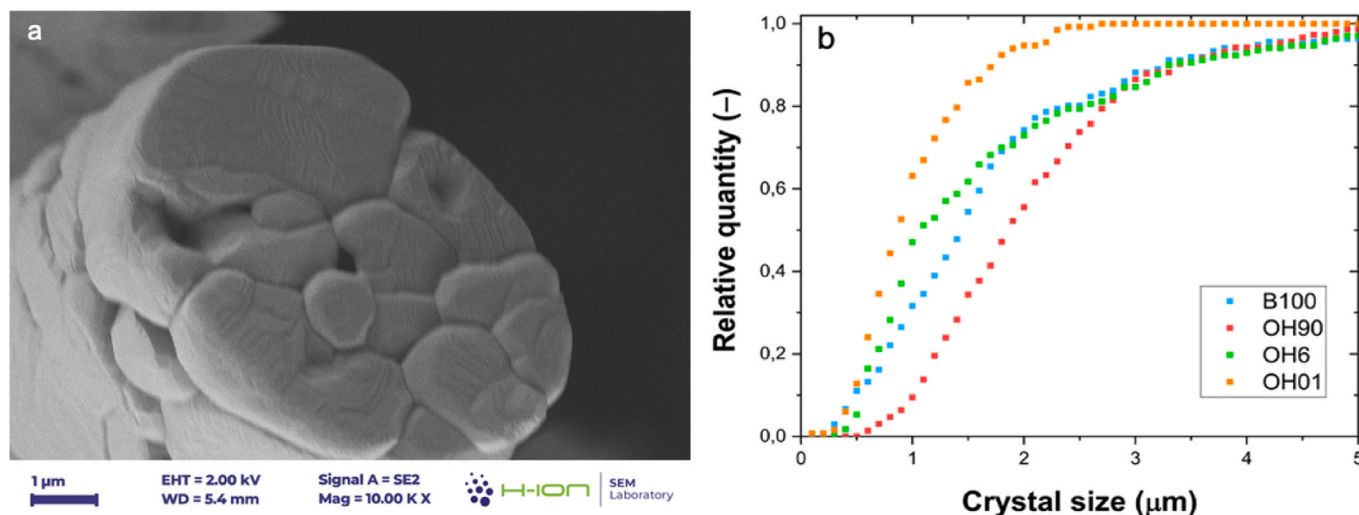


Fig. 8. Cross section of crystallized fibre (a) and size distribution of crystals measured from FESEM images.

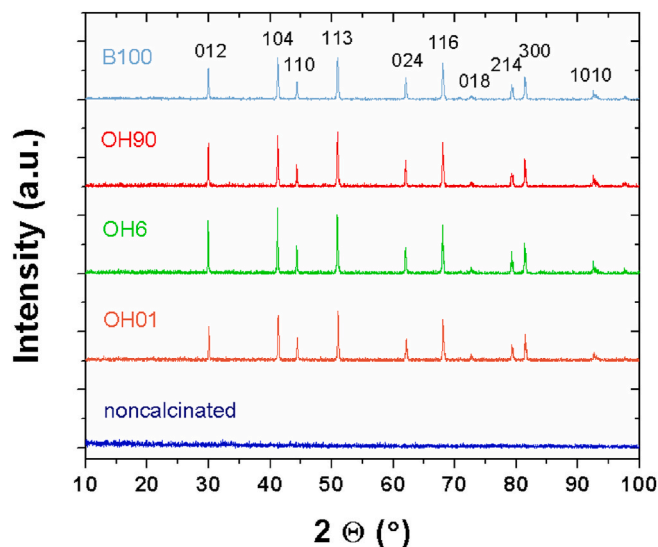


Fig. 9. X-ray diffractograms of vacuum formed samples.

leading to a denser system.

The 24 h long 1500 °C heat treatment indicates crystal growth: the binder particles disappear and both fibres and binder system show well developed crystals (Fig. 7).

Samples with smaller particle size binders, the size of the crystallized particles that formed is smaller. The crystal size observed with SEM is smaller when using nano-powder binder compared to micron-sized binder (Fig. 7). The average crystal size is half as large in the case of OH01 compared to OH90 (see Fig. 8).

During heat treatment, the nucleation stage is controlled the particle size, the surface of the particles acting as nucleation sites. The smaller the particles, the larger the surface area and the higher the number of nucleation sites [29]. The higher number of nuclei at the same time causes smaller crystals.

Based on FESEM images, the porosity of the fibres decreased but did not completely disappear. The original nano-size porosity of fibres is vanished, but in some places, new pores formed at the grain boundaries of the crystals (Fig. 8).

The crystal phase was examined by powder XRD. In case of samples without heat treatment peaks were not found in the diffractograms (Fig. 9). Probably the amorphous components (e.g.: fibres, flocculant) suppress the signal of binders. In great accordance with the SEM results all calcinated samples possess diffractograms with sharp peaks and all

samples have the same pattern. Crystal phase was identified as α -aluminium oxide, which is the most stable phase in the temperature range $>1300\text{ }^{\circ}\text{C}$ [30]. If XRD patterns are corrected with difference between the Co K α and Cu K α radiation, there have a perfect match to the JCPDS standard card NO.43–1484.

4. Conclusions

Pure aluminium oxide vacuum-formed fibre board samples were successfully prepared by different binding agents. Boehmite with 100 μm and aluminium-hydroxide with three different particle size (10 nm, 6,5 μm , 90 μm) were used as binder materials. Aluminium chlorohydrate was additionally used as flocculant. Samples were tested at high temperature (1500 $^{\circ}\text{C}$) for 24 h. During the heat treatment, samples shrink isotropically.

The mechanical properties (both modulus and compressive strength) are comparable commercially available boards. The measured mechanical data are proportional to density. In the view of chemical composition, Boehmite containing samples performs better. In case of aluminium-hydroxide containing samples, the size of the used binder particle affects the mechanical properties. The smaller particles result better mechanical and thermal performance.

The micro-scale morphology was studied by field emission scanning electron microscopy. In contrast to other samples only a few binder particles can be found in case of Boehmite containing boards. Calcinated samples show well-developed crystals. Both fibres and binder mixture become crystalline. The smaller binder particle size results smaller crystal size. The crystal phase was identified as α -aluminium oxide in all cases.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

We express our gratitude to R. Fekete to his technical support. The financial support of Hungarian Ministry of Finance and the European Union (grant number GINOP-2.1.2-8-1-4-16-2019-00907) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oceram.2024.100553>.

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