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Manufacturing of porous mullite fiber compacts by uniaxial hot-pressing of semi-crystalline MAFTEC® MLS-2 organic bound mats

Peter Mechnich*, Ferdinand Flucht, Martin Schmücker

German Aerospace Center (DLR)

Institute of Materials Research

51147 Köln, Germany

*corresponding author; e-mail: peter.mechnich@dlr.de

Abstract

Highly porous and fully crystalline mullite fiber compacts were fabricated by uniaxial hot-pressing of stacked short-fiber mats without binders or sintering aids. The special feature of this new fabrication method is the use of MAFTEC® OBM type fiber mats consisting of semi-crystalline “MLS-2” short fibers. In contrast to conventional, polycrystalline mullite fibers semi-crystalline MLS-2 fibers are consisting of amorphous silica and nanoscale transitional alumina. Due to this special microstructure MLS-2 fibers are less prone to fiber breakage upon shear load, therefore are well withstanding pressure-assisted consolidation. Hot-pressing of stacked OBM to highly porous fiber compacts is facilitated by the thermally driven softening of amorphous silica above 900°C, favorable deformation and consolidation rates are achieved above 1050°C. Above 1250°C mullite is crystallizing at the expense of amorphous silica, simultaneously deformation and consolidation comes to an end. Obtained MAFTEC OBM-derived fiber compacts only consist of crystalline mullite, therefore mechanical properties are favorably retained at high temperatures.

Introduction

Mullite represents a family of aluminosilicates having the general formula $Al_2(Al_4+_{2x}Si_{2-2x})O_{10-x}$. The most prominent and technologically important members of this solid-solution series are mullites with x=0.4 resulting in the composition Al_4SiO_8 or $2Al_2O_3•SiO_2$ (“2/1-mullite”) and mullites with x=0.25 resulting in the composition $Al_6Si_2O_{13}$ or $3Al_2O_3•2SiO_2$ (“3/2-mullite”). 2/1-mullites typically form in fusion-quench processes and are considered long-term stable only at high-temperatures (>1800°C). 3/2-mullites form in solid-state reactions and are considered long-term stable below 1800°C. Due to an outstanding combination of low thermal expansion and thermal conductivity, high creep resistance, and good strength and fracture toughness 3/2-mullites are frequently employed as structural ceramic materials for high temperature applications. Many studies on structure-property-relationships and applications of mullite are available, for example see references [1,2,3]

Due to its favorable high-temperature properties mullite is also an attractive material for continuous fibers which are employed as ceramic textiles or reinforcement of ceramic matrix composites. Alternatively to continuous fibers, mullite-based short fibers are usually employed as felts or blankets. Short fiber-based components exhibit high gas permeability as well a high inner surface area, consequently are also attractive as effective filters or catalyst carriers in hot and corrosive atmospheres such as exhaust gases. Due to their high chemical stability and low thermal conductivity, such blankets are well suited for low-weight thermal insulation materials for industrial applications.[4] Currently, similar short fiber materials are gaining attraction also as aerospace materials. The use of short fibers as structural materials, however, requires additional mechanical stabilization with the help of inorganic fillers or “rigidizers”, frequently consisting of liquid siliceous sols or dispersions which are infiltrated in to the fiber network, dried, and thermally solidified [5-15].

In recent years, special polycrystalline 3/2-mullite short fibers for long-term high-temperature applications in corrosive environments have been developed. These mullite fibers are chemically pure (72 wt-% Al_2O_3 and 28 wt-% SiO_2), have low shot content and a narrow fiber diameter distribution in the range between 5 and 7 μm. [16] Currently such mullite fibers are distributed by Mitsubishi Chemical Corporation (formerly Mitsubishi Plastics Inc.) under the trade name “MATFEC® MLS-2”. In contrast to other silica-rich, aluminosilicate short fibers MATFEC® MLS-2 exhibit good creep resistance and low shrinkage. MAFTEC MLS-2 fiber felts are typically needled in order to produce blankets exhibiting favorable tensile strengths. These blankets can easily be shaped, for example into insulating panels for furnace linings. A further important application for MAFTEC fibers is the durable support of automotive catalytic converters or diesel particulate filters [17]. For this purpose, needled MAFTEC MLS-2 fiber mats are additionally stabilized by organic binders. These so-called organic bound mats (OBM) are then wrapped around the catalyst or filter monoliths before mounting in their metal casings.

A special feature of MAFTEC OBMs is the fact that MLS-2 fibers are still semi-crystalline, consisting of nanoscale transition Al_2O_3 and amorphous SiO_2. This nanoscale microstructure is favorable in terms of fiber strength and is considered a key to the good shaping capability and long-term durability of MAFTEC OBM support mats. Moreover, diphasic alumosilicates are well known in the field of mullite ceramics processing technology. In order to overcome the low sintering activity of crystalline mullite powders, non- or semi-crystalline “chemical” mullite precursors with much better sintering behavior are being developed for many years. Many variants of mullite precursors, having different homogeneity levels and related crystallization temperatures, have been reported in literature [16]. Two basic types of mullite

precursors are commonly discerned: single-phase mullite precursors show chemical homogeneity up to the atomic level and crystallize directly to mullite at temperatures as low as approximately 950°C. Diphasic mullite precursors consist of nanoscale transition alumina phases (e.g. spinel-type γ-Al_2O_3) coexisting with non-crystalline, silica-rich phases. Due to the chemical reaction of both phases metastable, Al_2O_3-rich mullite (approximately 2/1-composition) forms at temperatures above 1200°C. At higher temperatures, metastable primary 2/1-mullite gradually transforms into stable 3/2-mullite. Following this basic classification, semi-crystalline MLS-2 fibers can be designated as fibrous, diphasic mullite precursors in “3/2”-mullite overall stoichiometry. The crystallization behavior of diphasic precursors gave rise to the assumption that non-crystalline SiO_2 may coexist in semi-crystalline MLS-2 fibers in a wide temperature range, hence may offer densification and sintering by viscous flow. In this work we demonstrate the uniaxial hot-pressing of MAFTEC-OBMs without conventional sintering aids such as siliceous rigidizers. The resulting highly porous and fully crystalline mullite fiber compacts promise superior high-temperature strength and creep resistance. A similar manufacturing approach was previously introduced in the authors’ laboratory, where stacked woven mullite-based, Nextel® 720 type fiber fabrics were employed to fabricate “matrix-free” composites by uniaxial hot-pressing [18]. In the present work we explore a processing window by taking advantage of the semi-crystalline, diphasic fiber microstructure of MAFTEC MLS-2 OBMs.

Experimental Procedure

MAFTEC MLS-2 organic bound mats (OBM) with a chemical composition of 72 wt% Al_2O_3 and 28 wt% SiO_2 were kindly provided by Mitsubishi Plastics Europe (now Mitsubishi Chemical Europe GmbH, Düsseldorf, Germany). Detailed information on properties and applications of MAFTEC-type fiber products is available on the company's website [19]. All experiments were performed with circular disks (h=8 mm) which were punched out of as received MAFTEC OBM mats with a hole-puncher. Dilatometry experiments were performed on single disks (d=25 mm) in a vertical arranged and inductively heated test system (ZMART.PRO, Zwick-Roell, Germany). Large specimen were fabricated by stacking six disks (d=70 mm) and subsequent uniaxial hot-pressing in a $MoSi_2$-heated chamber furnace (Thermal Technology, Bayreuth, Germany) using two cylindrical sintered silicon carbide dies (SiSiC, EkaSiC, ESK, now 3M Technical Ceramics, Kempten, Germany) also having a diameter of 7 cm. Further heat treatments were performed in a SiC-heated chamber furnace (HTC 03/15, Nabertherm, Lilienthal, Germany. Phase evolution was studied by differential scanning calorimetry (DSC) in an STA 449 F3 Jupiter (Netzsch, Selb, Germany) and by X-ray powder diffraction (XRD) (Siemens D5000, CuKa radiation, secondary graphite monochromator, EVA/Topas 4.2 software package, Bruker AXS, Karlsruhe, Germany). Microstructural analyses were performed in a DSM Ultra 55 scanning electron microscope (Carl Zeiss NTS, Wetzlar, Germany). The mechanical characterization of hot-pressed specimen was performed in the ZMART.PRO universal test system.

Results and Discussion

Phase evolution and deformation behavior of MAFTEC MLS-2 OBM

In general polycrystalline mullite fibers and mats are prone to fiber breakage upon mechanical load. Indeed, chopped fibers can be simply produced from fully crystalline mullite fiber mats by uniaxial pressing at room temperature. Fiber cleavage occurs at fiber contact points where mechanical stresses are concentrating. The fibers of MAFTEC-OBM mats, however, are consisting of non-crystalline SiO_2 and nanoscale transitional Al_2O_3, therefore are considered to offer a priori higher mechanical strength. Moreover, their semi-crystalline microstructure with amorphous SiO_2 present is supposed to provide plastic deformation at high temperatures, avoiding extensive fiber damage during uniaxial hot-pressing. It was therefore anticipated that hot-pressing of MAFTEC OBM mats can be performed prior to mullite crystallization. Consequently, detailed knowledge on the phase evolution of MLS-2 fibers is considered a key to a successful and optimized manufacturing process.

The fundamental crystallization behavior of MLS-2 fibers was elucidated by XRD-analysis before and after annealing for one hour at 1200, 1250 and 1300 °C, respectively (fig. 1). As received fibers exhibit the typical broad XRD peaks of transitional Al_2O_3 and the characteristic “amorphous hump” between 18 and 25° 2-theta caused by non-crystalline SiO_2. At 1200°C fibers remain mostly semi-crystalline, but the appearance of the (120+210) reflection pair at about 26° 2-theta indicates the presence of some mullite. At 1250°, the same XRD reflection indicates progressing mullite formation; however the major part of the fibers evidently remains semi-crystalline. The XRD profile changes drastically at 1300° where extensive mullite formation has occurred and broad XRD peaks from transitional Al_2O_3 have

mostly disappeared. From these results it was concluded that the upper temperature limit of a possible hot-pressing window lies between 1250°C and 1300°C.

In a following step a simulation of the hot-pressing was performed. We used a single OMB disk (d=25 mm) which was placed in a uniaxial test system between two Al_2O_3 dies. A constant load was applied and adjusted to a pressure of 2 MPa. Subsequently the pre-loaded OBM disk was heated with a constant heating rate of 10K/min to 1400°C while the concurrent deformation was recorded. The dilatometer curve plotted in figure 2 reveals that the onset temperature of the OBM compaction is at about 900°C which is obviously correlated to the softening of non-crystalline SiO_2-rich phase. The deformation rate increases with temperature and reaches a maximum at about 1190-1210°C. Above 1250°C compaction is slowing down and freezes abruptly at approximately 1270°C followed simply by linear thermal expansion. The only plausible reason for the sudden freezing at 1270°C is the crystallization of mullite and related consumption of low-viscous silica phase. Since XRD results indicate that mullite formation occurs in a relative narrow temperature range, the crystallization behavior of pulverized MLS-Fibers was also studied in detail by DSC and compared directly to dilatometry (fig. 2). The onset temperature of the exothermic mullite crystallization is around 1260°C, the peak temperature at around 1280°, and the crystallization appears to be mostly completed at 1290°C. Evidently the DSC results confirm the assumption that the onset of mullite formation is linked to the sudden stop of densification beyond 1270°C, emphasizing that hot-pressing of OBM fiber mats is viable only if sufficient amorphous SiO_2 is available. Note the relative high noise of the DSC signal which is explained by the use of pulverized MLS-2 fibers, i.e. the still mostly fibrous particle morphology is disadvantageous for packing density of the DSC sample and the resulting thermal flux.

The chemical composition and diphasic nature of MLS-2 fibers suggest that early formed mullite may still not be thermodynamically stable 3/2-mullite containing 71.8 wt% Al_2O_3 and 28.2 wt% SiO_2. Given the fact that Al_2O_3-rich mullites of about 2/1-composition are typically observed as primary crystallization product in diphasic precursors, a similar behavior is expected for MLS-2 fibers as well. A sensitive measure for the Al_2O_3-content of mullites is provided by the lattice parameters, which are easily accessed by analytical XRD profile fitting [20]. Figure 3 displays the well-known literature data for the correlation between lattice parameters and Al_2O_3 content of mullite [2]. Open circles represent calculated mullite lattice constants of MLS-2 fibers annealed for one hour at 1300°C. Similar to previous studies we observe an Al_2O_3-rich primary mullite containing 64.8 mol-% Al_2O_3 being in good agreement to the frequently observed formation of primary 2/1-mullite (66.6 mol-% Al_2O_3). On the other hand, this immediately raises the question about SiO_2 being not structurally bonded in mullite. Taking into account the bulk chemical composition of MLS-2 fibers and the calculated mullite composition approximately 5 wt-% free SiO_2 should be present after annealing at 1300°C. Evidently full crystallization of MLS-2 fibers requires annealing at temperatures far beyond their core crystallization range (1260-1290°C). This observation motivated a further series of one hour annealing experiments performed between 1300 and 1500°C. The thermal evolution of the mullites' "a" lattice constants and the estimated Al_2O_3 contents are presented in figure 4. Although there is significant Al_2O_3 depletion above 1300°C, annealing at 1500°C is required in order to approximate 3/2-mullite stoichiometry; also denoting complete consumption of free SiO_2. Note that the bulk Al_2O_3 content of MLS-2 fibers (72 wt%) is slightly richer in Al_2O_3 than 3/2 mullite (71.8 wt%) consequently the lowest possible Al_2O_3 content of present mullite is 60.25 mol%, i.e. mullite

composition will remain above the “theoretical” value of 60 mol% even if free SiO_2 is completely consumed.

Processing and characterization of hot-pressed MAFTEC MLS-2 OBM

Large OMB compacts were manufactured by means of uniaxial hot-pressing in a $MoSi_2$-heated chamber furnace. Taking into account the substantial densification observed in dilatometry, for each run 6 OMB disks were used in order to obtain sufficient sample dimensions. Punched OMB disks (d=70 mm) were aligned and stacked carefully, then positioned between highly dense EkaSiC SiSiC dies (d=70 mm). Such SiSiC dies exhibit high thermal conductivity (130 W/mK at RT, data published by manufacturer); therefore fast temperature equilibration can be expected resulting in minimal radial thermal gradients in OBM disks especially during heating. Moreover, SiSiC has a thermal expansion coefficient of 4-5 ppm/K which is close to the CTE of mullite, i.e. undesired radial stresses between dies and OBM disks are minimized during hot-pressing as well as cooling. On the basis of the dilatometry results an appropriate temperature-pressure profile was selected: First the OMB disk stack is heated to 1075°C with a rate of 10K/min. Then follows a fifteen minute dwell at 1075°C which provides temperature equilibration across the sample volume. During the final five minutes of the dwell a pressure of 2.5 MPa is slowly applied. Subsequently the temperature is raised with 5 K/min to 1275°C. After a second fifteen minutes dwell at 1275°C, hydraulic pressure and furnace heating are switched off simultaneously; then samples are cooled down freely. Although SiSiC underwent some thermal oxidation, the hot-pressed disks were detaching easily from the dies. Figure 5 shows the OMB stack (h≈48 mm) and the hot-pressed OBM compact (h≈6 mm). The total compaction ratio of approximately 7:1 or 87-88 % can also be calculated from as-received OBM density (0.16-0.17 g/cm^3; data published by

manufacturer) and the density of the OBM compact (1.34-1.36 g/cm^3). Taking into account the theoretical density of mullite (3.1-3.2 g/cm^3) the total porosity of the OBM compact is about 57 vol-% while the fiber volume content equals the density and is about 43 vol-%.

Like conventional short-fiber felts or blankets OBM mats show a random fiber alignment in the base plane (xy-direction) and a preferred fiber alignment perpendicular to the vertical z-direction, respectively. It is expected that compaction along the z-direction will augment this preferred fiber orientation. A representative cross section of a hot-pressed OBM compact is given in figure 6(a). The SEM image clearly shows that there is no obvious laminar meso-structure visible along the z-direction which could be associated with the OBM stack, i.e. the fiber volume content appears similar all across the hot-pressed body. Key factors for the integrity and stability of OBM compacts are the structural health and bonding of fibers, respectively. Mechanical strength will evidently suffer from widespread fiber breakage and/or insufficient bonding between fibers, both inhibiting load transfer. However, fibers appear mostly undamaged, i.e. the hot-pressing process did evidently not produce small and dusty fiber debris. The higher magnification SEM picture showing a polished cross-section (fig. 6b) is crucial for understanding the essential microstructural effects evolving during hot-pressing of OBM. Basically three scenarios are observed at fiber intersections (see respective marks): (1) fibers remain fully separated; (2) fibers well bonded without apparent interface but exhibit some cracking close to the sintering neck; (3) fibers are strongly bonded without apparent interface. Evidently, the absence of distinct fiber/fiber interfaces in (2) and (3) is associated with the initially diphasic MLS-2 fiber microstructure allowing fiber re-arrangement and viscous-phase sintering during hot-pressing. Crack-free fiber contact areas are considered dominant microstructural features of hot-pressed OBM:

they provide load transfer between fibers and thus are the reason for obtaining a ceramic body consisting of a rigid fiber network. Nonetheless, some cracking at fiber contacts may occur in later stages of the process when amorphous SiO_2 is mostly consumed and crystalline mullite becomes dominant, i.e. fiber deformability decreases while uniaxial pressure is still applied. It is anticipated that free standing or only partially bonded fibers contact areas are not contributing substantially to the structural integrity of OBM compacts. At this point it is unclear if an optimized temperature-pressure profile could effectively reduce fiber damaging or increase fiber bonding.

A first evaluation of the fracture behavior and mechanical properties of hot-pressed OBM was performed by means of standard 3-point bending tests at room temperature and at 1300°C, respectively. OBMs were tested in the as hot-pressed state and after subsequent annealing (1500°C, 1 h). Preliminary experiments at RT revealed a linear-elastic deformation, brittle fracture behavior, and no influence of the orientation of bending bars, i.e. an apparent strength difference between the xy-plane or the zx/zy-plane subjected to tensile loads was not observed. Accordingly, no apparent delamination effects were observed irrespective of the orientation of bending bars, emphasizing the “quasi monolithic” nature of hot-pressed OBM stacks. The two OBM variants tested in xy-orientation at 20°C (RT) and at 1300°C, the average bending strengths (solid bars) and elastic moduli (hatched bars) are compiled in figure 7, respectively. As hot-pressed OBM keep about 95% of their 27 MPa RT fracture strength at 1300°C, but the elastic modulus decreases considerably by almost 35%. The RT fracture strength of post-annealed OBMs is 10% higher (29.7 MPa), but is retained to only about 85 % at 1300°C. On the other hand, post-annealed OBMs exhibit almost the same modulus at RT but the elastic modulus decreases by about 15% only. For an interpretation of the observed mechanical

behavior bending tests were corroborated by high-resolution SEM analyses of MLS-2 fibers visualizing microstructural effects associated with post-annealing. The observation that as hot-pressed OBM almost retain their RT 3-point bending strengths at 1300°C can certainly be explained by the preservation of the nanoscaled microstructure, i.e. very sluggish growth of mullite grains. A high-magnification SEM image reveals that only few large grains appear in the apparently pore-free microstructure of as hot-pressed MLS-2 fibers (fig. 8a). Since no significant reaction of amorphous SiO_2 and primary "2/1"-mullite is expected at the bending-test temperature of 1300°C (see previous section), the presence of about 5 wt% residual amorphous SiO_2 is presumably the reason for the decreasing effective elastic modulus. Moreover, co-existing amorphous SiO_2 may also help to retain fracture strength by stress relaxation or re-distribution. On the other hand, there is no obvious rationale for the observed mechanical properties of 1500°C pre-annealed OBM. Since no substantial shrinkage was observed upon post-annealing, there is no plausibility for an increased fiber volume content contributing to the higher fracture strength. Post annealing of 1275°C hot-pressed OBM at 1500°C triggers the reaction of amorphous SiO_2 and primary mullite to "3/2"-mullite. Figure 8(b) shows the related effects: now the MLS-2 fiber microstructure is dominated by prismatic and isometric mullite crystals exhibiting grain sizes of about 0.2-0.5 μm. Dark spots randomly distributed across the fiber sections represent pores obviously formed by coalescence of nanoscale pores. At first glance mullite grain growth and pore coalescence seem to be in conflict with the observed increase of RT strength. However, two further microstructural features may be in effect: (1) additional bonding of formerly separated fibers. This would require much materials transport and/or deformation which seems highly unlikely for fibers mostly consisting of crystalline mullite. (2) Growing fiber contact areas and "healing" of cracks due to sintering. The

high resolution SEM image clearly shows mullite crystals in fiber contact areas where they “bridge” fibers. Although we cannot provide statistically supported evidence at this point, crack healing seems at least plausible (see arrows). Such microstructural effects may contribute to the observed, slight improvement of RT fracture strength of annealed OBM compacts. The relative higher strength loss at 1300°C accompanied by a less decreasing elastic modulus are obviously due to the consumption of residual amorphous SiO_2 and primary Al_2O_3-rich “2/1”-mullite to form fully crystalline, quasi-stoichiometric “3/2”-mullite.

General aspects of processing

The present manufacturing process for mullite fiber compacts offers advantages as well as disadvantages with respect to standard processing methods employing conventional short fiber felts or blankets. Fiber compacts are typically obtained by infiltration of short fiber products with liquid binders or particle dispersions which are subsequently shaped, dried and eventually heat-treated in order to obtain a rigid structure. The infiltrated liquids are typically containing SiO_2-rich constituents such as SiO_2-sols, silicate solutions (“water-glass”) or also classical ceramic binders like Al-(meta)phosphate. A first important feature of the process reported in this work is the fiber volume content of compacts. Whereas the fiber volume content is evidently not substantially changed in conventionally rigidized materials, the uniaxial compaction of MAFTEC OBMs by hot-pressing results in a fiber volume content increased by a factor of seven. Considering fibers as major load-bearing constituent of any fiber compacts, it is straightforward to rationalize the favorable strength of hot-pressed MAFTEC OBMs. The final fiber content is strongly depending on the fiber “packing density” of employed “green” MAFTEC fiber products. Although there are no

fundamental constraints, the availability of starting products e.g. mats with different needling will presumably remain limited.

A major feature of conventionally processed fiber compacts is the presence of excess of glassy/amorphous binder phases which inevitably will deteriorate high-temperature stability of fiber compacts: mullite can be chemically attacked by low viscous siliceous melts. Mullite grain boundaries, in particular at fiber contacts, can be wetted. Hence, deterioration of mechanical strength as well as possible creep deformation is expected even at relative low application temperatures. In contrast to this, the present manufacturing process does not require any kind of additional binders to yield rigid glass-free OBM fiber compacts which are able to preserve a major part of their mechanical stability at high temperatures and consequently can be applied as high-temperature structural materials such as stable insulation panels or any high-temperature structures exposed or penetrated by fluids such as gas filters. The porous and fibrous architecture of OBM fiber compacts is also considered ideally suited for vapor- or liquid-phase infiltration with functional materials such as catalysts. In general it may be stated that OBM fiber compacts could fill the application gap between low-strength, rigidized fiber felts and high-performance ceramic matrix composites reinforced by continuous fibers.

A fundamental drawback of the present manufacturing process is the limited component shape variability. Conventional processing allows rigidization of large, complex shaped components “in situ” (e.g. in furnace linings). Uniaxial hot-pressing is limited to quasi flat plates where dimensions are limited by existing hot-pressing facilities and tools. The availability of strong, creep-resistant SiSiC dies with low CTE mismatch to mullite is considered a key issue for successful upscaling: homogenous pressure application as well as minimized thermal gradients and radial stresses

between dies and plate become increasingly important for large-scale fiber compacts. An additional processing option would be the use of “plain” OBMs along with OBMs filled by “matrix” components not substantially affecting high-temperature properties. In a similar approach “fiber-laminate” composites were manufactured by alternating stacks consisting of matrix-infiltrated and non-infiltrated fiber fabrics and subsequent hot-pressing [21]. The present manufacturing process does offer the same flexibility, i.e. there are quasi unlimited possibilities to process filled and unfilled OMBs into a single compact. A promising approach would be the use of diphasic mullite precursor powders allowing co-processing due to their compatible crystallization behavior. By this conductivity or permeability of fiber compacts could be directed to towards specific demands.

Summary

Highly porous mullite fiber compacts were successfully manufactured by uniaxial hot-pressing of stacked MAFTEC organic bound mats (OBM) between SiSiC dies. The process takes advantage of as received diphasic MAFTEC MLS-2 fibers consisting of amorphous SiO_2 and transitional Al_2O_3, opening a suitable processing window where consolidation proceeds before final crystallization of fiber constituents to mullite. Since the compaction process does not require any additional binders or sintering aids, MAFTEC OBM fiber compacts exhibit favorable mechanical properties which are largely retained at high temperatures, therefore such compacts are considered well suited as high-temperature structural materials.

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Figure captions

FIGURE 1: XRD analysis of the crystallization behavior of MAFTEC MLS-2 fibers. As received material shows broad reflections characteristic for nanoscaled transitional Al_2O_3. Phase evolution was monitored upon annealing for one hour, respectively. At 1200°C traces of mullite are indicated by the 120/210 mullite reflections at about 26° 2-θ. Between 1250 and 1300°C mullite becomes the dominant phase.

FIGURE 2: Combined dilatometric and DSC analysis of the compaction and crystallization behavior of MAFTEC MLS-2 OBM mats. The deformation onset temperature is about 900°C whereas compaction abruptly stops at about 1275°C. A simultaneous exothermic DSC peak at approximately 1280°C is related to mullite crystallization.

FIGURE 3: Correlation between lattice parameters and Al_2O_3 contents of mullites as taken from literature (e.g. [2]). The lattice parameter refinement of MLS-2 fibers annealed at 1300°C reveals that the respective mullite has an Al_2O_3 content of almost 65 mol%. Note the almost perfect linear correlation of a.

FIGURE 4: Evolution of the “a” lattice parameter of mullites as detected in MLS-2 fibers. At 1300°C mullites show nearly 2/1-stoiciometry (2 Al_2O_3• SiO_2); annealing at 1500°C is required to approach stable 3/2 mullite (3 Al_2O_3• 2 SiO_2).

FIGURE 5: Stack of six MAFTEC MLS-2 OBM disks before and after uniaxial hot-pressing using process parameters given in figure 6. The total compaction ratio is about 7:1.

FIGURE 6: (a) Cross section of as hot-pressed MAFTEC MLS-2 OBM revealing a predominant fiber alignment perpendicular to the compaction direction z. There is no apparent laminar mesostructure due to use of stacked mats. (b) High-magnification of polished cross section. Three basic scenarios are observed: (1) fibers remain separated; (2) fibers are bonded but exhibit cracks close to bonded areas, (3) fibers are well bonded without defects.

FIGURE 7: Results of 3-point bending tests performed at room temperature and 1300°C. Solid bars refer to strengths, hatched bars to elastic moduli, respectively. Whereas as-hot pressed MAFTEC OBMs mostly retain strength at 1300°, modulus is decreasing significantly. Loss of HT-strength and -modulus is observed for post-annealed samples. Note beneficial effect of annealing at 1500°C for RT strength.

FIGURE 8: High-magnification SEM analyses of polished MAFTEC MLS-2 OBM cross sections: (a) In the as-hot-pressed state only few primary mullites grow larger than nanoscale (b) Post-annealing at 1500°C triggers formation of a homogeneous “mosaic”-type microstructure. Prismatic mullites are also bridging fibers and crack-healing is plausible. Dark spots designate pore coalescence.

Figure 1

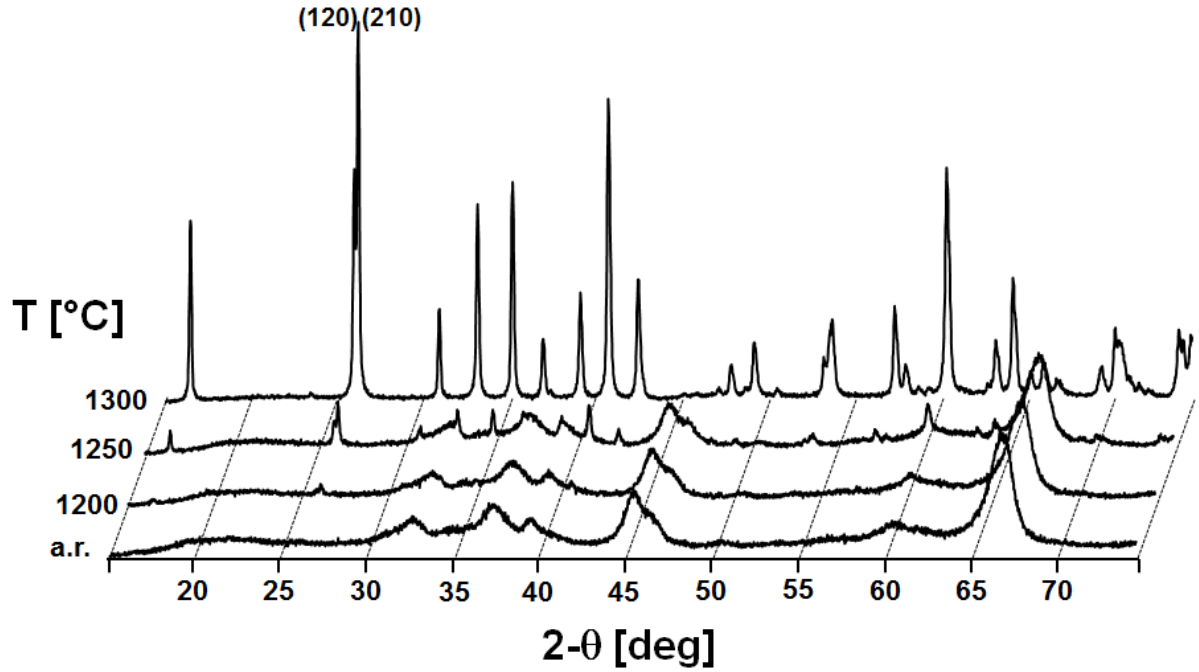

Figure 2

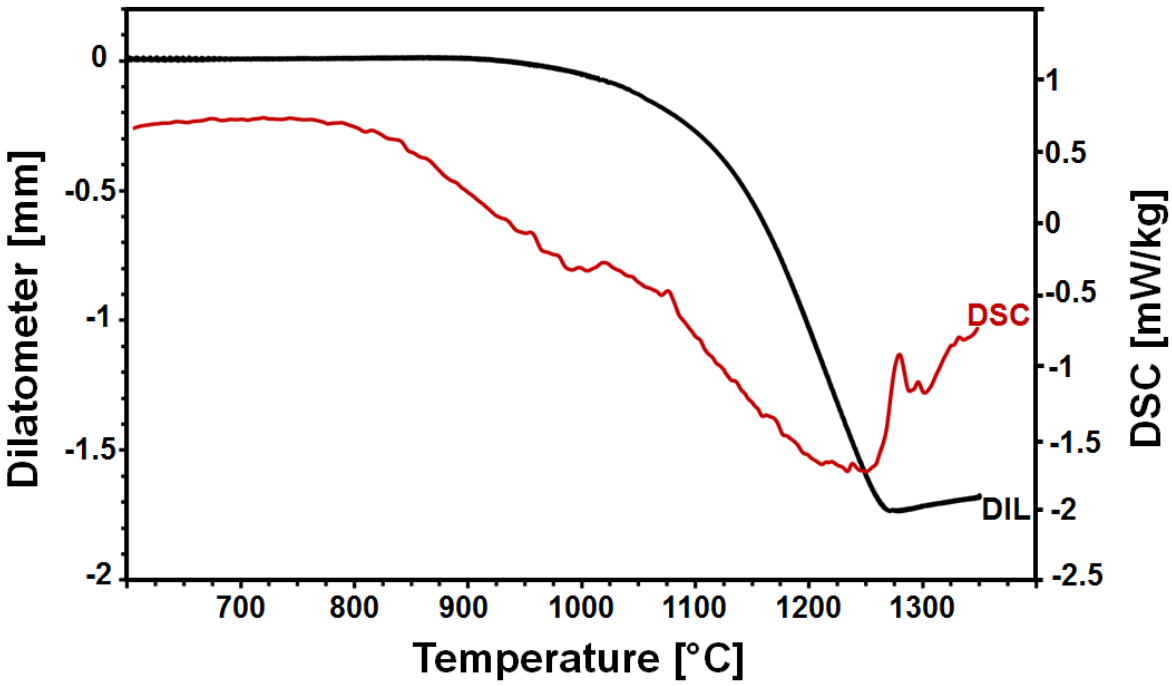

Figure 3

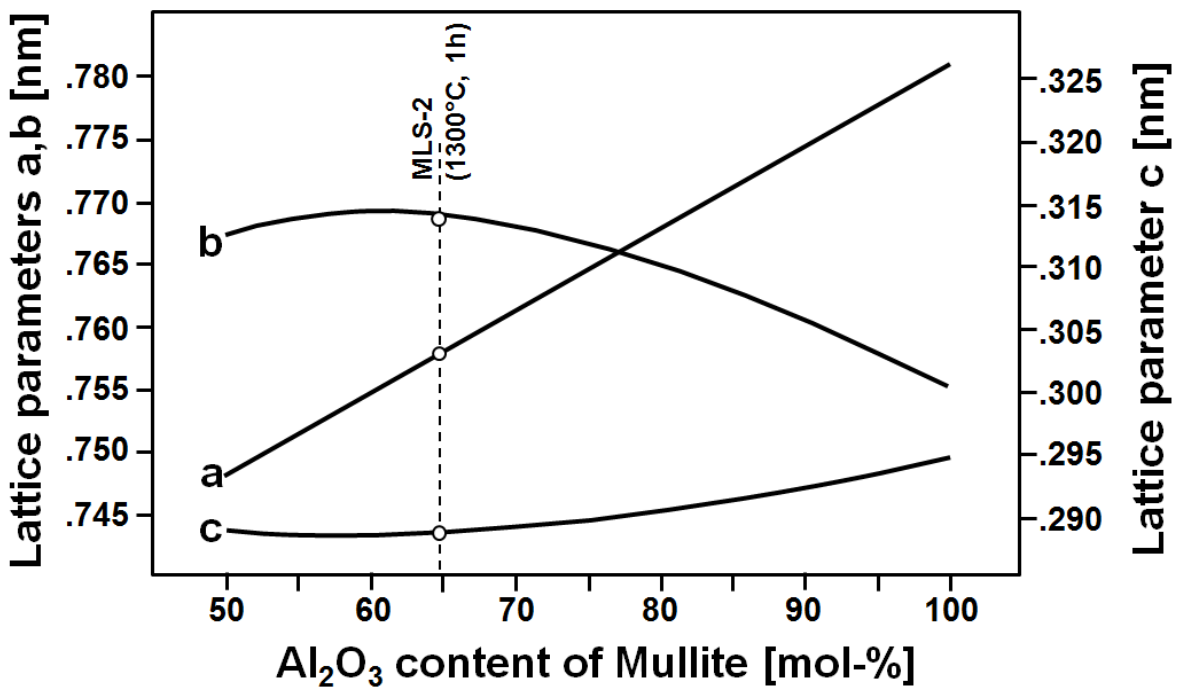

Figure 4

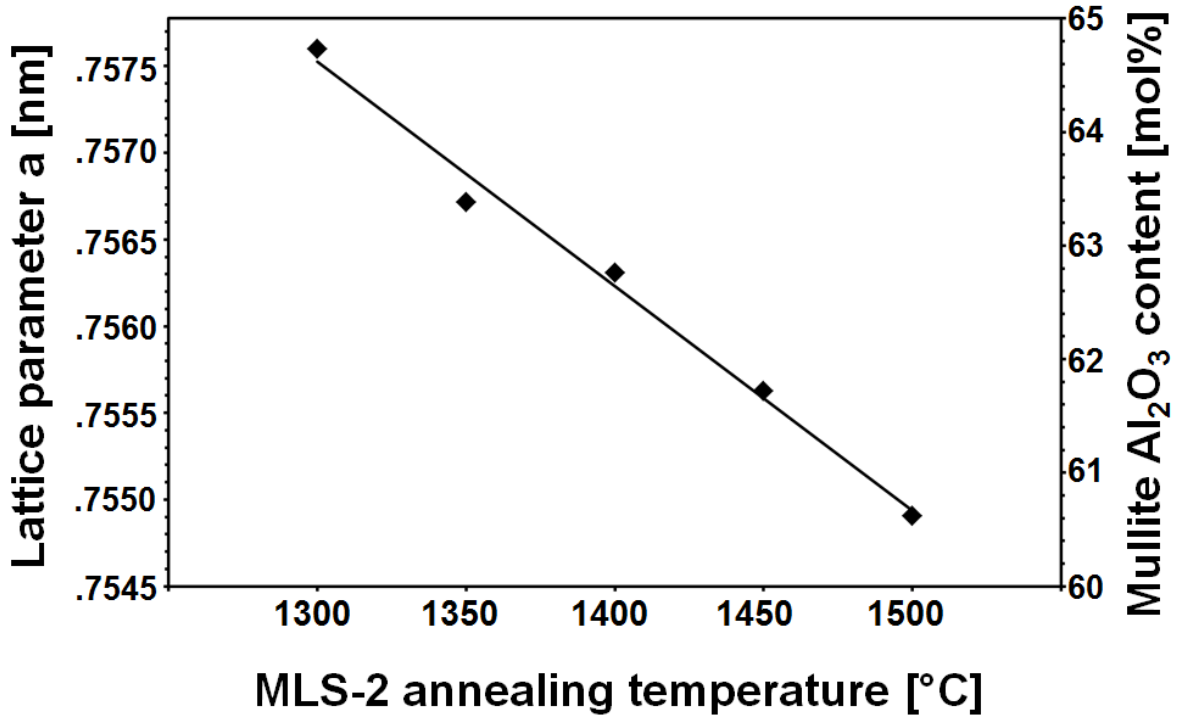

Figure 5

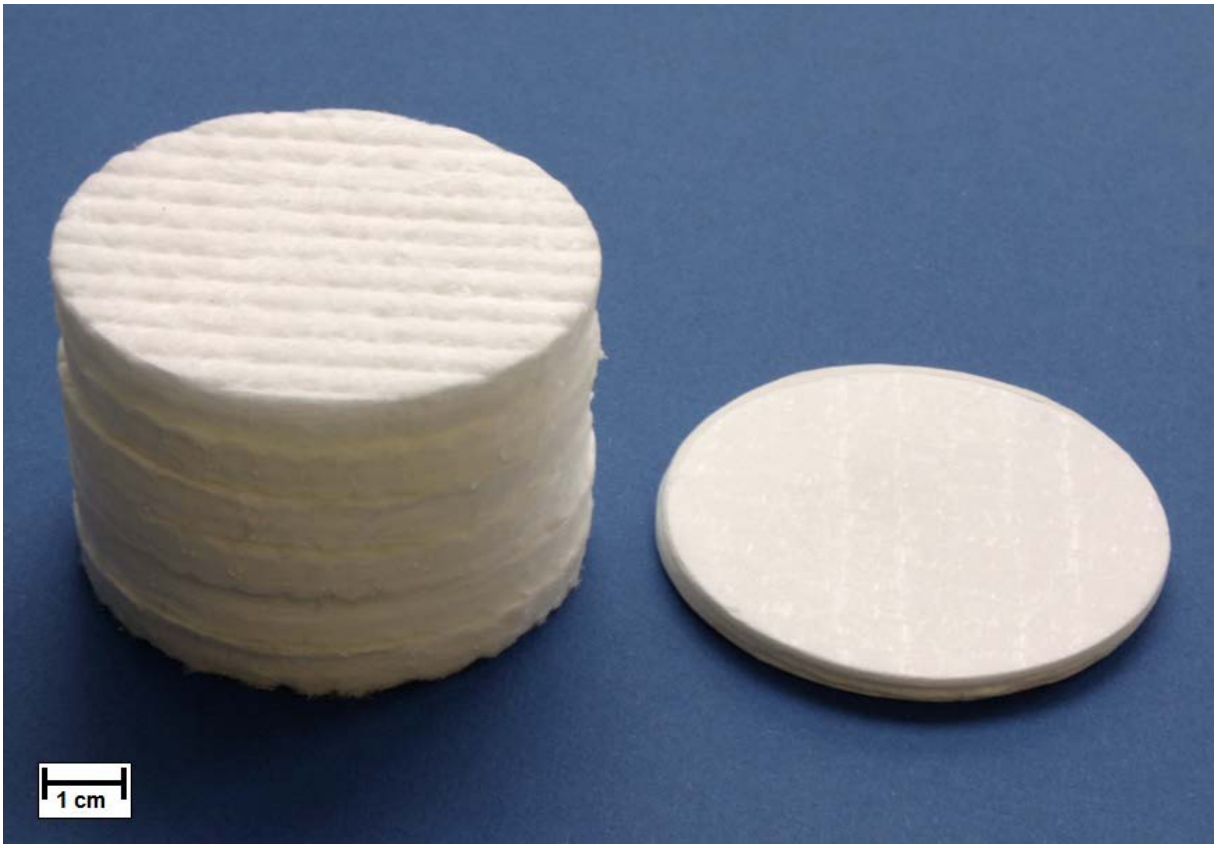

Figure 6

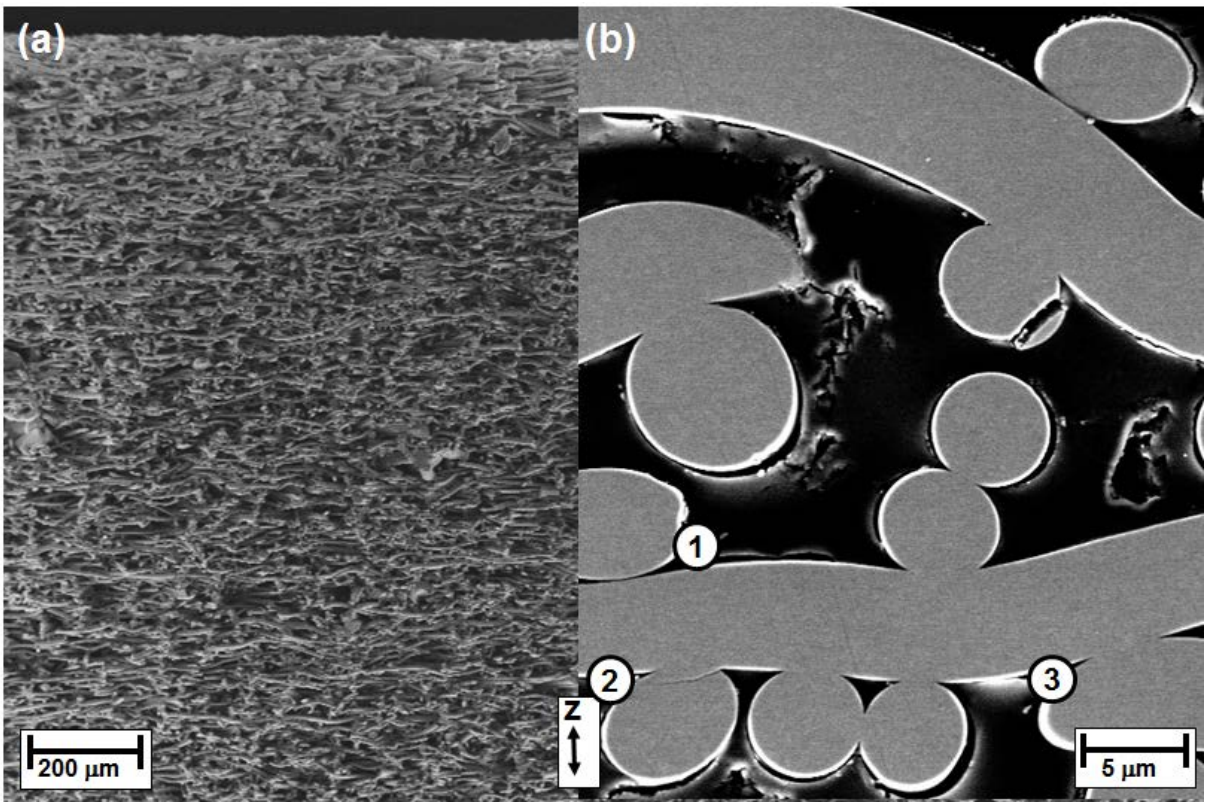

Figure 7

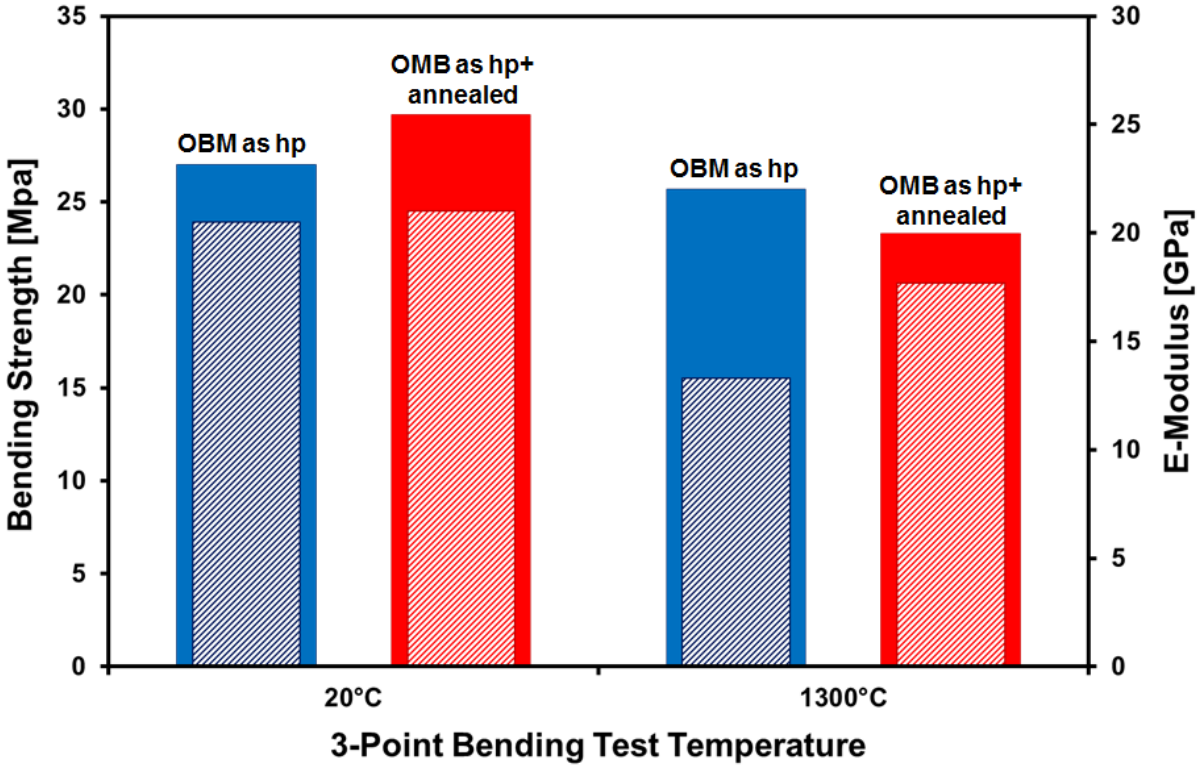

Figure 8