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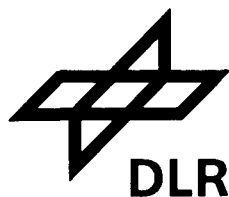
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Characterization of low temperature mullitization

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Various mullite precursors have been prepared by various synthetic methods using the various starting materials. It is generally considered that mullite forms directly from the amorphous phase at around 1000°C when the precursor is chemically homogeneous, but spinel phase forms preceding to mullite when the precursor is less chemically homogeneous. Recently, Nishio and Fujiki¹⁾, Hulling and Messing²⁾, and Schneider³⁾ independently showed mullitization at below 800°C. Since this new mullitization reaction is unclear yet in this study, low temperature mullitization reaction was characterized by magic-angle spinning nuclear magnetic resonance (MAS NMR), small angle X-ray scattering (SAXS) and powder X-ray diffraction (XRD) methods.

The precursor sample was prepared basically by Nishio and Fujiki method¹⁾. At first, 0.1 mole of aluminium nitrate nonahydrate, 0.2 mole of aluminium isopropoxide, and 0.1 mole silicon ethoxide were dissolved in 7.9 mole of de-ionized water and stirred for 2 days at the ambient temperature. The solutions were gelatinized and dried to xerogel at various temperatures from 70° to 250°C. A part of xerogels were further heat-treated at 250°C for 16 hours.

Low temperature mullitization was found to occur only when the precursor samples were dried and heat-treated at 250°C. Mullite started to crystallize as low as 450°C. Amount of mullite formed did not increase up to 800°C but significantly increased between 800° and 1000°C. Two peaks at -90 ppm and -105 ppm were observed in the ²⁹Si MAS NMR spectra of the sample, which showed low temperature mullitization. By SAXS measurement of the sample, existence of the particles in two different sizes was found. Two different structures in polymerization of SiO₄ tetrahedra in the sample, i.e. unpolymerized and polymerized SiO₄ tetrahedral structures were suggested from these results. The interface between these structures was considered to play an important role for nucleation of mullite phase at low temperature.

References

- 1) T. Nishio and Y. Fujiki, *J. Ceram. Soc. Jpn.*, 99 [8] 654-9 (1991)
- 2) J.C. Hulling and G.L. Messing, *J. Non-Cryst. Solids*, 147/148 213-21 (1992)
- 3) H. Schneider, private communication (1993)

EXAFS studies of Cr-doped mullite ceramics

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Results of extended X-ray absorption fine structure (EXAFS) measurements of the Cr K edge of Cr-doped mullite (up to » 10 wt% Cr₂O₃) are presented. The experiments were carried out on Beamline 7C at Photon Factory, National Laboratory of High Energy Physics (KEK), in Tsukuba, Japan. The X-ray absorption spectra were normalized by first subtracting a pre-edge background and then fitting a smoothly-varying cubic spline background in the region of the EXAFS. For all measured spectra the magnitude of the Fourier transform, which is related to the radial distribution function (RDF), is characterized by two pronounced peaks. The first peak is ascribed to the nearest-neighbour oxygen atoms making up the octahedra surrounding the central Cr atoms and the second peak is assumed to be due to aluminium. In order to get a more quantitative view, the EXAFS spectra were least-squares fitted to a model function, which was based on standard Gaussian lineshapes for the RDFs of oxygen and aluminium. It turned out that the aluminium peak could not be fitted satisfactorily with a Gaussian RDF alone. The discrepancy can be reduced by assuming that there exists an additional contribution to the Gaussian RDF of aluminium. Obviously, the additional contribution results from Cr atoms that do not occur at 'regular' octahedral lattice sites. Since these Cr atoms are not in the center of the aluminium coordination shell, the Al-RDF seen by those Cr atoms is broadened and slightly asymmetric. The data analysis showed that the contributions from both Cr-atom positions did not correlate significantly. Therefore, inclusion of the additional term is justified. The aluminium coordination shell is at » 3.27 Å from the first Cr atoms while it is between » 2.8 Å and » 3.7 Å from the second. The interpretation of the EXAFS with the occurrence of two different Cr³⁺ lattice sites in mullite is in excellent agreement with previous electron paramagnetic resonance (EPR) and crystal field spectroscopic results: These investigations yielded strong evidence for a Cr³⁺ incorporation at 'regular' (M(1)) and 'interstitial' octahedral positions.

Processing of mullite-based long fiber composites via slurry routes and by oxidation of Al:Si powder

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A novel technique to synthesize mullite by oxidation of Al:Si alloy powder has been utilized for the manufacture of Al_2O_3 long-fiber reinforced mullite composites. It includes (1) slurry infiltration/fiber winding of continuous Al_2O_3 yarns (ALMAX) and (2) slurry infiltration/ slip casting of ZrO_2 coated sapphire fibers (Saphicon). The nonaqueous slurry used consisted of Al:Si alloy, mullite and additives. During reaction bonding of the green matrices, the Al:Si alloy oxidizes and converts to mullite, below 1400°C in air. One advantage of this technique is that the oxidation causes an internal volume expansion of the matrix. This minimizes the sensitivity to crack formation due to reduced shrinkage stresses between the fibers and the matrix.

Si:Al spinel formation in Al_2O_3 - SiO_2 precursor-mullitization processes

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Mullite formation processes in three different kinds of monophasic gels, hybrid gel, spray dried/pyrolyzed powder and three types of diphasic gels (all have 3:1) show great variations. Intermediate spinel formation directs mullitization reaction in most cases. In some kinds of monophasic gels or powder it does not form at all but t-mullite formation is evident at 980°C exotherm. In order kinds, it develops shaply with exhibition of 980°C exotherm. From DTA analysis, alkaliketching experiments, and RDS study, the composition of this Si-Al spinel is found to be analogous to that of 3:2 mullite.

Purely heterogeneous diphasic gel does not exhibit 980°C exotherm but form γ - Al_2O_3 and α - Al_2O_3 prior to mullitization. Formation of former phase is confirmed by AEM, followed by EDS analysis. However, insitu diphasic gels forms only Si bearing spinel other than pure Al-spinel. Formation of mixtures of Al-spinel and Si-Al spinel out of four different insitu diphasic gels (varying in Al/Si ratios) have been monitored by QXRD techniques. The results reveal that intensities of both 46° and 67° 2Θ CuK_α peaks of spinel phase/phases increase with temperature.

Measured X-ray intensity at each peak is found to be greater than that of the expected γ - Al_2O_3 formation. This apparent excess intensity evidently substantiates the view that silica is present in the spinel and formation of it is also possible in heated diphasic gel. But unlike to monophasic gel it forms as early as 600°C and increases predominantly with exhibition of an exotherm at $\sim 1280^\circ\text{C}$ and thereafter it transforms to o-mullite with exhibition or another exotherm at $\sim 1320^\circ\text{C}$. Finally, the reasons behind the various paths of mullitizations have been discussed.

Mullite fiber/mullite matrix composites

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Mullite fiber/mullite matrix composites represent an important type of oxide/oxide composites that can have potentially very attractive high temperature properties. This work shows how to achieve tough mullite/mullite composites without fiber degradation or interfacial reaction. Colloidal processing of mullite matrix to lower the composite consolidation temperature and engineering of the interface between mullite fiber and mullite matrix by using thick BN (1mm) or BN/SiC double coatings on mullite fibers were employed. This allowed deformation mechanisms conducive to toughness enhancement such as fiber/matrix debonding and fiber pullout come into play. Significant improvements in the mechanical properties, especially those related to toughness and a noncatastrophic failure were achieved in mullite fiber/mullite matrix composites.

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Multiple toughening in reaction bonded mullite/SiC/ZrO₂ composites

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Low shrinkage mullite/SiC/Al₂O₃/ZrO₂ composites were fabricated based on the RBAO technology. A powder mixture of 40 vol% Al, 30 vol% Al₂O₃ and 30 vol% SiC was attrition milled in acetone with TZP balls which introduce a substantial ZrO₂ wear debris into the mixture. The precursor powder was isopressed at 300-900 MPa and heat treated in air by two different cycles resulting in various phase ratios in the final products. During heating, Al oxidizes to Al₂O₃ completely, while SiC oxidizes to SiO₂ only on its surface. Fast densification (at >1300°C) and mullite formation (at 1400°C) prevent further oxidation of the SiC particles. Because of the volume expansion associated with the oxidation of Al (28%), SiC (10%), and the mullitization (4.2%), sintering shrinkage is effectively compensated. The reaction bonded composites exhibit low linear shrinkages and high strengths: shrinkages of 7.2%, 4.8%, and 3%, and strengths of 610 MPa, 580 MPa, and 490 MPa, corresponding to compaction pressures of 300 MPa, 600 MPa, and 900 MPa, respectively, were achieved in samples containing 49-55 vol% mullite. HIPing improves significantly the mechanical properties: a fracture strength of 490 MPa and a toughness of 4.1 MPa·m^{1/2} increased to 890 MPa and 6 MPa·m^{1/2}, respectively. These strength and K_{Ic} data are at least a factor of three higher than those usually obtained for conventional mullite. More than 80 % of the dispersed tetragonal ZrO₂ particles transform on fracture, however, this alone cannot explain the strong increase. Hence we speculate that both nano- and ZrO₂-toughening are active.

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Sol-gel mullite matrix-SiC and -mullite 2D woven fabrics composites with or without zirconia containing interphase. Elaboration and properties

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Many advanced aerospace systems require or would benefit from new low density materials for structural applications. This is particularly true for those applications requiring materials temperatures above 800°C, e.g. aircraft engine parts. For these applications the most promising classes of new materials are ceramics woven fabrics-reinforced ceramic matrix composites. Strong and very tough ceramic and glass-ceramic matrix composites have been prepared using mainly one-dimensional fiber reinforcements. One of the most interesting matrix is mullite. The interest of the mullite matrix arises from its high thermal and chemical stability and from its relatively low dilatation coefficient. Its mechanical properties are good up to 1300-1500°C and its low toughness can be improved by zirconia dispersion. The mullite solid solution domain is increased in the case of sol-gel synthesis and mullite glass-ceramic can be obtained. In this paper we compare the properties of composites made with Nicalon NLM202 (Nippon Carbon) SiC or with Nextel 440 (3M) or Sumica (Sumitomo) mullite fibers.

The method used to make composites is a three-stage process [1]: *i*) the first is the preparation of an interface gel precursor impregnated fabrics by in situ gelification of a mixture of alkoxides, *ii*) the second is the deposit of a fine and reactive amorphous powder of matrix precursor on the impregnated fabrics, *iii*) the third step is the hot-pressing of the stacked fabrics in a carbon mold. Three or five sheets are used.

Composites have been studied by SEM and TEM. Three points flexural strength was measured at R.T. and at 900°C, in air. Local Young's modulus, microhardness and interfacial shear stress have been determined at R.T. Micro-Raman spectra and X microanalysis were used to study the fiber-interface reactions. Using a mixture of aluminium-silicon ester and tributylborate as interface precursor, we obtain a carbon free SiC-mullite sliding interface. The use of a complementary ZrO₂-GeO₂ gel interface precursor allows to obtain dense composites (open porosity <4%) at moderate temperature (~1300°C) exhibiting good mechanical properties (ultimate value of the linear behaviour ~180 MPa, even after 30 days annealing in air). The effects of a zirconia interphase on the mechanical properties of mullite-mullite composite is also discussed. The achievement of a R.T. and 900°C non-brittle composite is related to the absence of reaction between the zirconia interphase and the fibers. Microwave properties are discussed.

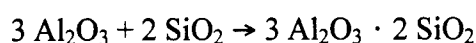
[1] Ph. Colomban, M. Menet, E. Mouchon, C. Courtemanche and M. Parlier, Patent Fr 2672 283, EP 92400235-5, US (pending)

Thermomechanical properties and creep behaviour of mullite issued from rapidly quenched powders

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Monolithic mullite was prepared by reaction sintering starting from an ultra rapidly quenched powder mixture, following the reaction:



The quenching technique was chosen in order to lead to an amorphous, highly reactive powder, which allowed us to obtain fully dense material at relatively low sintering temperatures.

The mechanical properties (strength resistance, toughness) of the fired bodies were measured both at room and at high temperatures. At room temperature, the ceramic shows a rising R-curve effect as a consequence of its particular microstructure composed of bimodal grain size distribution.

The creep behaviour of mullite was also assessed under the following conditions: temperature range from 1250 up to 1350°C, stress range from 60 to 120 MPa. By subtracting the viscoelastic contribution to creep, it was possible to approach the true steady state creep rates and then to determine the stress exponent and activation energy parameters of the conventional steady creep equation.

On the basis of these creep parameters, an attempt of deformation mechanism, involving liquid phase diffusion rather than the most often encountered solid state diffusion, is proposed.

New aqueous mullite precursor synthesis: Structural study by ^{27}Al and ^{29}Si NMR spectroscopy.

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Mullite precursor gel has been prepared by an aqueous route. The starting solution is made by hydrolysing tetraethoxysilane (TEOS) in a solution of aluminium nitrate. Urea is then added as a base generator. By storing at 80°C, ammonia is slowly formed in situ by thermolysis of urea and homogeneously hydrolyses the aluminium nitrate. At the beginning of the reaction, a silica gel is formed in a few hours by a catalytic effect of urea. This gel is then slowly digested by partially hydrolysed aluminium species which break the Si-O-Si bonds and link to the gel. After three days a clear colloidal sol is obtained and the particle size continues decreasing towards aluminosilicate species where the silicon atoms are in a single environment, linked to three hexacoordinated aluminium atoms and a hydroxyl group, as in natural imogolite. After a week the hydrolysis of aluminium is completed, the colloidal particles are crosslinked and a final gel, precursor of mullite is obtained. This gel, chemically very homogeneous, when washed, dried and heat-treated, crystallizes to mullite at 980°C. The structural evolution, from the first gel to the ceramic, has been followed by ^{27}Al and ^{29}Si liquid- and solid-state NMR spectroscopy.

The crystallization process of high alumina mullites

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Mullite has been commonly described to exist in a solid solution series of composition $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ with an observed compositional range of $0.18 < x < 0.55$ (57 - 74 mole% Al_2O_3). A new synthesis route in a sol-gel process yielded mullites up to 92 mole% Al_2O_3 . These mullites were synthesized with aluminum sec-butyrate and silicon chloride as starting materials corresponding to an Al/Si-ratio of 4:1. After homogenization of the admixture, hydrolysis was carried out by addition of H_2O which resulted in a vigorous reaction. After calcination at 700°C , a high alumina mullite, γ -alumina, and a residual non-crystalline phase were formed.

The lattice constants a and b of mullites from two different syntheses are shown in the figure as a function of the calcination temperature. Both mullites show a similar development of the lattice constants and consequently a similar behavior in the incorporation of aluminum which is linearly related to the a lattice parameter. At an annealing temperature of 700°C the mullite-type phase exhibits a very high Al_2O_3 content (≈ 88 mole%), documented by $a > b$ lattice constants. With increasing temperatures up to 1000°C , the Al_2O_3 content further increases (up to ≈ 92 mole%). Beyond this point, the alumina content decreases yielding a "normal" mullite at 1250°C with $a < b$ and an alumina content of about 73 mole%.

It should be noted that the mullites are orthorhombic in space group Pbam at all stages of the calcination. The cross over of a and b is just a coincidence which does not affect the orthorhombic symmetry. The lattice constants were refined in a Rietveld analysis, thus allowing an unambiguous assignment of a and b .

A third synthesis run yielded mullites at 950°C of sufficient quality for a crystal structure analysis. The results showed that the additional aluminum atoms reside on a new highly distorted site forming T_4O -groups.

Processing and mechanical properties of laminated composites of mullite/woven fabrics of Si-Ti-C-O fibers

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A sol-gel-processed mullite powder (specific surface area $3.2 \text{ m}^2/\text{g}$, equivalent diameter $0.59 \text{ }\mu\text{m}$) and woven fabric of Si-Ti-C-O fibers ($8.5 \text{ }\mu\text{m}$ diameter) were formed into laminated composites by filtration or doctor blade method using aqueous mullite suspensions containing polyacrylic ammonium (PAA) and methyl cellulose (MC) at pH 8.8. In the filtration method, aqueous mullite suspensions containing 52 vol% solid and PAA of $10.5 \times 10^{-6} \text{ mol carboxyl group per m}^2$ of powder surface were poured into the spaces separated with Si-Ti-C-O fiber fabrics with a thickness of $270 \text{ }\mu\text{m}$. In the doctor blade method with a blade clearance of $500 \text{ }\mu\text{m}$, mullite green sheets with $200 \text{ }\mu\text{m}$ thickness were formed from aqueous suspensions containing 40-45 vol% powder, PAA of $4 \times 10^{-6} \text{ mol carboxyl group/m}^2$ and MC of 2.0 mass% against weight of mullite. The green composites were hot-pressed to near full density at $1500\text{--}1650^\circ\text{C}$ for 1 h under a pressure of 39 MPa in a N_2 atmosphere. The four-point flexural strength over the spans of 30 mm (lower span) and 10 mm (upper span) and fracture toughness by the single edge precracked beam (SEPB) method over a span of 30 mm were measured at a crosshead speed of 0.5 mm/min at room temperature. Unfortunately, the dense composites ($>99\%$ of the theoretical density) fractured with a linear relation of stress and strain. The strength of mullite hot-pressed at 1650°C was $328 \pm 18 \text{ MPa}$. The strength ($292 \pm 36 \text{ MPa}$) of laminated composites with 6 vol% of Si-Ti-C-O fibers, hot-pressed at 1650°C , was comparable with that of monolithic mullite. However, the composites hot-pressed with 10 vol% of Si-Ti-C-O fibers at 1500°C showed a lower strength of $171 \pm 31 \text{ MPa}$. The fracture toughness increased from $1.6 \text{ MPa m}^{0.5}$ for monolithic mullite to $3.9 \text{ MPa m}^{0.5}$ for the composite hot-pressed at 1650°C . Above mechanical properties would be analyzed in relation to the structure of interface between mullite and long fibers.

Investigation of mullites by X-ray absorption spectroscopy at the K-edges of silicon and aluminium

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Measurements of X-ray absorption spectra near the absorption edge of a selected element (XANES = X-ray absorption near edge structure and EXAFS = Extended X-ray absorption fine structure) give detailed information e.g. about the valency of the excited atom, type and number of the neighbour atoms in the first and second coordination shell and the radial distance of these atoms to the atom under investigation. EXAFS is described analytically whereas the information from the near edge structure is derived in a fingerprint method using spectra of well characterized reference compounds.

As compared to other techniques, X-ray absorption spectroscopy as a tool for the structural analysis of amorphous materials has some important advantages:

- a long range order is not necessary
- there is atomic selectivity and
- in situ measurements are possible.

The here reported measurements were carried out with synchrotron radiation from the electron storage ring ELSA of the Bonn University. All spectra were taken with the standard X-ray absorption technique.

Three types of mullites were investigated at the Si and the Al-K-edge by measuring the corresponding near edge structure (XANES). As reference compounds for the various possible coordinations of Al a-Al₂O₃ (6), andalusite (5,6), and sanidine (4) were included in this investigation.

The observed differences at the Si-K-edge of the three mullites were rather small whereas significant differences were observed at the Al-K-edge. From the comparison position form and intensity of the "white line" of the mullites with those of the reference compounds it is evident that the mullite samples differ significantly in their composition from Al in various coordinations. In principle, a quantitative analysis of this composition seems possible so that a correlation of the structure with the observed properties can be tried.

We would like to thank PD Dr. Schneider from the DLR in Cologne for providing mullite samples and reference compounds. This work was partly supported by the BMFT under contract No. 05 433 AXI.

Shock wave effects in polycrystalline 3/2-mullite

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Mullite ceramics produced by pressureless sintering and hot isostatic pressing of sol-gel derived mullite powders were used as starting materials. Shock wave compression experiments were carried out by planar impact techniques employing a highly explosive device. The mullite samples, 0.5 mm thick and 20 mm in diameter, were embedded in a steel container. Shock wave pressures ranging between 25 to 60 GPa were generated by explosively accelerated steel plates of different thickness. The peak pressures transmitted into the samples were determined by independent calibration tests and impedance reflection matching using Hugoniot data for steel. After shock loading the samples could be recovered from steel container in the original position to shock wave propagation.

X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and infrared spectroscopy (IR) techniques were used to characterize residual shock effects. Shock pressures up to 25 GPa caused intergranular fracturing of ceramic samples but no phase decompositions. At higher shock loading pressures gradual decomposition of mullite to corundum (α -Al₂O₃), transition alumina, and non-crystalline silica were observed. The transition alumina of the order of 1 nm developed very small crystallites. The shock-induced decomposition of mullite to alumina and silica is similar to shock transformations occurring in the structurally similar alumina silicates andalusite and silimanite.

Quantitative characterization of mullite by ^{27}Al NMR

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A recent development of ^{27}Al MAS NMR (MAS Magic Angle Sample Spinning) called Satellite Transition Spectroscopy [1] enables a distinct progress for quantitative investigations of crystalline and amorphous solids. Satellite Transition Spectroscopy is nothing else than the standard MAS experiment. However, rather than observing the so-called central transition (CT) MAS spectrum, the MAS spinning sidebands of the inner satellite transitions are acquired. The advantages of this new approach are explained and verified by several examples.

^{27}Al NMR Satellite Transition Spectroscopy has been used for a quantitative investigation of the microstructure of polycrystalline 2/1-type mullite ($\gg 76 \text{ wt}\% \text{ Al}_2\text{O}_3$, $24 \text{ wt}\% \text{ SiO}_2$) [2] and 3/2-type mullite ($\gg 72 \text{ wt}\% \text{ Al}_2\text{O}_3$, $28 \text{ wt}\% \text{ SiO}_2$). Using this method the chemical shifts, quadrupole interaction parameters and relative amount of Al in the various coordination polyhedra have been obtained with high accuracy. The improved spectral resolution of the ^{27}Al MAS spinning sidebands of the inner satellite transitions allows the unambiguous detection of three different AlO_4 units. The three AlO_4 -resonances with isotropic chemical shifts at 68 ppm, 53 ppm and 45 ppm are associated with AlO_4 polyhedra in the tetrahedral double chains ($\text{AlO}_4(\text{T})$), the tetrahedra adjacent to the oxygen vacancies ($\text{AlO}_4(\text{T}^*)$) and the tetrahedra $\text{AlO}_4(\text{T})$ linked by Oc^* with $\text{AlO}_4(\text{T}^*)$, respectively. Our NMR study of a polycrystalline sample supports the results of previous single crystal studies of Angel et al. [3], especially the exclusion of silicon from the tetrahedral sites linked by Oc^* in 2/1 mullite.

- [1] C. Jäger, Satellite Transition Spectroscopy, in: *NMR Basic Principles and Progress* 31 (1994) 135, Springer Verlag, Berlin Heidelberg 1994
- [2] G. Kunath-Fandrei, C. Jäger, P. Rehak, S. Steuernagel, H. Schneider, submitted to: *Solid State Nucl. Magn. Reson.* (1994)
- [3] R.J. Angel, R.K. McMullan, and C.T. Prewitt, *American Mineralogist* 76, 332 (1991)

Oxide ceramic matrix composite for aerospace applications

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Continuous fiber reinforced ceramics combine the advantages of monolithic ceramics such as high temperature resistance and low density with the damage tolerance, i.e. low brittleness of composites. A new composite was developed based on Al-Si-B-O (Nextel) fibers and a multiphase matrix containing mullite as a major constituent. The composite is manufactured by infiltration of fibers with a slurry containing a diluted polymer and mullite powder, curing in an autoclave and subsequent heat treatment with pyrolysis of the polymer.

A variety of tests demonstrated that the material can be used in oxidizing atmosphere (air) up to a temperature of about 1000°C. Long term stability was shown for 10 000 hours. The high damage tolerance was proven by mechanical tests which revealed non-brittle fracture behaviour with elongations up to 0.5%. Because of the unique properties and the ability to produce complex and thin walled structures, this light weight material is well suited for hot aerospace components. One component now under development is a ceramic exhaust tube for aeroengines, that saves half of the weight compared to the standard metal components at similar costs. Since 1992 a prototype tube was tested in a DO 228 aircraft under flight conditions.

Single phase and diphasic aerogels and xerogels of mullite: Mechanism of crystallization and densification

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Single phase mullite composition gels have been synthesized using tetraethoxysilane [$\text{Si}(\text{OC}_2\text{H}_5)_4$] and aluminum nitrate nonahydrate as precursors. Diphasic mullite gels have been prepared using colloidal silica and boehmite as precursors. Xerogels and aerogels of both the above gels have been obtained by ordinary drying in air and critical point drying in methanol, respectively. Single phase xerogels show an intense exothermic peak at about 980°C while their counterparts, aerogels, do not show any detectable exotherm by differential thermal analysis (DTA). These results suggest that the structure of single phase gels changed during critical point drying and the structural changes as investigated by solid-state ^{27}Al MAS NMR will be presented. No differences between diphasic xerogels and aerogels could be detected by DTA because there was little or no effect of drying on the discrete silica and alumina phases. Crystallization and densification appear to be simultaneous processes in diphasic mullite gels which show identity of colloidal particles up to the crystallization of mullite. Nucleation of mullite is postulated to occur at the interface of $\text{SiO}_2/\delta\text{-Al}_2\text{O}_3$ phases in the diphasic gels.

Sintering and annealing of mullite/zirconia composites prepared by reaction sintering

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Two types of zirconia/mullite composites were prepared by reaction sintering of zircon and alumina (RS2) and that of silica, alumina and zirconia (RS3). Chemical composition of mullite and incorporation of ZrO_2 in the mullite formed under various firing and annealing conditions were investigated from lattice constant of mullite and by chemical analysis using transmission electron microscope (AEM). The composites were prepared by conventional process through mixing of the respective powders, ball milling, forming and sintering at 1570-1635°C. The RS2 samples fired at 1635°C for 12h were annealed at 1520-1635°C for 12 - 144 h.

As shown in Fig. 1, mullites formed in the RS2 were richer in Al_2O_3 composition than those in the RS3. Mullites formed in the higher temperature showed trend to incorporate ZrO_2 . These results implied existence of amorphous SiO_2 in the RS2 and it was found in the grain boundaries by the AEM observations. Fig. 2 shows the relation of the length of a-axis and b-axis of mullite in the RS2 fired at 1635°C for various durations. As longer the duration by 12 h, the data moved parallel to the pure mullite line toward Al_2O_3 -rich composition. Then, the data moved toward the pure mullite line by only changing the length of a-axis over 12 h duration and approached to pure mullite with 63 mol% Al_2O_3 . According to this change in mullite grain growth was observed in the microstructure. Annealing at 1570°C caused the data shift toward pure mullite with 60 mol% Al_2O_3 as longer the duration. Mullites formed in the RS2 were found to be in transient state even when they were formed at high temperature unless they were fired long duration.

Mullite/zirconia composites prepared by reaction sintering of zircon and alumina were found to show much larger variation in the composition of mullite than those of silica, alumina and zirconia and were considered to be necessary to shift the bulk composition as Al_2O_3 -rich to avoid amorphous SiO_2 formation in the grain boundaries.

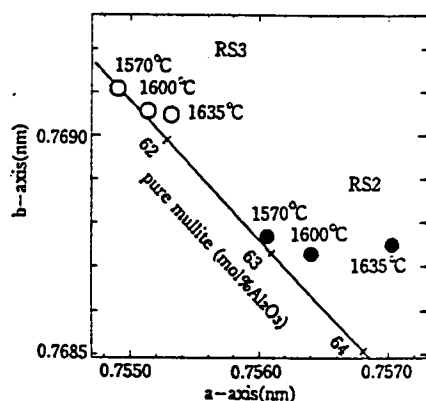


Fig. 1 Relation between a- and b-axes of mullite in the composites fired at various temperatures for 12 h.

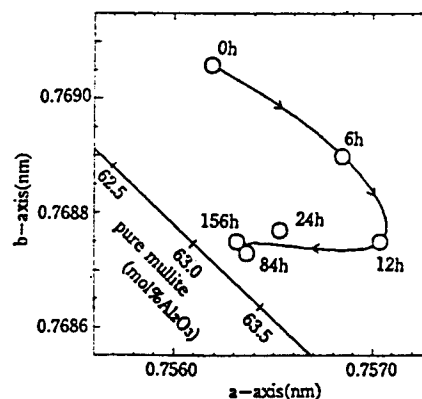


Fig. 2 Relation between a- and b-axes in the RS2 fired at 1635°C for various durations.

Thermomechanical behaviour of mullite-X sialon composites

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Mullite-X sialon composites were prepared by hot pressing starting from different precursors.

One route consists in reaction sintering of silicon nitride and an amorphous alumino-silicate synthesised by sol-gel. The second route is the direct sintering of carbothermally nitrated powders. Various ratios of X sialon/mullite were assessed.

The microstructure analysis of dense materials revealed that carbonitridation leads to composites containing a large amount of glassy phase and showing many defects resulting in a bad corrosion resistance during chemical etching and in poor mechanical properties. Composites prepared by reaction sintering show a better behaviour. Mechanical resistance at room temperature is comparable to mullite matrix ($\sigma_f = 300$ MPa, $K_{Ic} = 3$ MPa $\sqrt{m}$). However, the mechanical properties decrease from 25 to 600°C, as a consequence of sub-critical crack growth ($n = 15$ at RT and 8.7 at 600°C). At higher temperature, healing of defects by oxidation of X sialon phase leads to an increase of mechanical properties. Similar behaviour has already been observed for some silicon nitride ceramics. Some preliminary tests gave evidence of a very high creep resistance in comparison with monolithic mullite: $\dot{\epsilon} = 1.610^{-9}$ s⁻¹ and 1.110^{-9} s⁻¹ at 1200°C for composite and monolithic mullite, respectively.

The effect of reaction atmospheres on the formation of mullite from kaolinite

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In addition to its importance as a high-technology ceramic, mullite is also an intermediate phase in the formation of non-oxide ceramics (sialons) by carbothermal reduction of clay minerals. This reaction involves the formation of mullite under non-oxidising atmospheres and in the presence of carbon. The effect of eight different reaction atmospheres on mullite formation from kaolinite in the presence and absence of carbon was studied by XRD, ^{27}Al and ^{29}Si MAS NMR. The amount of mullite formed at 1200°C is generally greater under vacuum and reducing atmospheres, but the precise effect of the atmosphere can be modified by the presence of carbon. Vacuum and reducing atmospheres also produce mullites of composition nearer 3:2 than 2:1 (estimated from unit cell measurements) and containing higher proportions of tetrahedral Al associated with an oxygen defect (estimated from NMR measurements). Reaction systems containing either nitrogen or ammonia in the presence of carbon show NMR evidence of previously unreported early stage formation of Si-O-N bonds. Thermodynamic calculations are discussed which clarify details of the complex interactions between the aluminosilicate, carbon and the various gas atmospheres.

Anisotropic grain growth of mullite

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Anisotropic grain growth in a sol gel-derived mullite was investigated as a function of sol gel preparation method, mullite whisker seeding, and boria concentration. The precursor gels were prepared from either a colloidal boehmite-silica sol or a polymeric aluminum nitrate-tetraethoxysilane sol. The addition of acicular mullite seeds plus boria resulted in well faceted, anisotropic grains of $>20\text{ }\mu\text{m}$ length and $\sim 3\text{ }\mu\text{m}$ diameter in both gels. Pore elimination in the mullite is discussed in terms of the relative rates of mullite crystallization, sintering and anisotropic grain growth. Anisotropic grain growth in the mullite system is described in terms of transport phenomena and grain growth kinetics.

Germanium mullite: Structure and vibrational spectroscopy

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The $\text{Al}_2\text{O}_3\text{-GeO}_2$ and $\text{Al}_2\text{O}_3\text{-SiO}_2$ phase diagrams exhibit common features. In particular, a mullite phase with an extended range is found in both systems. However, Al and Ge mullites differ for the composition and the temperature of their existence domain. The substitution of silicium by germanium strongly decreases the fractarity and hence helps to densify mullite composites [1]. The mullite phase is the only alumino-silicate formed at atmospheric pressure whereas two other compounds exist with germanium: Al_2GeO_5 (isostructural with the high-pressure silicate kyanite) and $\text{Al}_2\text{Ge}_2\text{O}_7$ [2-3].

Raman spectra of these compounds will be discussed and interpreted in relation with structural modifications and order-disorder phenomena depending on the non-stoichiometry. The replacement of Si by Ge and Al by Ga is used for the assignment of vibrational bands.

A comparison is made with the spectra of amorphous gels and glasses prepared by slow hydrolysis polycondensation of aluminum and germanium alkoxide mixtures.

[1] Ph. Colomban and E. Mouchon, this meeting

[2] M. Perez y Jorba, *Rev. Int. Hautes Temp. Réfract.*, **6**, 283 (1969)

[3] V. Agafonov, A. Kahn, D. Michel and M. Perez y Jorba, *J. Solid State Chem.*, **6**, 402 (1986)

Mullite-silicoaluminate glassy matrix layered substrates by reactive coating

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The interfacial reaction between alumina and kaolinite has been studied in kaolin-Al₂O₃ layered substrates obtained by sequential slip casting at 1650°C. Two kinds of mullite have been identified: a) 2:1 mullite layer with ≈ 2 mm thickness at the alumina-kaolinite interface and b) needle like 3:2 mullite randomly distributed in a glassy matrix with mullite-silica eutectic composition.

Taking into account these results, low permittivity value substrates for electronic applications were designed.

These layered substrates were obtained by reactive coating of alumina on a preheated kaolinite substrate at 1650°C. The sintered substrates are formed by a thin mullite layer ($<10\mu\text{m}$) at the surface and a bulk with silicoaluminate glassy matrix reinforced with mullite whiskers.

Characterization and sintering behaviour of a 2:1 alumina-silica gel

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Complete characterization of a 2:1 commercial alumina-silica gel has been performed. The evolution of this gel treated at different temperatures has been studied by XRD, SEM and TEM. For thermal treatments as high as 1800°C, it was not possible to obtain a single phase 2:1 mullite powder and Al₂O₃ secondary phase was always detected.

Dilatometric studies have been performed up to 1550°C. Dense samples have been obtained by pressureless sintering and hot pressing. The microstructure and the properties of these materials have been comparatively analyzed.

Effect of aging temperature for structure of mullite precursor prepared from tetraethoxysilane and aluminum nitrate in ethanol solution

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Since structure of mullite precursor in solution was considered to be important relating to the mullitization route study, structural change of mullite precursor in sol solution by aging under the various temperatures was investigated by ^{29}Si and ^{27}Al liquid-state NMR and small angle X-ray scattering (SAXS) methods. The sol solution was prepared by dissolving 0.24 mol/l of tetraethoxysilane (TEOS) and 0.72 mol/l of aluminum nitrate nonahydrate (AN) in ethanol. It was aged under the various temperatures of 25°, 40°, 50° and 60°C for 5 days.

As higher the aging temperature, polymerization of SiO_4 tetrahedra progressed and formed a framework structure. Since the peak of ^{29}Si NMR spectrum became very broad in the 60°C aged specimen, the formed framework was suggested to be largely distorted and irregular. On the other hand, no apparent structural change was detected in the coordination state of Al ions in the solution. The solubility of AN in ethanol largely increased by higher the aging temperature. The average sol particle size measured by the SAXS increased and the sol particles over 20 nm in size were observed in the specimen aged at 60°C. The main crystalline phase obtained by rapidly firing the specimens at 1000°C was mullite when the specimens were aged at 60°C whereas that was spinel phase when the specimens were aged at lower temperature than 60°C. The crystalline phases formed by firing at 1000°C were, therefore, concluded to depend largely on the aging temperature but not to depend largely on the aging time.

Structure of mullite precursor to cause direct mullitization at around 1000°C has been considered to be in a molecularly mixed state in SiO_2 and Al_2O_3 components, however, the structural state of the precursor prepared by TEOS and AN was found to be not in such a homogeneous state actually. The important points for mullite precursor to cause direct mullitization in this case were, therefore, concluded to be as follows: (1) Forming SiO_4 tetrahedral framework structure with Al ion in the opening of the framework, and (2) High solubility of Al ion for the solvent.

Mechanical properties of mullite materials

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A comprehensive high temperature (up to 1400°C) mechanical characterization under critical loading conditions has been performed on two mullite materials with different purity grades. The measured properties have been: modulus of rupture, modulus of elasticity and fracture toughness. The obtained values are analyzed as a function of microstructure and the main impurities present in both materials.

The influence of loading rate on the K_{Ic} values and its relation to the fracture surface features has been established at two temperatures of interest for this kind of materials (RT and 1300°C). According to this last analysis, the importance of loading rate on the fracture behaviour is evidenced.

Phase equilibria of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system: Role of solid state chemical reactions

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Disagreements in phase equilibria in the high- Al_2O_3 compositions of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system have appeared in the literature. Although details of the procedures followed are generally presented, attempts to explain and understand the reported differences have not been made. In the spirit of the workshop approach of this meeting, an analysis and a discussion of the reported results, on the basis of solid state reactions and thermodynamics, should lead to an understanding and explanation of the differences that have been reported.

The function of a phase equilibrium diagram is to present the chemical and structural compositions of the individual phases and mixtures of phases that form from a given chemical composition at a given temperature and gas composition (usually atmospheric). These assemblages presumably represent phase compositions in the lowest free energy state. Therefore, if the determination reactions were done correctly, only one diagram represents stable phase equilibria, and the others - metastable phase equilibria.

Normally, an investigator follows one of two reaction paths to determine phase equilibria:

1. The starting materials (equivalent to a given final composition) are homogenized at a high enough temperature to form a single liquid phase which is then heat-treated at a given temperature to obtain equilibrium phase compositions for that temperature by precipitation;
2. The starting materials in the form of powders are heat-treated at a given temperature to obtain the equilibrium phase composition by the solid state reaction route.

Logical comparative analyses of the results should lead to an understanding and identification of the stable phase equilibria. The qualitative approach with use of solid state chemical principles is most useful and applicable in reaching this goal.

Interpretation of mullite HREM images

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Order/disorder phenomena of oxygen vacancies and coupled cation shifts cause an incommensurate modulation of the mullite structure and have been investigated by HREM in the present paper.

To examine these phenomena, extensive HREM contrast simulations of simple supercell structure models throughout a range of defocus and thickness values have been performed to interpret contrast patterns of 200kV- and 300kV-HREM images of 3:2- and 2:1-mullite with beam directions parallel to [001], [010] and [100]. The calculations clearly indicate that contrast variations are correlated with enhanced vacancy concentrations. Further investigations with supercells consisting of more than 2000 atoms reveal a direct relationship between the intensity of the defect-induced changes and the vacancy concentration along the actual beam direction. Additionally applying image processing methods to digitized HREM images, it has been possible to determine domains with higher vacancy concentrations which exhibit a specific ordering scheme.

Summarizing the results, the ordering scheme of the ac-plane shows linear arrangements of vacancies along $\langle 102 \rangle$, with periods of $1.5a$ and $2c$. In comparison, the bc-plane exhibits arrangements parallel to $\langle 012 \rangle$ and $\langle 001 \rangle$ resulting in an average direction parallel to $\langle 013 \rangle$ with a period of $1.5b$ and a five to sixfold period along [001]. In contrast to HREM images of Al-rich mullites ($x \geq 0.48$) [1], it is obvious that the investigated mullites ($x=0.25$, $x=0.40$) do not show long-range ordered arrangements of the oxygen vacancies. In the ac- and bc-planes, short-range ordered domains with high vacancy concentrations are distributed in a matrix with a minor degree of order, already indicated by the diffuse shape of the satellite reflections and additional diffuse scattering throughout reciprocal space. Extension and distribution of these domains show a close dependence to the chemical composition.

Although distinct ordering directions have been determined from HREM images, there are still some questions concerning the 3-D arrangement of vacancies in mullite, since the image contrast changes occur due to a projection of various vacancy arrangements along the incident beam. A determination of the 3-D vacancy arrangement and possible correlations within and between individual domains can be carried out by applying computer-based videographic real structure simulations and reconstructions, presented in a second paper.

[1] Ylä-Jääski, J.; Nissen, H.-U. (1983). *Phys. Chem. Minerals* 10, 47-54.

Mullitization and densification of $(3\text{Al}_2\text{O}_3 + 2\text{SiO}_2)$ powder compacts microwave sintered

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Many studies have been recently devoted to microwave sintering of ceramics. Microwave treatments have been reported to lead to a decrease in the temperature of sintering. In alumina, the decrease could be as large as 400°C , which has suggested the existence of a „microwave effect“. The microwave effect has mostly studied in the case of densification, with no chemical reactions, but one can think that if it is not artefact it would affect chemical reactions as well. Very few studies have been carried out on microwave reaction-sintering. The present work was devoted to the preparation by reaction-sintering of mullite ceramics to compare the influence of conventional (3 kW electric furnace) and microwave (1.2 kW, 2.45 GHz microwave furnace) heat treatments.

Two tests were developed to calibrate temperature measurement in the microwave cavity. Quantitative X-ray diffraction experiments and SEM observations conducted on small specimens cut from samples treated by microwaves showed that those samples had been subjected to large thermal gradients during the reaction-sintering stage.

The study does not invalidate the possibility of a „microwave effect“, which would favor both reaction and densification. However, the decrease in temperature associated with such an effect is less than 50°C , which is much lower than what was claimed in the case of alumina. The gradients of temperature that are always present in microwave heated samples play a prominent role to explain the specificity of microwave sintering.

Time resolved fluorescence spectroscopy of Cr^{3+} in mullite

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Mullite containing up to 10 wt% Cr_2O_3 was investigated by time resolved fluorescence spectroscopy in a wide time range at 300K and 77K. Selective and non-selective excitations were used for the measurements. A strong deviation from an exponential decay was observed for all bands down to low temperature (22K), which was explained to be due to energy transfer between the different Cr^{3+} sites. The ${}^4\text{T}_1 \rightarrow {}^4\text{A}_2$, ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ and ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission bands were easily separated. Emitting level energies and decay times were used to determine Cr^{3+} ions in high field sites (HFS) and in low field sites (LFS). At least two families of Cr^{3+} can be distinguished in LFS. In addition to the HFS band at 14480 cm^{-1} band of Cr^{3+} ions a band at 14000 cm^{-1} with long decay time was observed. It is assigned to a family of intermediate field Cr^{3+} sites. The ${}^2\text{E}$ character of the emitting state of this band is retained despite its unusual low energy.

At high Cr_2O_3 contents Cr^{3+} ions occur almost in LFS only. These sites correspond to a ${}^4\text{T}_2$ level as lowest emitting state. The increase of the Cr_2O_3 content of mullite produces a preferential incorporation of Cr^{3+} ions at interstitial sites (LFS) together with a $\text{Cr}^{3+} \rightarrow \text{Al}^{3+}$ substitution on octahedral Al^{3+} (M(1)) sites (HFS).

Cr-doped mullite precursors

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Mullite precursor doped with 3 wt% Cr₂O₃ was investigated with X-ray diffractometry (XRD), electron paramagnetic resonance (EPR) and optical absorption spectroscopy. The main interest of the study was to characterize the structural development of the precursor at different temperatures prior to crystallization to mullite (< 1250°C).

The EPR measurements revealed different temperature controlled types of Cr short-range-orders for the precursor. The first temperature range is between 450 and 800°C with a characteristic Cr EPR signal at $g = 1.96$. Above 800°C and up to $\approx 1250^\circ\text{C}$ the Cr EPR signal is similar to that of glasses containing Cr. Above $\approx 1250^\circ\text{C}$ the typical Cr³⁺ spectrum of Cr-doped mullite arises. The precursor exhibits the EPR signals of Cr₂O₃ at temperatures between 800 and 1250°C.

EPR spectroscopy normally is sensitive to Cr³⁺ and Cr⁵⁺ only, while Cr²⁺ and Cr⁴⁺, though being paramagnetic, are rarely observed due to physical reasons. However, Cr ions, in the valence state between +2 and +6 can be detected by optical absorption spectroscopy. According to the optical absorption spectroscopy the precursor contains Cr⁶⁺, Cr⁵⁺, and Cr³⁺ in different concentrations depending on the calcination temperature. The amount of Cr⁶⁺ and Cr⁵⁺ gradually decreases with increasing temperature. At >1100°C Cr⁶⁺ and Cr⁵⁺ vanish and an optical absorption spectrum of Cr³⁺ similar to that of Cr-doped mullite appears.

Videographic simulations and reconstructions of the mullite real structure

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HREM investigations of mullite, obtained in a previous paper, indicate a complex ordering scheme of the oxygen vacancy distribution. Besides satellite reflections in $h0l$ - and $0kl$ -diffraction patterns, this scheme causes additional diffuse scattering phenomena in $hk^{1/4}$ -, $hk^{1/3}$ - and $hk^{1/2}$ -planes which have been determined by [1, 2]. Based on the videographic method, real structure simulations have been performed to explain some of the diffuse scattering phenomena.

Especially the $hk^{1/4}$ -plane is characterized by more or less circular shaped diffuse regions, centered at 10 - and 01 -positions. These regions are connected by additional diffuse streaks, running parallel to $\langle 110 \rangle^*$. The results of 2-D videographic real structure simulations yielded, that the ordering scheme can be described by definite vector correlations between the oxygen vacancies [3, 4, 5, 6]. The typical diffuse scattering phenomena are mainly caused by inter-vacancy vectors of the following directions: $\frac{1}{2}\langle 310 \rangle$, $\frac{1}{2}\langle 130 \rangle$, $\frac{1}{2}\langle 200 \rangle$, $\frac{1}{2}\langle 020 \rangle$.

Videographic image reconstructions [7] reveal the real structure of mullite to be consisting of "domains" with enhanced vacancy concentrations which show an ordering scheme and furthermore exhibit an additional specific correlation with each other. The sizes and arrangements of the domains are closely dependent on the actual chemical composition. In the range of $x = 0.4$ - 0.7 the domain size in the ac -projection is inversely proportional to the vacancy concentration. For higher x -values ($x \geq 0.7$) the domains occasionally form "twin boundaries", causing a splitting of the satellite reflections in the $h0l$ -diffraction pattern.

- [1] Tokonami, M.; Nakajima, Y.; Morimoto, N. (1980). *Acta Crystallogr.* A36, 270-276.
- [2] Welberry, T.R.; Withers, T.L. (1990). *Phys. Chem. Minerals* 17, 117-124.
- [3] Rahman, S.H. (1991). Habilitation, Universität Hannover.
- [4] Rahman, S.H.; Paulmann, C. (1991). *Optik Supplement* 4(88), 018.
- [5] Paulmann, C.; Rahman, S.H.; Weichert, H.-T. (1992). *EUREM92*, Granada, Spain, Vol. 2: 445-446.
- [6] Butler, B.D.; Welberry, T.R.; Withers, R.L. (1993). *Phys. Chem. Minerals* 20, 323-332.
- [7] Rahman, S.H. (1993). *Acta Crystallogr.* A49, 56-68.

IR-spectroscopical investigation of the lattice vibrations of 2:1 and 3:2 mullite

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First results of 2:1 mullite ($\text{Al}_2(\text{Al}_{2.8}\text{Si}_{1.2})\text{O}_{9.6}$) single crystal reflection measurements in the infrared spectral range are presented. The real and imaginary parts of the dielectric function were calculated using Kramers-Kronig analysis and were fitted using Lorentz oscillators. The spectra show strong anisotropic behaviour with a considerable larger number of modes for the $E//[100]$ and $E//[010]$ compared to the $E//[001]$ lattice direction. The results are explained using group theoretical assumptions for the space group Pbam of the average structure with the modes being assigned to 4-5 B_{1u} (z), 9-13 B_{2u} (y) and 9-13 B_{3u} (x) species. Details of the spectra can be explained with the assumption of two limiting cases of hypothetical ideal mullite structures. In particular, we are able to assign the compositional variations of the well known 1100 cm^{-1} mode(s) [1] evidently to the building units involved in the exchange reaction $2\text{Al}^{3+} + \text{L} = 2\text{Si}^{4+} + \text{O}^{2-}$. This result is supported comparing the single crystal spectra with absorption spectra of powdered samples of 2:1 and 3:2 mullites embedded in KBr disks.

[1] W.E. Cameron, 1977, *Am. Ceram. Soc. Bull.*, 56, 1003.

Fabrication of continuous fiber reinforced mullite matrix composites

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For the high-temperature applications in the oxidizing atmospheres, mullite is one of the best candidates among the high-performance ceramics. As its predecessors, mullite is brittle and needs to be reinforced in order to increase its damage-tolerance. Fabrication of continuous fiber reinforced ceramics which fundamentally display a high amount of volume shrinkage during green processing as well as during sintering has been always very difficult and requires application of sophisticated methods.

Reaction-bonding of metal powders has been suggested as a suitable method to process continuous fiber reinforced ceramics, in which case a near-net-shape production with a negligible volume change can be acquired. Reaction-bonded-silicon nitride (RBSN) and aluminium oxide (RBAO) are the best examples of the materials obtained with this method, and some studies have been devoted to fabricate mullite ceramics with this method. Mullite formation has been reported to start at about 1450°C, however to achieve a reasonable amount of mullite, long holding times (5h) and higher temperatures (1550°C) are required. Although the method is promising for fabrication of continuous fiber reinforced mullite ceramics, the polymer-derived oxide-based fibers are stable only up to 1400°C. Above about 1400°C, an extreme grain-growth and consequently a sharp decrease in the tensile strength of the fibers are observed. Therefore, the final fabrication temperature and holding time of the process for such ceramics should not exit 1500°C and 1 hour, respectively.

In this context, fabrication of continuous fiber reinforced mullite matrix composites by reaction-bonding-method is carried out by employing an optimized mixture of metal and precursor powders. Before mixing, the powders are individually milled and homogenized. The milling process is rather crucial for reducing the oxidation and mullitization kinetics. The oxidation and reaction conditions are simulated by DSC measurements which are coupled with SEM / XRD observations. Mullite formation begins already at about 1200°C and a substantial amount of mullite, coexisting with corundum is present at 1500°C after 1h of processing. The interfacial reactions between the fiber and the matrix are very important in order to process composites with good properties. Therefore, fibers are coated with an oxide-based coating by means of a high frequency sputtering. Microstructural observations by SEM are conducted in order to establish the properties of the interface and to optimize the processing conditions.

Synthesis and microstructural development of chromium doped mullite ceramics

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Mullite recently has become a good candidate for interconnective substrate materials. For such applications, the most desired properties are lower dielectric constant, lower thermal expansion coefficient and relatively good mechanical properties. Sol-gel derived high purity mullite precursor powders have very fine uniform particles and are easy to sinter to full density at lower temperatures. Incorporation of Cr^{3+} into the mullite lattice should improve the properties of mullite, so that ceramics with appropriate properties for substrates can be produced.

Mullite precursor powders were synthesized from TEOS and aluminium-sec-butylate and were doped with Cr_2O_3 in proportions of 1, 3, 6 and 9 wt% by using chromium-acetylacetonate. Chromium incorporation resulted in a progressive change in the microstructure of the mullite ceramics. Microstructural and compositional development of the doped- and undoped-ceramics were investigated by SEM, TEM, and XRD techniques. Influence of incorporation was discussed in terms of lattice parameters, thermal expansion coefficient and high temperature mechanical properties.

Microstructure and strength of technical aluminium silicate fibers

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Aluminium silicate fibers are used in a wide variety of applications, e.g. furnace seals, thermocouple insulation or as reinforcement of high performance ceramic composites. In the presented study two commercial aluminium silicate fibers were investigated by means of TEM, XRD, and single fiber tensile strength testing: Nextel 440 (3M) with a bulk composition of 70 wt% Al_2O_3 , 28% SiO_2 , 2% B_2O_3 and Altex 2K (Sumitomo Chemical Co.) with 72 wt% Al_2O_3 and 28% SiO_2 .

Microstructural development and phase transformation during heat treatment and their influence on mechanical properties was of particular interest. As-received Nextel fibers consist of nanometer sized $\gamma\text{-Al}_2\text{O}_3$; the tensile strength is 2100 MPa with 4.9 Weibull modulus. Up to 1050°C no change in microstructure and strength was observed. In the temperature range between 1100 and 1200°C $\gamma\text{-Al}_2\text{O}_3$ -nanocrystals transform to mullite. Transformation kinetics are determined by quantitative X-ray phase analysis. Firing at 1200°C leads to complete transformation to mullite of 50 to 150 nm grain size, and tensile strength of the fibers decreases to $\approx$ 1600 MPa. Between 1200 and 1400°C mullite grains coarsen moderately and polygonization of the crystals is observed, and the tensile strength decreases to a value of 1100 MPa at 1400°C. Above 1500°C secondary grain growth leads to micron-sized mullite crystals.

Altex fiber starting material consists of mullite with a grain size of 50 to 400 nm. The tensile strength is 1250 MPa with a Weibull modulus of 6.1. Up to 1400°C only slight coarsening of the mullite crystals is observed and tensile strength remains nearly constant. Microstructure and strength of the as-received Altex fiber are similar to those of Nextel fibers heat-treated at 1400°C.

Mechanical properties of high purity mullite at elevated temperatures

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Fracture strengths, creep resistance, and microstructures of high purity mullite body sintered between 1650°C and 1750°C were studied. Fracture strengths at 1400°C and 1500°C decreased, but fracture strength at 1600°C and creep resistance increased with sintering temperature. Application of high purity mullite for conveyor belt furnace was also introduced.

Formation of Al_2O_3 -Al composites by reactive metal infiltration of mullite

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Ceramic-metal composites have been made to near-net-shape by infiltrating reactive metals into dense ceramic preforms. In low $p(\text{O}_2)$ atmospheres and at temperatures above about 900°C , molten Al reduces mullite to produce Al_2O_3 and silicon. For Al, the general form of the reaction is $(y+2)\text{Al} + (3/x)\text{MO}_x = \text{Al}_2\text{O}_3 + \text{M}_{3/x}\text{Al}_y$ where MO_x is an oxide that is wet by molten Al and for which the Gibbs energy for reaction with Al is strongly negative. The Al-mullite reaction has a $\Delta G^\circ(1200\text{K})$ of -967 kJ/mol and a theoretical volume change on reaction of less than 1%. Experiments with commercial mullite containing a SiO_2 grain boundary phase average less than 2% volume change on reaction. Property measurements show that the composite has a modulus and expansion coefficient near that for Al_2O_3 , and fracture toughness of 6 to $9 \text{ MPa}\cdot\text{m}^{1/2}$. The infiltration reaction produces a fine-grained microstructure of mutually-interconnected oxide and metal phases. Reaction layer thickness varies as the square root of time, which allows metal-ceramic composite coatings to be fabricated by controlling the infiltration time.

Thermodynamic calculations indicated that other compositional systems also are candidates for in-situ reaction synthesis. The thermodynamic predictions have been tested by sintering mixtures of ceramic and metal powders and analyzing the products by X-ray diffraction. Reactive metal infiltration may be a general route to composite synthesis with the prospect for near-net-shape processing.

Phase transformation and grain refinement of submicron ZrO_2 in zirconia/mullite composites

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ZrO_2 /mullite composites (ZMC) with homogeneously dispersed ZrO_2 grains were prepared either by hot-pressing or by pressureless sintering. The ZMCs were obtained from three different sources, including ground crystalline or dissociated zircon powders reaction sintered with alumina, or a mixture of colloidal pseudo-boehmite ($\gamma\text{-AlOOH}$), zirconia, and silicic acid gel. The sintered composites in various stages were analyzed by using XRD, SEM and analytical TEM. Different types and sizes of ZrO_2 grains in ZMC, especially the one prepared from sol-gel methods which grew the ZrO_2 from near tens of nanometer to submicron size. The effects of addition of ultra-fine ZrO_2 on retarding the grain growth of mullite, increasing the amount of metastable t-phase ZrO_2 and the growth mechanism of fine ZrO_2 grains will be reported.

Local structural information of mullite obtained from diffuse X-ray scattering

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A complete description of the structure of mullite cannot be obtained from information provided by the usual average crystal structure analyses which use Bragg diffraction data only. This is because Bragg data contain only information regarding one-site properties such as the occupancies, atom positions, and mean-squared displacements of atoms on the various crystal lattice sites and do not contain any information about the distribution of the oxygen vacancies and the accompanying cation and anion shifts. The degree to which the oxygen vacancies and atomic displacements are ordered over short and intermediate ranges is evidenced by the very structured diffuse scattering, that is observed in diffraction patterns of mullite. Such diffuse X-ray scattering occurs when there are local deviations of the structure from the long-range average and contains a wealth of information regarding local chemical and displacement correlations. Unfortunately, the extraction of this information has proved to be a difficult task for even relatively simple systems and success in obtaining such information has been mostly limited to alloys and simple oxides.

We have found it useful for more complex materials such as Mullite to employ various atomic modelling methods (typically based on Monte Carlo methods) where the diffraction patterns of several plausible models are computed and compared with the diffraction data. We applied such methods to an $x=0.4$ mullite. In this earlier study it was found that nearly all of the observed diffraction features could be reproduced from simple 2D models of **ab** layers of the mullite structure. Although subsequent 3D modelling was somewhat less successful these models were useful in providing a qualitative understanding of the local interactions controlling the ordering of the oxygen vacancies in mullite and were the first to address all the available 3D diffuse diffraction data. Most importantly, *the study demonstrated that it is possible to describe all of the prominent diffuse features with a model that contains only a description of the oxygen vacancy ordering with the $T \rightarrow T^*$ cation and $O_c \rightarrow O_c^*$ oxygen shifts following in a predictable way from this ordering.*

This fact that the diffraction pattern can be described in terms of a single set of oxygen-vacancy ordering parameters indicates that it is possible to formulate a mathematical description of the diffuse intensity from mullite which contains only the oxygen-vacancy correlations as free parameters. It is possible then using appropriate analysis techniques for the data to yield directly these short-range correlations and provide a more complete description of the structure of mullite than has previously been reported. In the present study, such a mathematical description has been derived, and least-squares used to obtain a fit to the observed data.