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Electrostatically Deposited Surface Seeding and Promotion of Crystallization of Sol-gel Derived $LaAl_{11}O_{18}$ Coating on Oxide Fibers

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Abstract

For the use as interface material in oxide/oxide-continuous fiber-reinforced composites, $LaAl_{11}O_{18}$-fiber coatings have been developed. The magnetoplumbite structure has an attractive property, due to the presence of mechanically weak cleavage planes between the stacked spinel blocks. Thus, easy cleavage or crack deflection resulting in reduction in energy release rate at the fiber/matrix interface can be provided during the fracture of an oxide/oxide-composite. The synthesis of $LaAl_{11}O_{18}$ via sol–gel route required high processing temperature which causes the instability of fibers. An optimization of the process, in terms of elimination of occurrence of an intermediate phase and promotion of complete crystallization at temperatures $\leq 1200\,^{\circ}C$ was necessary. This study describes a method to obtain continuous and well-crystallized $LaAl_{11}O_{18}$ fiber-coatings at temperatures as low as 1100 °C, benefiting from both the sol–gel-process and the seeding concept. © *1999 Elsevier Science Ltd. All rights reserved.*

Keywords: coatings, fibre-coatings, $LaAl_{11}O_{18}$, seeding, sol–gel processes.

1 Introduction

The use of new materials in aircraft engines provides distinct economical and ecological advantages. Oxide/oxide-fiber-reinforced composites are one of the most attractive materials for this purpose, relying on their oxidation resistance and favourable high-temperature properties. However, due to the high diffusion rates, in oxide/oxide-systems, the strong interfacial reactions and/or bonding between fiber and matrix are unavoidable. Therefore, there is an essential need to develop an interfacial material which provides crack deflection and/or crack bridging at or around the fiber, eventually leading to the fiber pull-out.[1–5]

Lanthanum hexaluminate, $LaAl_{11}O_{18}$, is an interesting interface material for oxide/oxide-composites. Its magnetoplumbite structure yields weakly mirror-plane bonded stacking of spinel blocks.[6] This is in turn enables fracture-toughening to occur at the fiber/matrix interface by cleavage and crack deflection along these weak planes.[7,8,10] Sol-gel processing of this interface material has presented some difficulties, mainly due to its crystallization behaviour.[8,9] The formation of an intermediate $LaAlO_3$ phase at about 900 °C results in a two-phase material at 1200 °C. Further heating to 1400 °C is required in order to eliminate the $LaAlO_3$ phase and obtain pure $LaAl_{11}O_{18}$.[8] The use of organic starting materials and the optimization of the sol–gel process may help to overcome the intermediate crystallization of $LaAlO_3$.[9] $LaAl_{11}O_{18}$, obtained from organic precursors, however, is somewhat amorphous at 1200 °C and full-crystallization requires temperatures as high as 1400 °C. For fiber coatings, such temperatures are extremely high and can cause serious fiber damage.

Another possibility is to improve the sol–gel-chemistry and utilize seeding. It is known that in many sol–gel-systems, the addition of 2–5 wt% seeds into the sol prior to gel formation promotes the crystallization of the desired phase.[11,12] Electrostatic forces are created through opposite surface

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charges of particles. This latter technique has been often used to coat fibers, cloths and whiskers with fibrous boehmite,[13] α-Al_2O_3[14] and mullite[15] coatings. Surface charge modification has been obtained by employment of an adsorbing polymer, namely ammonium polymethacrylate,[15] polyacrylate[14] or polyvinylsulphate.[13] In this case, the aim was to exclude problems related to the wetting of fibers in tows, the use of high viscosity liquid precursors or sols and bridging of fibers. Although this method has worked fine for relatively large individual fiber filaments (Textron-SiC-fibers of 125 μm,[14] for small diameter fibers in a tow, the deposition was incomplete (less than 40%) with discrete islands of particles developing rather than uniform monolayer coverage.[15] A repetitive coating sequence in order to improve the coverage, may result in the loss of previous deposition, due to change of the surface charge of the previous coating. Furthermore, the bonding of the coating on the surface with this method is not very strong, resulting in partial loss of the layer during handling and composite processing. Coverage was poor at tow–tow crossover points, especially in the coating of cloth.[15]

This study combines two techniques in order to achieve adequately covered and fully crystallized $LaAl_{11}O_{18}$ coatings on oxide fibers. The aim is to coat the fibers first with a monolayer of fine crystalline $LaAl_{11}O_{18}$-particles, followed by a homogeneous sol which promptly yields $LaAl_{11}O_{18}$, without crystallizing into $LaAlO_3$. The fine $LaAl_{11}O_{18}$ seeds are expected to promote the crystallization of the $LaAl_{11}O_{18}$-sol at temperatures lower than that where fiber damage occurs ($< 1200\,^{\circ}C$).

2 Experimental

2.1 Sol preparation

The procedure for synthesizing lanthanum hexaluminate ($LaAl_{11}O_{18}$) sol is outlined in Fig. 1. The starting materials used in this study were lanthanum acetylacetonate hydrate, $[CH_3COCCH=C(O\text{-})CH_3]_3La.x.H_2O$, (Aldrich, Milwaukee, WI) and aluminum tri-sec-butoxide $[C_2H_5CH(CH_3)O]_3Al$ (Aldrich, Milwaukee, WI). Initially, a stoichiometric amount of lanthanum acetylacetonate was dissolved in 2-methoxyethanol (2-MOE) in a flask and distilled to remove water of hydration. The distillation process was repeated three times with the addition of fresh 2-MOE to ensure complete dehydration. The total volume of the solution after distillation was reduced to about 100 ml and refluxed in an argon atmosphere at 125 °C for 6 h. A stoichiometric amount of aluminum tri-sec-butoxide was added to the anhydrous lanthanum precursor solution and refluxed in 2-MOE at 125 °C for 8 h to form the lanthanum hexaluminate precursor solution. This precursor solution was cooled to room temperature and adjusted to a pH of 10 using nitric acid.

2.2 Coating of fibers

The flow chart for the seed coating of fibers is shown in Fig. 2. Nextel 720 tows are desized by washing with ethanol overnight. In the case of continuous coating applications, it is also common to heat fibers at 1100 °C for a few seconds while pulling the fiber tows through a tube furnace in order to remove the sizing. Prior to seed-coating, the surface characteristics of the $LaAl_{11}O_{18}$-particles and Nextel 720 fibers were determined by comparing particle mobility (measured with a zeta potentiometer, Coulter Delsa 440SX, Amherst, MA) as a function of pH and/or the concentration of the polyacrylate solution. The pH adjustment

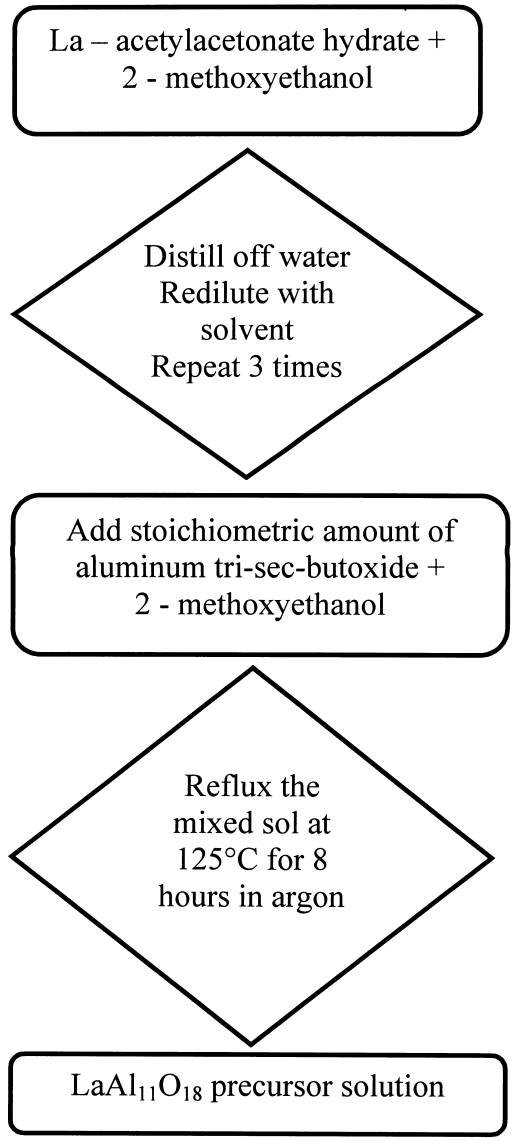

Fig. 1. Flow chart of sol–gel synthesis of $LaAl_{11}O_{18}$-sol.

was carried out with either concentrated acetic acid or with ammonium hydroxide (NH_4OH). The isolectric point (IEP) defines the pH above which the mobility (zeta potential) is negative and below which it is positive.

Seed particles of $LaAl_{11}O_{18}$ were prepared by heat-treating the sol–gel-derived powder at 1650 °C for 5 h and ball-milling for 36 h with alumina balls. Ball-milled and fully crystalline $LaAl_{11}O_{18}$ particles (5–10 g L^{-1}) were dispersed in water at pH 5 (adjusted by acetic acid). After this suspension was allowed to settle for 4 h, the fine portion which remained suspended in the liquid part was collected and used for seed-coating of fiber tows. SEM investigations of the seeds collected from the suspension showed that the particle sizes ranged between 0·3 to 5 μm, although the particles were mostly in the range of 1–2 μm. The morphology of the seeds was mixed with some elongated plate-like and some equiaxed grains.

Surface-modified Nextel 720 fibers were dried and subsequently submerged for several minutes into the seed suspension (suspension maintained through stirring). Upon removal from the suspension, the fibers were dried and then immersed into the La, Al-sol for film-coating. Seed-coated fibers were also investigated by SEM. These seeds displayed a finer particle size (0·3–1·5 μm) with a similar morphology as reported above (Fig. 3).

To promote immediate gel formation of the film, the dip-coated fibers were pulled through a water bath. This film-coating process could be repeated in order to obtain a certain thickness. In this study, dip-coating was carried out three repetitive sequences with a sol of relatively low viscosity ($4{\cdot}5-5\times10^{-3}$ Pa.s), to obtain a sufficient coating thickness. At this stage, the fiber tows were mantel-coated and dried overnight in a vacuum oven at 200 °C. The final fiber-coating thickness was achieved after 1 h of heat-treatment at 1200 °C.

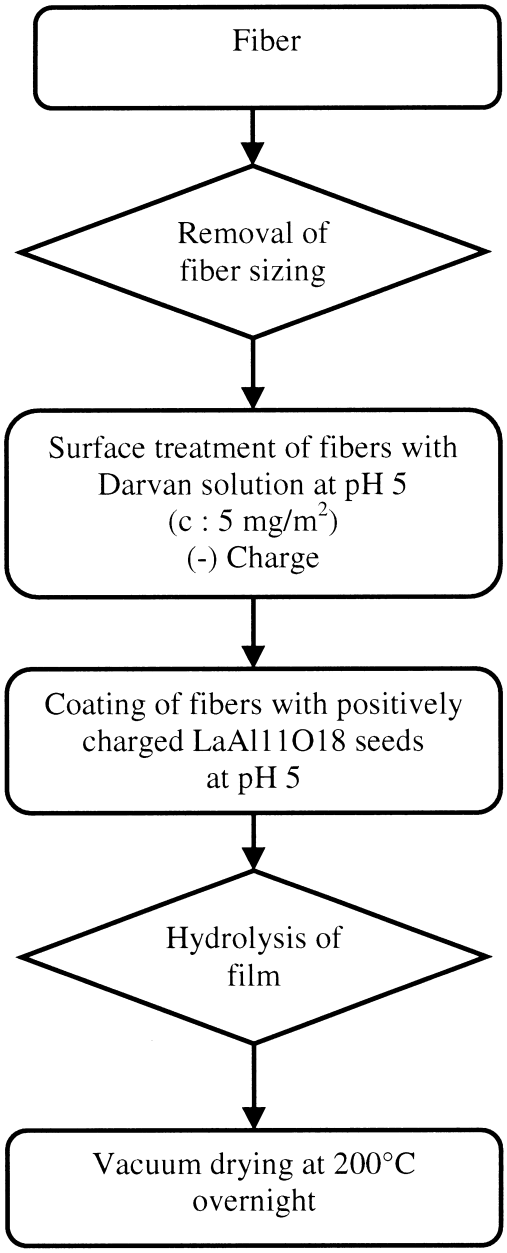

Fig. 2. Flow chart for seeding-coating of fibers with $LaAl_{11}O_{18}$ on Nextel 720-fibers.

2.3 Characterization of coated fibers and seeded gels

After seed coating, film coating and calcination at 1200 °C, fibers were individually characterized by field-emission scanning (FE-SEM, Leo) and scanning electron microscopes (SEM-ISI DS 130, Akashi Beam Technology Corporation, Tokyo, Japan) and by energy dispersive X-ray spectroscopy (EDS). Seeded gels were calcined for 1 h at temperatures varying from 200 to 1200 °C. Coated and heat-treated fibers and seeded gels were X-rayed at 10–80° 2Θ with an X-ray diffractometer (Model DMC 105, SCINTAG, Santa Clara, CA) with Ni-filtered CuKα radiation. Particle size measurement of the seeds was carried out by SEM.

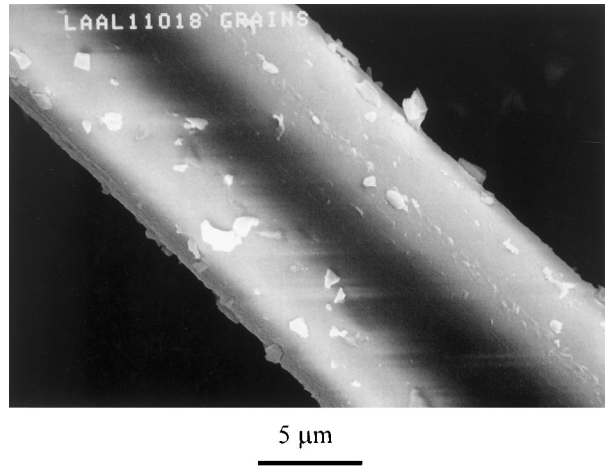

Fig. 3. Scanning electron micrograph of the electrostatically seed-coated fiber.

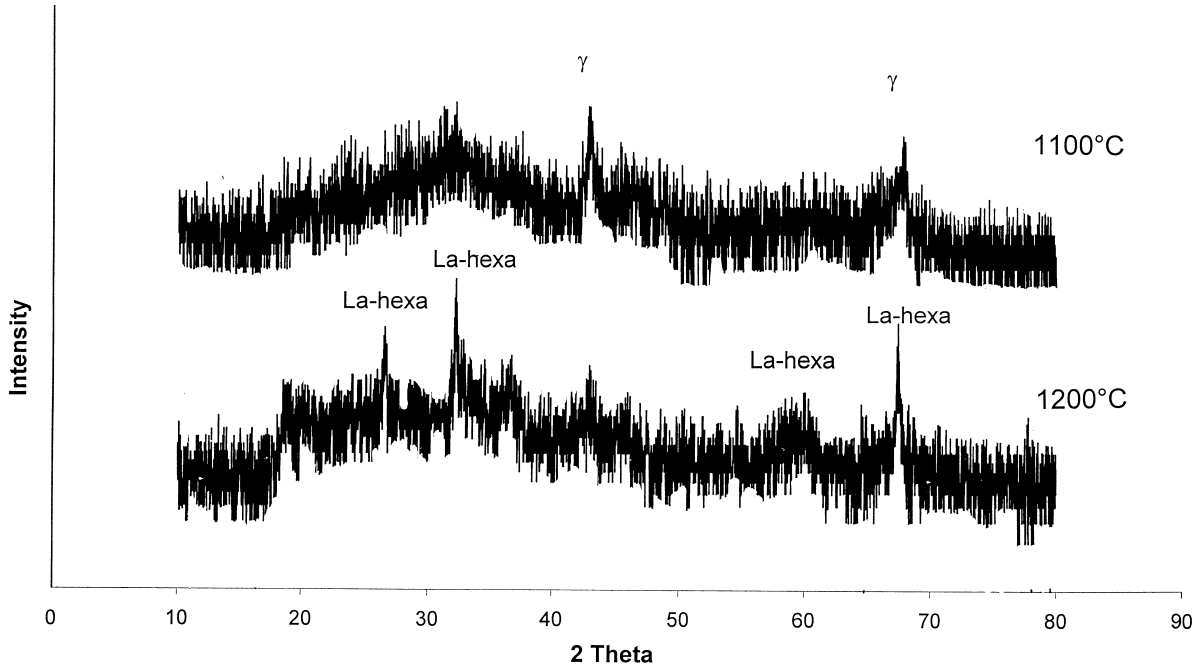

Fig. 4. Crystallization behaviour of the gels synthesized using lanthanum acetylacetonate and aluminum tri-sec-butoxide starting materials at temperatures 1100 and 1200 °C (unseeded).

3 Results

3.1 Sol preparation

Fig. 4 shows the crystallization behaviour of the gels synthesized using lanthanum acetylacetonate and aluminum tri-sec-butoxide starting materials unseeded at temperatures of 1100 and 1200 °C. At 1100 °C, there exists only weakly crystalline γ-Al_2O_3. Crystallization of $LaAl_{11}O_{18}$ occurs at about 1200 °C, without intermediate formation of $LaAlO_3$. However, the presence of a high background and the absence of the strongest peak in $LaAl_{11}O_{18}$ (2Θ 33·94°) indicates that the degree of crystallization is fairly low.

3.2 Coating of fibers and vacuum-drying

The mobility of $LaAl_{11}O_{18}$-seeds and Nextel 720 fibers in distilled water as a function of pH is given in Fig. 5. The surfaces of seeds and fibers display similar characteristics under these conditions, both having an IEP-point between $pH_{IEP} = 6{\cdot}8$ and 7·5. Therefore, it was necessary to modify the surface charges of one of the components in order to provide a strong electrostatic attraction between the particles and the fiber. To impart a negative charge on the fiber surface, the fiber tow was immersed in an ammonium polyacrylate solution (Darvan 821-A, Vanderbilt Co., Norwalk, CT) for adsorption of the polymer and consequent modification of the

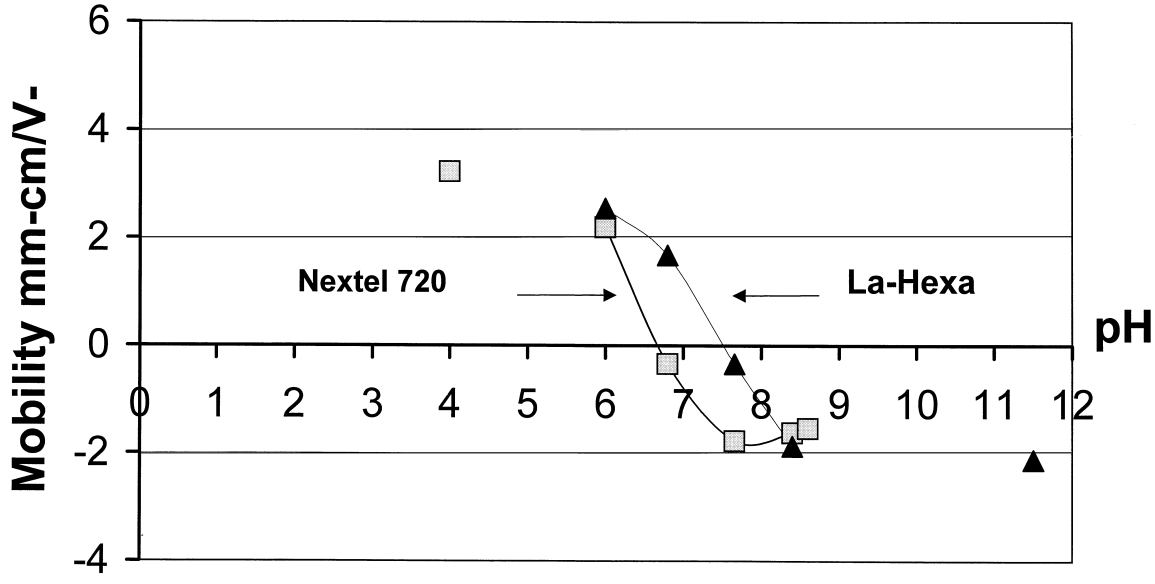

Fig. 5. Mobility of $LaAl_{11}O_{18}$-seeds and the Nextel 720 fibers in distilled water as a function of pH.

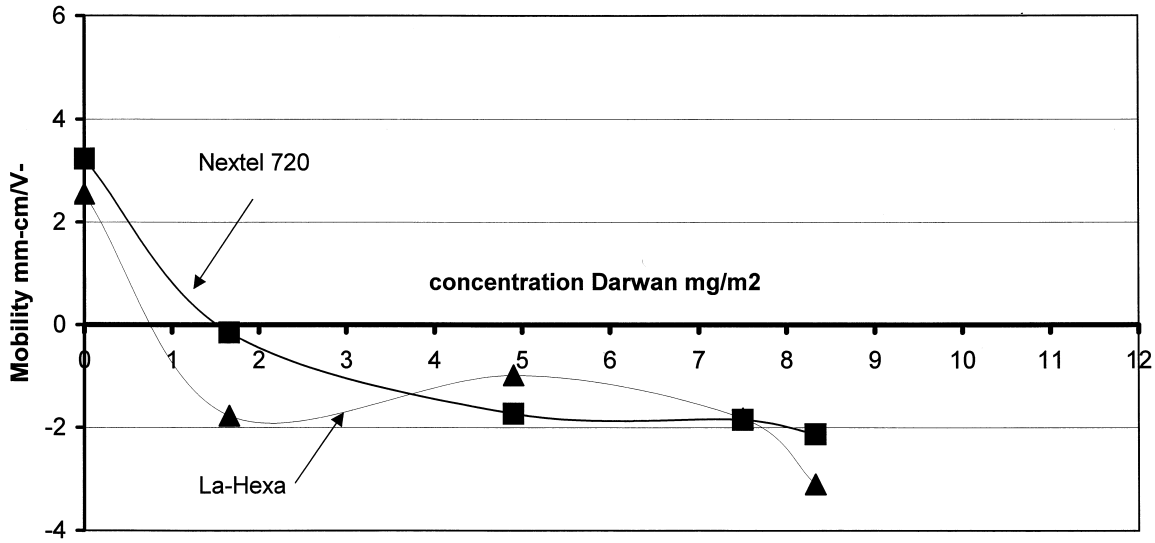

Fig. 6. Mobility of Nextel 720 and crystalline $LaAl_{11}O_{18}$-particles in ammonium polyacrylate solution at pH 5.

surface charge of the fiber. Change in the IEP-point of fibers through the addition of various concentrations of Darvan 821-A at constant pH (= 5) is presented in Fig. 6. A concentration of as low as $1{\cdot}66\,mg\,m^{-2}$ was enough to change the surface charge of fiber to negative. It appears that an increased amount of Darvan 821-A had little influence on the surface charge. Nevertheless, to assure the effectiveness of the adsorbed polymer, a Darvan concentration of $5\,mg\,m^{-2}$ was selected for seed-coating.

Negatively-charged fibers were immersed in a constant pH $LaAl_{11}O_{18}$-suspension where particles were positively charged. SEM-observation of the seed-coated fibers displayed a coverage of low packing density of monolayer $LaAl_{11}O_{18}$-particles of 0·3–1·5 μm on the fiber surface. The intention was not to obtain a full coverage of the fiber surface with the particles. Instead, the aim was to provide a seeding-effect in a fully deposited sol–gel film.

On dip-coating, fiber tows were mantled by the sol, filling the capillary between the individual fibers. A low temperature solvent evaporation reduced the volume of the surrounding gel-coating. If the gel is immediately dried out, however, a large amount of fiber-bridging is unavoidable.

Therefore in this study, fiber tows were processed under vacuum with a very slow drying rate between 40 and 200 °C. SEM-observations of dried fibers revealed that the fibers were coated individually and completely with no visible fiber–fiber contact occurring.

After 1200 °C heat-treatment, the coated fibers were examined by SEM and EDS. A La-mapping on the fiber surfaces showed that a homogeneous distribution throughout the fiber surface was achieved (Fig. 7). Fibers were covered with a continuous and corn-like morphology with some elongated grains, and exhibited an orientation in *x*- and *y*-axes. This indicates an alignment parallel to the *z*-axis, i.e. the fiber basal plane (Fig. 8).

X-ray diffraction spectra of the coated and 1200 °C heat-treated fibers contained two distinct phases: mullite and $LaAl_{11}O_{18}$. Although the Nextel 720 fiber should consist of mullite and α-Al_2O_3, no corundum was detected.

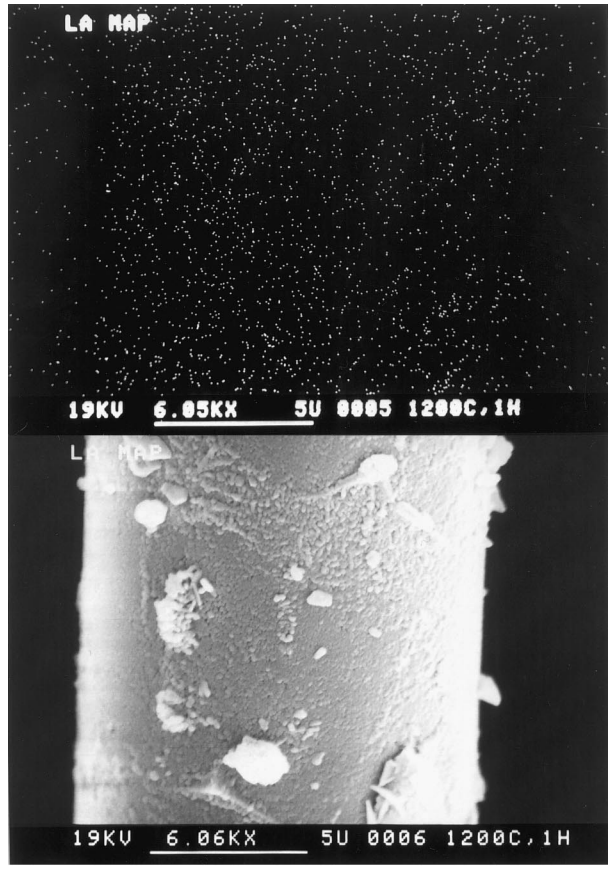

Fig. 7. Scanning electron micrograph of a fiber after seed and sol-coating and heat-treatment at 1200 °C with the corresponding La-mapping of the area.

3.3 Effect of seeding on crystallization behaviour of $LaAl_{11}O_{18}$

In order to determine the least amount of seeds required to achieve full-crystallization of $LaAl_{11}O_{18}$ at 1200 °C and to evaluate the crystallization behaviour, gels with defined amounts (2 and 4 wt%) of $LaAl_{11}O_{18}$-seeds were prepared. Gel formation of sols including seeds were forced by adding 1 mol of distilled water for 3 mol of aluminum, under vigorous stirring. Gels, which were soft and formable at this stage, were dried under vacuum overnight at temperatures between room temperature (RT) and 200 °C. This step was included to obtain a comparable condition between seeded gels and the coated fibers. Fig. 9 exhibits the X-ray spectra of gels containing (a) 2 wt% and (b) 4 wt% seeds between 200 and 1200 °C, after 1 h of heat-treatment. If no seeds are introduced, the (La, Al)-sols that are prepared as described in the experimental section, remain amorphous up to 1000 °C. Above this temperature, formation of poorly crystalline γ-Al_2O_3 was observed. Crystallization of $LaAl_{11}O_{18}$ occurs at about 1200 °C,

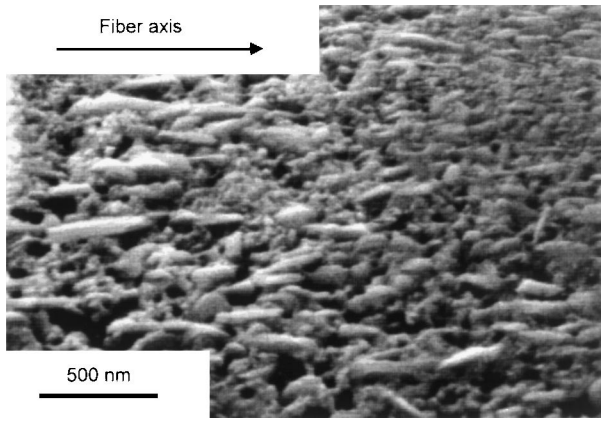

Fig. 8. Scanning electron micrograph of the coated fiber surface.

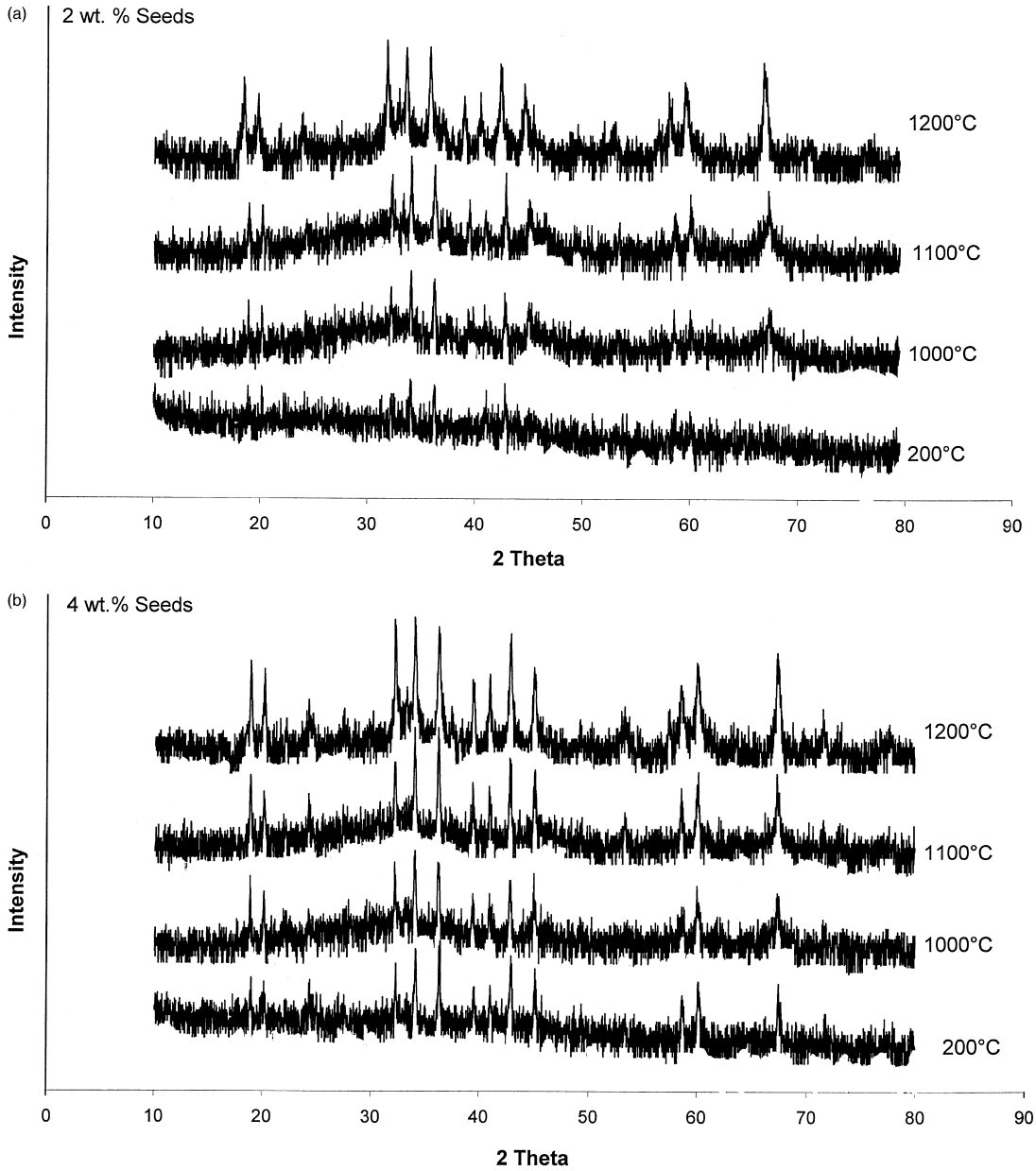

Fig. 9. Crystallization behaviour of $LaAl_{11}O_{18}$-gels seeded with 2 wt% (a) and 4 wt% (b) crystalline $LaAl_{11}O_{18}$-particles.

although not completely. At 200 °C both of the seeded gels displayed the strongest peaks of $LaAl_{11}O_{18}$, due to the presence of seeds. These peaks increased in intensity and yielded a well-developed spectra as the temperature increased to 1200 °C. With 2 wt% seeded gel, at about 1000–1100 °C, the typical peaks of (2Θ: 45 and 67°) γ-Al_2O_3 were detectable; 4 wt% seeded gel showed only $LaAl_{11}O_{18}$ at all heat-treatment temperatures. Conclusively, one needs $LaAl_{11}O_{18}$-seeds above 2 wt% with this seed particle size (1 μm), in order to achieve single phase formation in the temperature range of 200–1200 °C.

4 Discussion

4.1 Sol properties

Previous studies related to the synthesis of $LaAl_{11}O_{18}$ reported that the crystallization of the perovskite type of lanthanum monoaluminate ($LaAlO_3$) delays the formation of $LaAl_{11}O_{18}$ as a single phase, requiring an increase in the process temperature to as high as 1400 °C. This temperature is extremely high considering the stability of commercially available oxide fibers and makes sol–gel synthesis of $LaAl_{11}O_{18}$-coating for fibers unfavorable. The starting materials which were used in these studies were mainly colloidal precursors[8] combined with either nitrates or alkoxides.[9,16] Colloidal starting materials are known to yield diphasic sols, owing to the achievement of nano-scale homogeneity as opposed to the atomic scale-mixing in all-alkoxide precursors. Nitrate-based starting materials usually contain six or more moles of crystal water and are prone to form hydroxides in their ionized solutions. Considering the highly alumina-rich stoichiometry in $LaAl_{11}O_{18}$, it is likely that these hydrolyzed species would tend to form preferentially 1:1-compounds, such as $LaAlO_3$, as has been observed in the case of nitrate-based precursors.

In general, alkoxide-derived starting materials yield a homogeneous mixture in multiple-compound systems. However, starting materials such as metal-acetates and acetylacetonates may be hygroscopic, containing OH-groups attached on the monomer surfaces, or they may contain crystal water. These make it difficult to maintain sol homogeneity and may result in the formation of secondary and/or intermediate phases.

One of the starting materials used in this study is lanthanum acetylacetonate hydrate, containing approximately 3 mol of crystal water which normally may cause spontaneous hydrolysis of aluminum tri-sec-butoxide on mixing. Aluminum tri-sec-butoxide is a very hydrolysis prone alkoxide. Therefore, a distillation process of lanthanum acetylacetonate hydrate was necessary, prior to the preparation of the mixed-precursor. Care was taken to employ only pure substances and no additional chelates or dopants were used. Given that the hydrolysis of aluminum tri-sec-butoxide was impedded, formation of condensed aluminum-species was promoted and thus, achievement of alumina-rich stoichiometry of $LaAl_{11}O_{18}$ was facilitated. Addition of chelates such as acetylacetonate (AcAc), even in the presence of water species in the starting material, may help to obtain relatively homogeneous sols by occupying one or more OR-sites of the alkoxide.[16] The difficulty, however, is the elimination of excess acetylacetonate or carbon-containing species. Especially in the case of thin films, this may lead to detrimental results such as spalling and/or cracking of the coating if the evaporation and/or decomposition of carbon species were not carried out under controlled conditions. It is even more detrimental to form graphite type species which may cause carbon embrittlement of the fiber by diffusing into the fiber at higher temperatures. The resulting 1200 °C X-ray spectra of the $LaAl_{11}O_{18}$-coating obtained by addition of chelates (AcAc) also show poor crystallinity.[16]

4.2 Seeded fiber coating

Particle coating by electrostatic adsorption was introduced as an alternative coating method for fibers.[13–15] Convincing results, obtained earlier in the case of colloidal Al_2O_3-coating/Textron SiC-fibers, indicate that coating thickness is a function of the concentration of amine in the solution and the particles in the suspension. If the method is used as the only coating source, it faces limitations for thin fibers ($\phi < 20\mu$m). Some disadvantages found in the above study are incomplete surface coverage and/or poor tow–tow crossover coating in woven cloth, and low-strength bonding to fiber resulting in difficult handling. However, the experimental data provided by the previous studies are valuable to understand particle deposition, change of surface characteristics (e.g. surface charge and surface area) and usage of long chained polymers.

The principle of seeded sol–gel coating of fibers in this context is schematically shown in Fig. 10. Seed-coating was carried out in order to provide crystallization sites for $LaAl_{11}O_{18}$-sol. In outlining the crystallization and growth mechanisms in thin coating systems, Vaidya *et al.*[17] suggested that preferential grain growth with specific orientations is favored, when the structures of the film and the substrate are similar or identical with a reasonable lattice mismatch. On single crystal substrates such as Sapphikon fibers the epitaxial grain growth

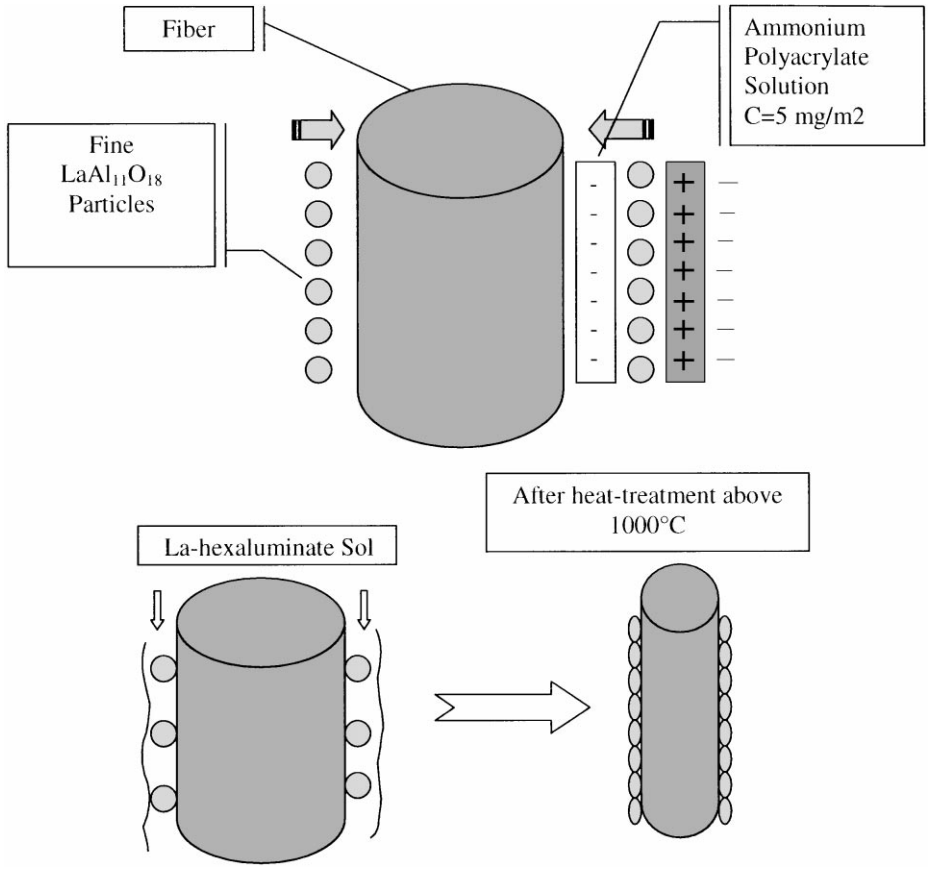

Fig. 10. Principles of seed-coating of fibers via the sol–gel-route.

cannot be avoided due to anisotropic interfacial energies.[18] In cases where structural similarities are not apparent, epitaxial grain growth is delayed until normal grain growth within the film produces a columnar microstructure where grains with a specific orientation initiate.[17] If the film consists of grains with a preferred out-of-plane orientation, these grains can form 'seeds' to initiate the epitaxial growth in the film. The observations of this study agree well with this theory. Previous experiments[11,12] on seeding of gels showed that the finer the seed particles, the more effective the seeding. The use of nano-scale particles < 500 nm is expected to further promote crystallization resulting in higher degree of crystallization at lower temperatures with a lower amount of seeding (≤ 2 wt%).

As Fig. 8 suggests, most of the newly-formed $LaAl_{11}O_{18}$ grains show an alignment parallel to the basal plane of the fiber, though some equiaxed and some extremely fine (< 20 nm) particles can also be observed. This heterogeneous grain distribution may relate to the initial distribution and morphology of the seed particles on the fiber surface. The processing conditions of this study can indeed introduce a physical alignment of the seeds. Withdrawal of the fibers from the sol along with the drainage and the primary drying processes creates a flow which is directed axially along the fibers. Relatively lighter seeds will be dragged and aligned in this flow direction. The certain orientation of $LaAl_{11}O_{18}$ grains on the fiber length, as shown in Fig. 8, may be a result of this. However, a more adequate alignment in the coating can be achieved by control of the seed size and morphology.

$\langle 11\ \bar{2}0\rangle_{\text{Ln-hexa}}\langle 10\ \bar{1}0\rangle_{\text{sapph}}$ in-plane and $(0001)_{\text{Ln-hexa}}$ $(0001)_{\text{sapph}}$ out-of-plane orientation of $LaAl_{11}O_{18}$ in thin films occurred unintentionally as the perovskite ($LaAlO_3$) layer reacted with the sapphire substrate to form $LaAl_{11}O_{18}$.[17] Out-of-plane orientation occurrence was explained due to similarities in the hexagonal oxygen symmetry between the substrate and the coating. For in-plane epitaxial relations, however, a 30° rotation of oxygen planes was responsible, according to TEM-observations.[17] Considering the polycrystalline structure of fiber (mullite/corundum) used as substrate in this study, attainment of a fully oriented thin layer would be rather difficult. In the La-magnetoplumbite structure, 1/6 th of the Al^{3+} ions are tetrahedrally coordinated, whereas the larger La^{3+} is coordinated by 12 oxygen. In mullite, the Al is tetrahedrally and octahedrally coordinated in chains running parallel to *c*-axis. The configuration of oxygen stacking at the mullite/$LaAl_{11}O_{18}$ interface is the deciding factor if an orientation was to be achieved. Hence, it is crucial to start with preoriented crystalline seeds to promote an aligned

crystallization. The seeds used in this study had the same structure (magnetoplumbite). Although some particles showed needle-like morphology, it is unlikely that aligned single crystals were present. Control of this parameter may lead to more successful results.

Moreover, it was reported that reducing both the thickness of the conduction layer and the in-plane compressive stresses by reducing La-oxygen distances in the mirror plane may promote an aligned orientation.[17] It has been reported[6,10] that the addition of M^{2+} ions may promote the crystallization of $LaAl_{11}O_{18}$. However, its effect in terms of orientation is doubtful, since M^{2+} ions preferentially occupy tetrahedral sites in spinel blocks, increasing their packing density, but not the compaction of the mirror planes. Another suggestion may be that M^{2+} additions could segregate to and affect surface energies if not being incorporated into the bulk structure. This can have a significant effect on preferred orientation. Hence, the correct selection of the M^{2+} is a crucial point. M^{2+} cations such as Mg, Ca, Fe tend to incorporate with the fiber or the matrix material at the processing temperature, yielding undesired results.

5 Conclusions

Fully crystalline $LaAl_{11}O_{18}$ coatings on thin fibers were achieved. The use of pure alkoxide precursors and the employment of electrostatically adsorbed seeds facilitated the crystallization of $LaAl_{11}O_{18}$ at temperatures $\leq$1200 °C. Electrostatic adsorption was provided by the modification of surface charges of the fiber and the seed particles. Although surface coverage with particles was not complete, this was not disadvantageous, because the fiber surface subsequently was covered with a complete sol–gel layer by multiple coatings. Upon crystallization of these multiple layers, a full coverage of fiber surface with partly aligned $LaAl_{11}O_{18}$ grains was achieved.

Acknowledgements

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