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Electrophoretic deposition infiltration of metallic fabrics with a boehmite sol for the preparation of ductile-phase-toughened ceramic composites

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The infiltration of commercially available metallic fibre mats by a boehmite sol using the electrophoretic deposition (EPD) technique was investigated. The nanosized boehmite particles were positively charged in a colloidal suspension at pH 4 and migrated upon application of an electric field to the metallic fabric acting as the negative electrode. Three different type 316L stainless steel fabrics were considered and it was found that the quality of the infiltration depended on the fibre architecture. The EPD parameters, i.e., the applied voltage and deposition time, were optimized for obtaining a high solids loading in between the fibre tows and a firm adherent deposit. The infiltrated fibre mats, being of high quality, i.e., low macroporosity and absence of significant microcracking, serve as prepregs for the manufacture of alumina matrix composites reinforced with a two- or three-dimensional metallic phase. © *1998 Chapman & Hall*

1. Introduction

The best results in terms of increasing the fracture tolerance and imparting a pseudoductile fracture behaviour to brittle matrices is achieved with continuous fibre reinforcement, including unidirectional and cross-ply fibre alignment, and two- and three-dimensional fibre architectures. The vast majority of work concerned with fibre reinforcement of ceramics has focused on using oxide and non-oxide ceramic fibres, including carbon, SiC yarn (Nicalon), SiC monofilament, alumina–zirconia (type PRD-166), polycrystalline alumina, single-crystal alumina (Saphikon) and mullite (Nextel) [1–4]. The reinforcement of ceramic matrices by continuous ductile elements has been much less investigated, despite the advantages that they may have over their ceramic counterparts. These include increased resistance to damage during composite processing due to the intrinsic ductility of metallic fibres and the possibility of exploiting their plastic deformation for composite toughness enhancement [5]. Moreover, it has been suggested [6] that, if an optimized matrix–reinforcement interface bonding strength is achieved, both plastic deformation of the reinforcement and frictional sliding between the components can be utilized in the composite, leading to a significant fracture toughness improvement. A penalty is paid in these composites, certainly, owing to the relatively low thermal capability and poor chemical resistance of the metallic reinforcement, limiting the application temperature and environment. Besides a few reports on continuous ductile reinforcement of glass matrices [5, 7, 8], no significant research has been devoted to metallic fibre reinforcement of ceramics and certainly even less work has been carried out using two-dimensional metallic fibre mats to reinforce brittle matrices [9]. The research interest concerning ceramic–metal composites has focused traditionally on discontinuous particulate reinforcement [10–12] and, more recently, has shifted to composites with three-dimensional interpenetrating microstructures prepared by chemical reaction processes, metal infiltration of porous ceramic preforms or sol–gel techniques [13–15]. The fabrication technologies in these cases, however, are complex. One probable reason for the previous lack of interest in metal fibre reinforcement may have been the general unavailability of suitable small-diameter fibres. In recent years, however, small-diameter inexpensive titanium and stainless steel fibres have become available, which have been used in the production of antistatic and conductive textiles and for the fabrication of filters [16]. A few studies have been conducted regarding the use of these

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fibres as a discontinuous reinforcement element (chopped fibres) in brittle matrices, including hydroxyapatite [17], borosilicate glass [18] and bioglass [19], and as unidirectional reinforcement in borosilicate glass matrix [8]. As metallic fibre mats have become available also, it was thought worth investigating their use as reinforcement in ceramic matrices, bearing in mind the more isotropic mechanical properties obtained with two-dimensional reinforcing elements over unidirectional fibre reinforcement, as demonstrated, for example, with silica matrix composites reinforced with woven ceramic fibre mats [20].

When using fibre mats as reinforcement, it is normally extremely difficult to achieve complete infiltration of the matrix material into the fibre tows, where the openings are of the order of 100 nm. Electrophoretic deposition (EPD) of colloidal ceramic sols has been shown recently to be a simple and inexpensive method for achieving complete infiltration of tightly woven fibre performs [20–22]. Briefly, the EPD process relies on the presence of small charged particles within a colloidal suspension which, on the application of an electric field, will migrate towards and deposit on either the anode or the cathode. Movement of the particles occurs because the particle surfaces are charged with respect to the suspending medium [20–22], and this charge governs the electrode to which they migrate. If the deposition electrode is replaced by a conducting fibre preform, the suspended particles will be attracted into the fibre preform and deposited within it, resulting in complete infiltration. The movement of ceramic sol particles in an aqueous suspension within an electric field is governed mainly by factors such as the field strength, the pH of the solution and the ionic strength of the solution [21, 23]. For a complete description of the EPD technique and its applications in ceramic technology, the reader is referred to a recent review article by Sarkar and Nicholson [23]. The EPD technique has been employed for infiltrating silica and alumina sols into ceramic fibre preforms, such as SiC (Nicalon) [20, 21] and alumina (Almax) woven mats [22, 24]. Recently, a silica sol has also been used to infiltrate metallic fibre mats [25]. The previous studies have showed that EPD provides more efficient infiltration and stronger adhesion between the fibre and the matrix than a simple slurry dipping technique and thus allows the preparation of high-quality fibre performs for ceramic matrix composite manufacture. In the present work, the possibility of infiltrating woven metallic fabrics with a ceramic sol, as the first step for the fabrication of two-dimensional ductile-phase-toughened ceramic composites, was explored. A boehmite sol is used which, upon the high-temperature consolidation process, should yield an alumina matrix material.

2. Experimental procedure

From the variety of metal fabrics commercially available (Bekaert SA, Zwevegem, Belgium) [16], the following fibre architectures were chosen: (i) a woven stain fabric (Bekitherm FA), (ii) a sintered solid filter felt (Bekipor ST) and (iii) a three dimensional web of loose fibres in a non-woven labyrinth structure (Bekipor WB). All fabrics were made of 100% standard type 316L stainless steel and the individual fibres had an average diameter of 12 μm. There are other fibre mats available also, made from alloys such as Inconel 610, Hastelloy X and Fecralloy, which have better high-temperature properties than type 316L stainless steel does but, for this study, the more cost-effective type 316L stainless steel was considered adequate to demonstrate the use of this particular processing technology. The maximum using temperature for the type 316L steel in an oxidizing atmosphere is 900 °C and

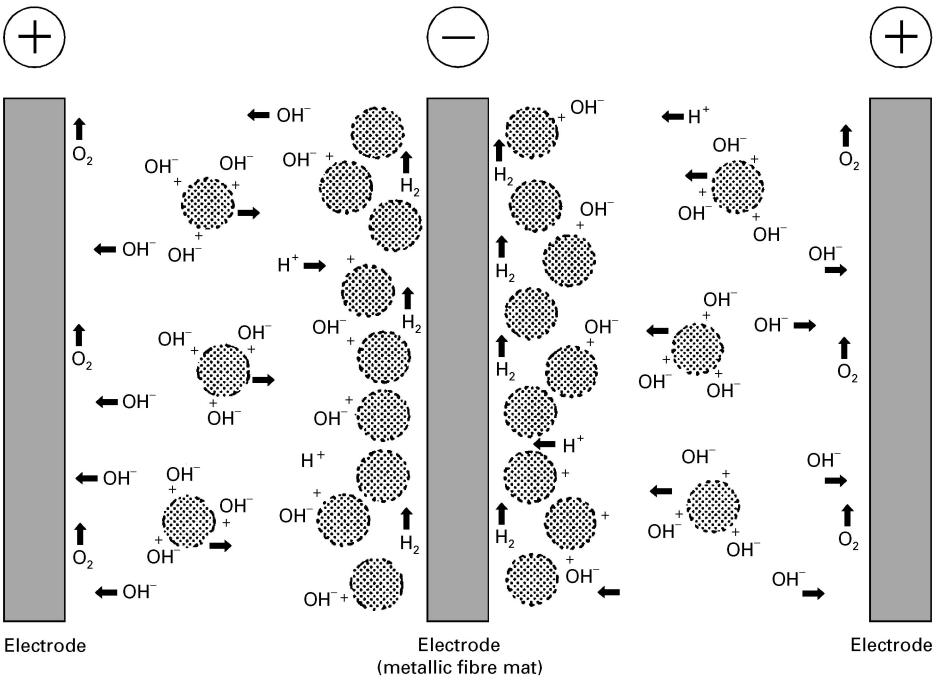

Figure 1 Schematic representation of the EPD cell for a boehmite sol in aqueous solution.

the thermal expansion coefficient (20–700 °C) is 16.8×10^{-6} °C^{-1} [26, 27]. Because of the relatively low thermal capability and oxidation resistance of the metallic fibre used, a ceramic matrix precursor had to be chosen, which would allow the densification step to be carried out at moderate temperatures (about 1200 °C or less). A commercially available boehmite sol (γ-AlOOH) (Remal A20, Remet Corporation, USA) was chosen as the matrix precursor in this study. The sol contains 20 wt % solid and the pH is 4. The particle morphology and the relative spatial arrangement of the particles within the sol were investigated by transmission electron microscopy (TEM) (Philips CM20). The choice of this precursor was based on several studies in the literature, where it has been shown that α-Al_2O_3 of high relative density (about 99%) can be produced at sintering temperatures as low as 1180 °C from similar boehmite sol–gel precursors [28, 29]. For this to be achieved, the boehmite sol–gel precursor must be seeded with fine (about 0.1 μm) α-Al_2O_3 particles in a low concentration (less than 2.0 wt %) [29]. For the EPD experiments, 15 mm × 15 mm squares were cut from the as-received metallic fibre performs. They were placed in the boehmite sol and then vacuum degassed before being infiltrated by EPD. During EPD the fibre mats served as the negative "deposition" electrode and a stainless steel plate as the positive electrode, as schematically shown in Fig. 1. This is because the boehmite particles in colloidal suspension at the working pH (about 4) have a positive charge, as shown in the literature [30]. A standard direct-current (d.c.) power supply was used to provide the electric field. A constant d.c. voltage was applied to the electrodes, which were 3 cm apart. The applied voltage and the deposition time were varied in order to find the optimum for the complete infiltration of the sol into the intratow regions, and for obtaining the desired thickness of the deposited surface layer on the mat. The infiltrated fibre fabrics were dried slowly in a humid atmosphere (about 80% humidity) to avoid microcracking. The dried impregnated fibre mats were impregnated in resine and polished to a 1 μm finish for optical and scanning electron microscopy (SEM) examination and SEM energy-dispersive X-ray analysis (EDXA). Some dried impregnated fibre mats were heat treated for 1 h at temperatures between 900 and 1200 °C. Matrix material from the intertow and intratow regions was removed, powdered and analysed using X-ray diffractometry (XRD). The purpose of this analysis was to investigate the crystallization evolution of the boehmite sol used.

3. Results and discussion

Fig. 2 shows a transmission electron micrograph of the boehmite sol used. The particles have a mean particle size of 50 nm and a fibrillar morphology. Figs 3–6 are scanning electron micrographs showing

Figure 2 Transmission electron bright-field imaging micrograph of the boehmite sol at pH 4, showing the nanosized particles and their fibrillar morphology.

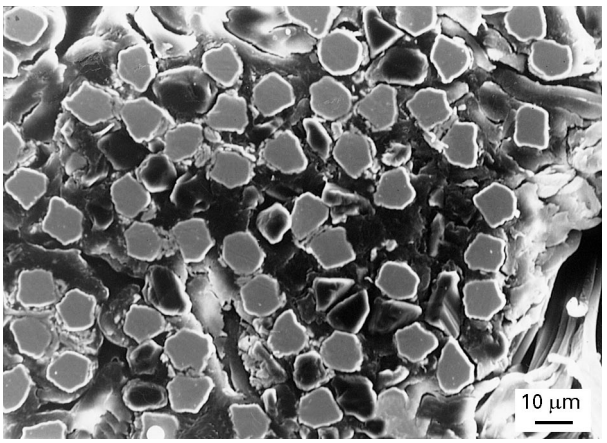

Figure 3 Scanning electron micrograph of an impregnated Bekitherm fibre mat, showing that during EPD the boehmite sol has infiltrated fully the intratow regions. The voltage and deposition time used were 4 V and 1 min, respectively.

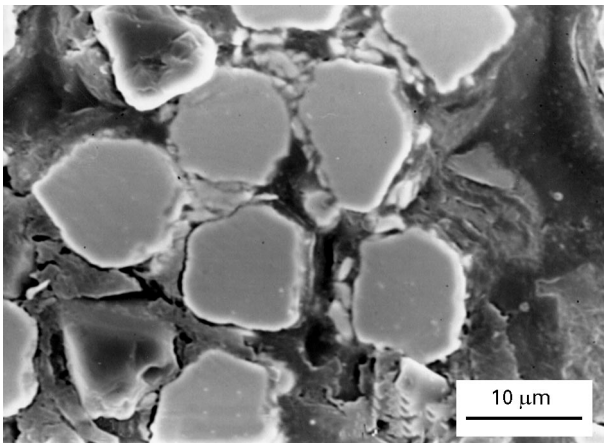

Figure 4 Scanning electron micrograph of the same sample in Fig. 3 but at a higher magnification to show the high solid content of the deposit.

the different metallic fibre fabrics after infiltration with boehmite sol by EPD. In general, all the fibre fabrics investigated could be infiltrated with the boehmite sol and a firm matrix deposit which adhered to the fibres was produced. Some differences were noted, however, between the infiltration quality of the different fabrics. It can be observed that EPD is capable of producing a high level of particle infiltration into the electrically conducting fibre tows for the Bekitherm (Figs 3 and 4) and the Bekipor WB (Fig. 6) fabrics. Owing to the small particle size of the ceramic sol used, they could infiltrate the spaces within the fibres tows efficiently. It is suggested that the infiltration process is enhanced in these fabrics by opening up the spaces in the fibre tows through the mutual repulsion of the charged fibres. The presence of ceramic material in the intratow and intertow spaces was confirmed qualitatively by spot EDXAs by detecting the peak for aluminium. This is shown for example for the Bekipor WB material in Fig. 7. The best particle packing and the highest solids loading was achieved for the Bekipor WB mats. This is due to the looser architecture of this fabric. On the contrary, the most difficult mat to infiltrate was the Bekipor ST fabric (Fig. 5), which consists of a very tight and rigid labyrinth structure. As the

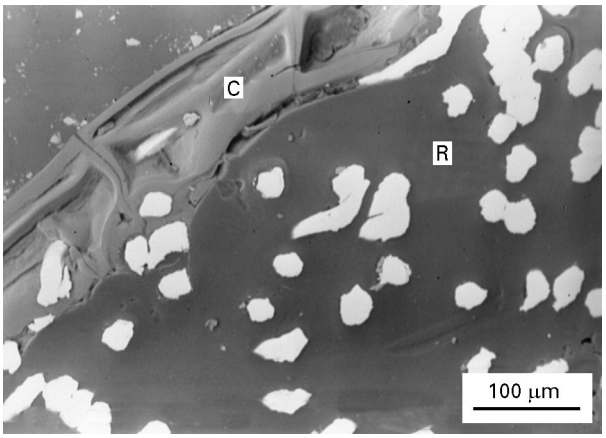

Figure 5 Scanning electron micrograph (back-scattered) of an impregnated Bekipor ST fibre mat, showing that during EPD the boehmite sol has not infiltrated fully the intratow regions. The light-grey area C represents the infiltrated ceramic (as confirmed by EDXA), while the dark area R in between the fibres represents the resin in which the samples were embedded prior to polishing. The voltage and deposition time used were 4 V and 3 min, respectively.

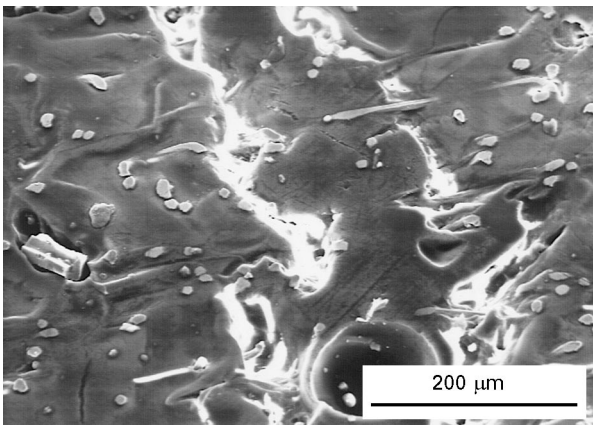

Figure 6 Scanning electron micrograph of an impregnated Bekipor WB fibre mat, showing that during EPD the boehmite sol has infiltrated fully the intratow regions. The voltage and deposition time used where 4 V and 1 min, respectively.

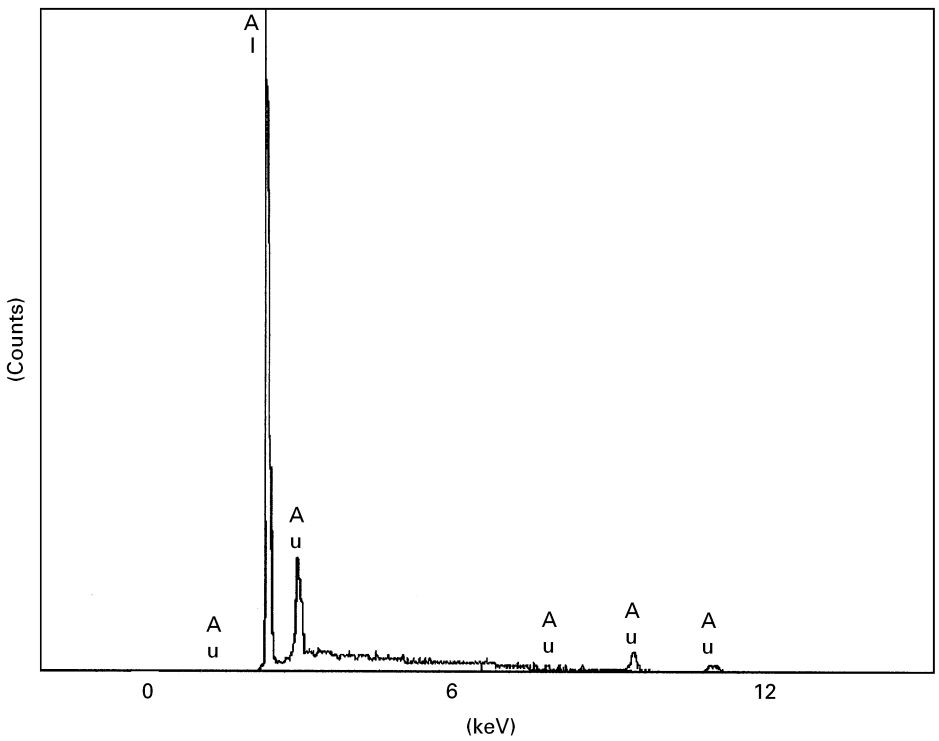

Figure 7 Spot EDXA of the deposited material between the fibres within the fibre tows of a Bekipor WB mat, showing the presence of aluminium, an element absent in the type 316L fibre composition, and hence confirming that boehmite particles have migrated to the negative electrode during EPD.

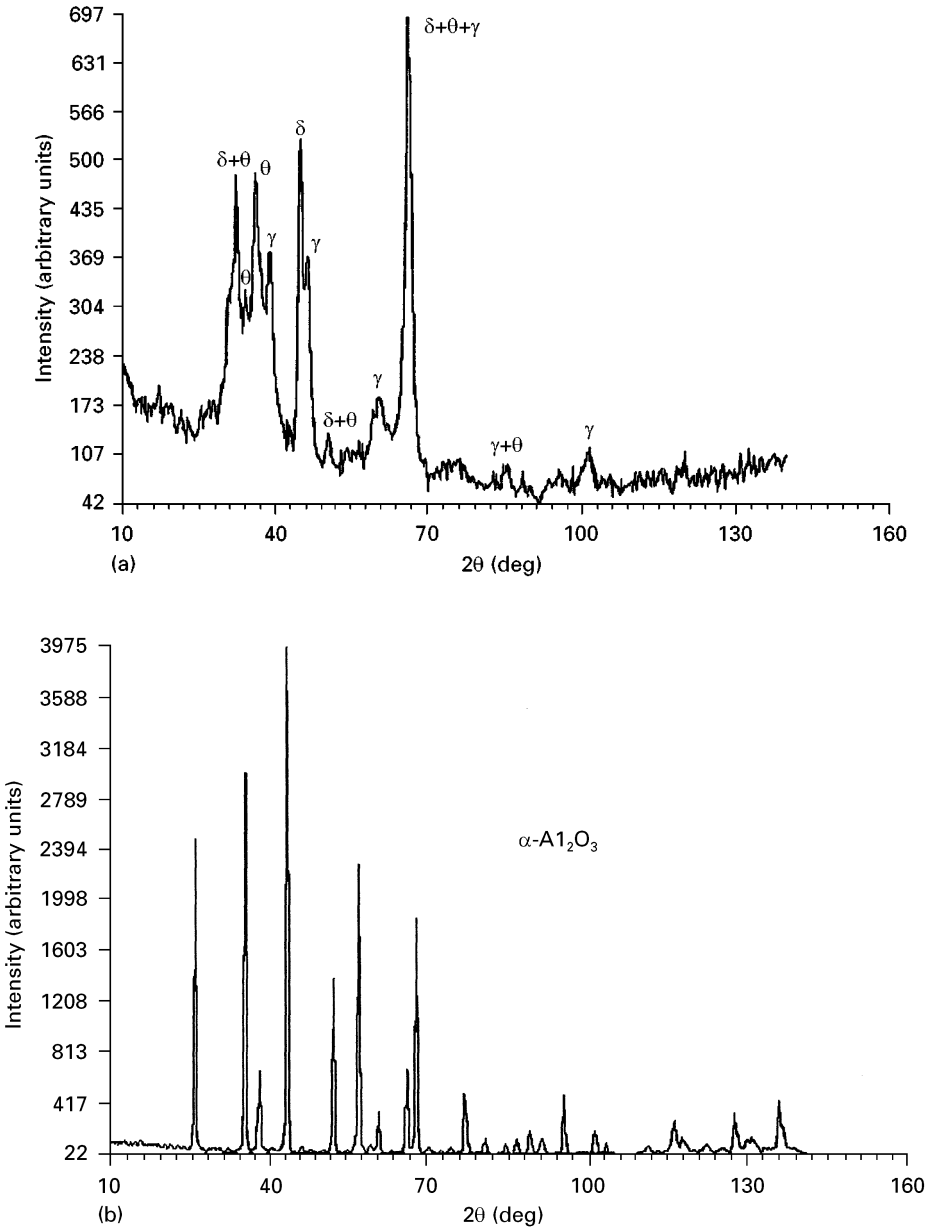

Figure 8 Powder XRD pattern of ceramic material deposited onto a Bekipor WB fibre mat by EPD after heat treating for 1 h at (a) 970 °C and (b) 1200 °C. The crystalline phases identified are indicated. Note that, at 1200 °C, α-Al_2O_3 is the only phase present.

back-scatttered SEM image in Fig. 5 shows, infiltration of the boehmite sol was only partially achieved for this fabric, even after a deposition time of 3 min; the light area corresponds to the ceramic material effectively infiltrating the outer region of the mat, but the dark area in between the fibres is the resin, the medium where the samples were embedded prior to polishing. Indeed, as this metallic web is designed to be used as a filter medium with high holding capacity and gel retention capability [16], the poor infiltration achieved by the ceramic sol is not surprising.

The optimum voltage and deposition time in each case were determined by a systematic approach. In agreement with previous studies on EPD of silica and mullite sols onto SiC Nicalon fibre mats [20, 21], increasing the voltage over 4 V resulted in significant formation of bubbles between the deposited particles. This is a consequence of oxygen and hydrogen evolution at the anode and the cathode, respectively, due to the electrolytic decomposition of the aqueous medium [20]. For the Bekitherm and the Bekipor WB fabrics, a deposition time of 1 min was found to yield complete infiltration while keeping the deposited layer thickness low enough to prevent significant cracking upon drying in air. Thin films (i.e., less than 1 μm thick) can be dried in air without cracking because the tensile stresses generated on shrinkage are too low to cause the growth of cracks from microscopic flaws [31]. The infiltrated fibre fabrics in this study were dried slowly in a humid atmosphere (about 80% humidity); as a consequence, crack formation in the ceramic matrix between the fibres was minimized.

The infiltrated metallic fabrics of Bekitherm and Bekipor WB type are of sufficient quality (high infiltration, no macroporosity and minimal microcrack development) to be used as preforms for the fabrication of alumina matrix composites. The subsequent steps would involve a slurry dipping procedure of the

infiltrated fibre mats to achieve the desired ceramic volume fraction and even out the non-uniform nature of the EPD deposit, the formation of the composite green body by stacking the prepregs, and the high-temperature consolidation by pressureless sintering or hot pressing. The development of suitable technology is the focus of current work. One critical aspect to be considered is the requirement of attaining full densification of the matrix at moderate temperatures due to the low thermal capability of the metallic reinforcement employed (less than 1200 °C). It is evisaged that the choice of a suitable nanosized boehmite sol precursor as matrix material will allow this. Boehmite undergoes dehydration at 500 °C to form γ-Al_2O_3, which then transforms to δ-Al_2O_3 and θ-Al_2O_3 before undergoing a subsequent phase transformation to α-Al_2O_3 between 1100 and 1200 °C. The crystallization development of the boehmite sol used is shown in Fig. 8. For a heat treatment of 1 h at 970 °C, only the transitional aluminas (δ-Al_2O_3 and θ-Al_2O_3) are present (Fig. 8a). The formation of α-Al_2O_3 was detected after a heat treatment of 1 h at 1200 °C, as shown in Fig. 8b. Preliminary investigations on the densification behaviour of this material showed that compacts made from the calcinated boehmite gel (uniaxially pressed) were only 74% dense after sintering for 2 h at 1200 °C [32]. In order to enhance the densification behaviour of the boehmite gel, therefore, the original sol will need to be seeded with fine (about 0.1 μm) α-Al_2O_3 particles in low concentration (less than 2.0 wt %), according to the method proposed by Messing and Kumagai [28] and Kumagai and Messing [29] mentioned above.

4. Conclusions

It has been demonstrated that the EPD sol infiltration technique can be used to infiltrate successfully a boehmite sol into different commercially available type 316L stainless steel fabrics. The quality of the infiltration depended on the architecture of fibre mat employed. The parameters of the EPD infiltration process, i.e., the voltage applied and deposition time, were optimized to obtain a high solids loading in the intratow regions and a firm ceramic deposit adhered to the fibres. The ability to prepare dense deposits of ceramic material on metallic fibre preform by the EPD technique opens up the possibility for the fabrication of two- and three-dimensional metal-phase-toughened ceramic matrix composites. The full potential of the present processing approach is still to be demonstrated, however, since densification of the matrix material at moderate temperatures (below 1200 °C) is a requirement. For a boehmite matrix precursor this may be possible, since the densification can be enhanced by seeding the original sol with submicrometer α-Al_2O_3 particles in low concentration, as reported in the literature [28, 29].

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