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Templated epitaxial coatings on magnesium aluminate spinel using the sol-gel method

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Abstract Polycrystalline magnesium aluminate ($MgAl_2O_4$) spinel has attractive properties for a range of applications including radomes, windows, and ballistic protection. A wet chemical approach using solutions of magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ in 2-methoxy-ethanol (2-MOE) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) in ethylene glycol, was developed for spin coating on coarse-grain, polycrystalline spinel substrates. The coated substrates were subjected to isothermal heat treatments in the temperature range 1000–1400 °C, and subsequently examined using low voltage scanning electron microscopy, EBSD (electron back scattered diffraction), and transmission electron microscopy. The results showed that for annealing at 1200–1400 °C, the coatings were converted to crystalline $MgAl_2O_4$ which was epitaxial with the substrate grains. Heat treatment at lower temperatures, however, resulted in porous, fine-grained polycrystalline coatings. Thermal faceting of the grain surfaces was observed to occur. The observations suggest that faceting occurs preferentially on {100} and {110} planes. The morphology of the faceting was discussed in terms of the reported relative surface energy values for the low index planes in $MgAl_2O_4$ spinel. Finally, the influence of the coating process on spinel substrates which had been lightly abraded prior to spin coating was investigated.

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Introduction

The excellent transmission of magnesium aluminate spinel ($MgAl_2O_4$) in the mid-IR (infrared) region makes it an attractive material for a variety of window and dome applications [1–4]. An advantage spinel has over other candidate materials such as sapphire and aluminum oxynitride (ALON), is that its usable range of IR transmission extends to longer wavelengths [2]. Further, for $\lambda = 4.8$ μm (a wavelength which is of specific interest for military applications), the relative degree of improvement in transmission improves with increasing temperature. Spinel is also being considered for transparent armor for personnel protection and windows for ground vehicles [5, 6]. As is the case for the majority of hard ceramics, mechanical finishing is a time-consuming and expensive process. This is clearly even more critical for lens and window components, where an optical quality surface finish is required.

Surface modification via the application of coatings would seem to be one possible approach to the fabrication of spinel components. For example, work by Park and Chan [7] on sapphire showed that the application of a reactively formed coating could result in an improvement of the surface finish. The aim of the present work was to test the viability of a sol-gel derived method to develop a homo-epitaxial coating on a polycrystalline, transparent spinel substrate. This is somewhat analogous to the solid state conversion and templating processes which have been reported in the literature for other ceramic systems, e.g., barium titanate [8, 9], lead magnesium niobate [8, 10, 11], and alumina [12, 13]. Generally speaking, these types of studies have utilized single crystal substrates and seed crystals with low index surface orientations as templates, as opposed to a polycrystalline substrate. For storage device applications, epitaxial thin films of magnetic spinels have

been fabricated by magnetron sputtering and pulsed laser deposition, using single crystal substrates such as MgO, $SrTiO_3$, and yttria-stabilized zirconia (see for example the review by Suzuki [14]). There have also been a number of studies of sol-gel spinel coatings [15–20], but for the most part these have focused on non-epitaxial thin films, and the substrates utilized were silicon or glass. Pasquier et al. [21] studied the effect of seeding on the sol-gel synthesis of $MgAl_2O_4$ spinel, and reported that the addition of spinel crystallites resulted in a lower formation temperature of the $MgAl_2O_4$. This effect was attributed to the seeds providing preferential nucleation sites for the spinel transformation. To the authors' knowledge, there have been no reports of sol-gel derived epitaxial coatings of spinel on polycrystalline substrates.

Experimental

Dense polycrystalline samples of magnesium aluminate spinel ($MgAl_2O_4$) were provided by Technology Assessment and Transfer Inc., Millersville, MD 21108. The specimens, which were polished and optically transparent, were cut by diamond saw into roughly rectangular pieces, approximately 2 × 2 cm^2, thickness ~4 mm. The formulation of the coating solutions was derived from the work of Sedlar and Pust [19] for $NiFe_2O_4$ thin films, but adapted for $MgAl_2O_4$. Precursor solutions were prepared as follows. Magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ was dissolved in 2-methoxy-ethanol (2-MOE) by stirring and heating to 60 °C (solution A). Similarly, a solution of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) in ethylene glycol was prepared under similar conditions (solution B). The concentrations of solutions A and B were 0.641 g cm^{-3} (2.5 M) and 1.251 g cm^{-3} (3.33 M), respectively. Preliminary experiments showed that a mixture of the precursor solutions (in the correct molar ratio) yielded a liquid which was too viscous for spin coating. Accordingly, the solution was diluted by adding more ethylene glycol. The make-up of the solution (by volume) which was found to be suitable for spin coating was 10% solution A + 15% solution B + 75% ethylene glycol.

Thin films of the sol-gel solution were spin coated at ~3500 rpm. Prior to coating, the samples were washed in acetone and dried. To promote wetting, various commercial surfactants were tested. The best results were obtained using polyvinyl pyrrolidone (PVP), at a concentration of 15 g per 100 cm^3 of solution. The coated samples were allowed to dry over night under ambient conditions, and subsequently annealed at temperatures ranging from 1000–1400 °C, with the duration of the heat treatment varying from 2 to 24 h. The furnace ramp rate (both heating and cooling) was 10 °C per minute. The spinel samples were examined using low voltage scanning electron microscopy (SEM; Hitachi S-4300 SE/N, Tokyo) at an accelerating voltage of 5 keV. Electron backscattered electron diffraction (EBSD; TexSEM Laboratories Inc., Draper, UT) was utilized to obtain grain orientation information in the SEM. For selected samples, electron transparent thin sections were prepared by focused ion beam milling (FIB; FEI Strata DB 235, Hillsboro, OR). These were examined in a transmission electron microscope (TEM; JEOL 2200 FS, Tokyo, Japan) fitted with an in-column energy filter (Omega, JEOL, Tokyo, Japan) and aberration corrector (ION,CEOS, Heidelberg, Germany).

Results and discussion

General

Examination of the spin-coated samples annealed at 1000 °C revealed that the coating had developed into a porous, fine-grained surface layer overlying the spinel substrate (see Fig. 1). The coating appeared homogeneous, and there was no evidence of the structure of the underlying spinel grains. The annealing time at this temperature did not have a pronounced effect on the microstructure of the coating. In contrast, for heat treatment at 1400 °C, the coarse grain structure of the spinel was readily visible. At low magnification (less than 1000×), the general appearance of the SEM images (see Fig. 2) was very similar to that of the as-received, uncoated samples. When the samples were observed at higher magnification, however, it was apparent that the grain surfaces had undergone thermal faceting. Spinel samples annealed for either 10 or 24 h showed very similar microstructures.

For the intermediate heat-treatment temperature (1200 °C), samples that had been coated and heat treated for 10 h

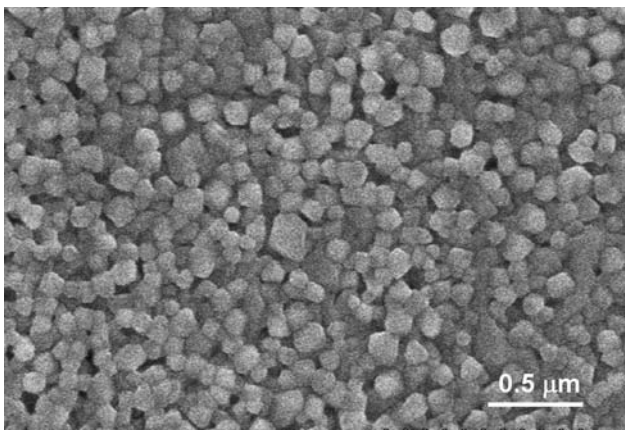

Fig. 1 Appearance of sol-gel coating after heat-treatment at 1000 °C for 2 h (SEM, 5 keV accelerating voltage)

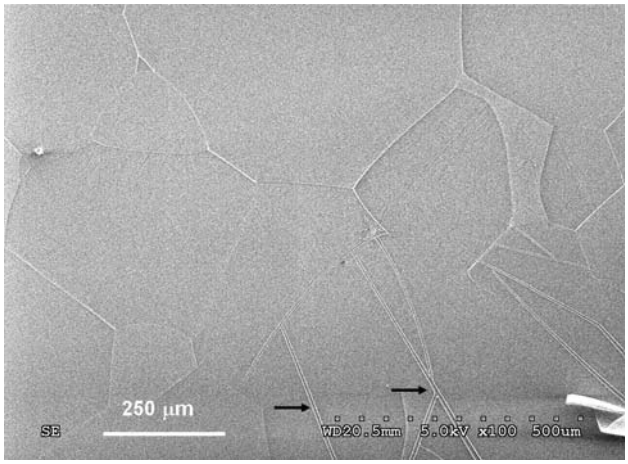

Fig. 2 Sol-gel coated spinel heat-treated at 1400 °C for 10 h (SEM, 5 keV accelerating voltage). Arrows indicate fine breaks in the coating

exhibited a mixture of grain surface morphologies. In some grain regions, the coating consisted of a porous aggregate of fine grains (see Fig. 3a). For other grains, however, the coating surface was uniform, and reflected the underlying grain structure. Individual grains exhibited either a 'rumpled' appearance or micro-faceting. The degree of faceting, however, was less pronounced than for the 1400 °C samples. An example of the latter type of behavior is shown in Fig. 3b.

In general, the 1400 °C heat-treated films were dense and crack-free, with the exception of isolated, fine breaks, which were sometimes observed at the periphery of the coated regions (see for example the features marked by arrows in Fig. 1). By either tilting the sample or examining regions where the coating had retracted and peeled upwards, it was possible to estimate the thickness of the sintered coating. Measurements were made for different areas on a given sample and for different coated samples. For single spin coatings, thickness values ranged from 0.6 to 1 μm. The variation is attributed to slight differences in the size of the droplet of solution used for the spin coat.

Epitaxial conversion

As stated earlier, one of the aims of the study was to establish whether sol-gel derived coatings could be converted by heat treatment to be epitaxial with the substrate. For the coated samples annealed for 10 h at 1400 °C, the surfaces of the spinel grains revealed fine-scale faceting when viewed at higher magnification (>10,000×). Particular attention was paid to regions where narrow cracks in the coating enabled direct comparison between the morphology of the faceting in the coated and uncoated regions, within a given grain. It was found that for most (>95%) of the more than 20 regions studied, the appearance of the faceted surfaces did not change from the coated to uncoated region of the grain. An example of this faceting behavior is shown in Fig. 4. The results suggest strongly,

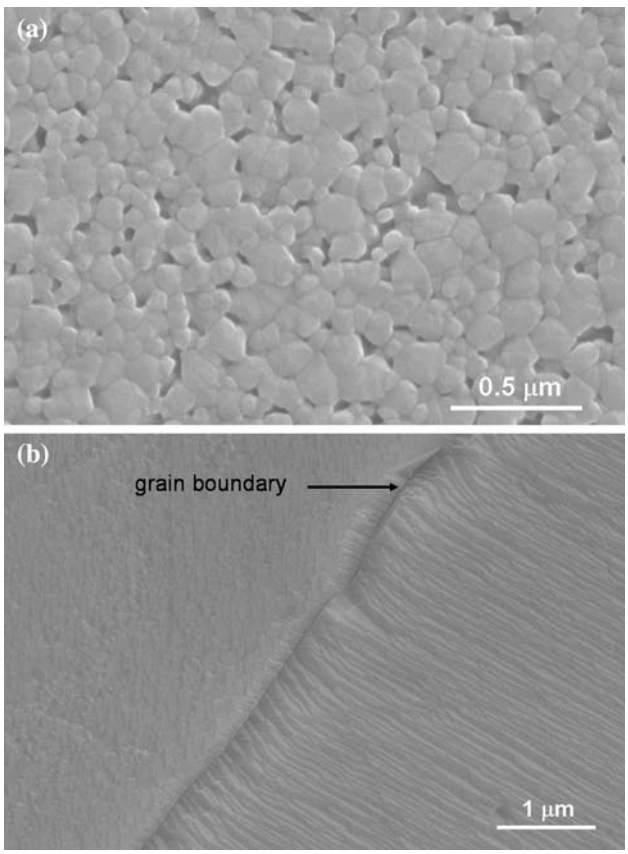

Fig. 3 **a** Region of sol-gel coating exhibiting fine, granular structure (heat-treatment at 1200 °C for 10 h) (SEM, 5 keV accelerating voltage). **b** Region of sol-gel coating exhibiting micro-faceting (heat-treatment at 1200 °C for 10 h) (SEM, 5 keV accelerating voltage)

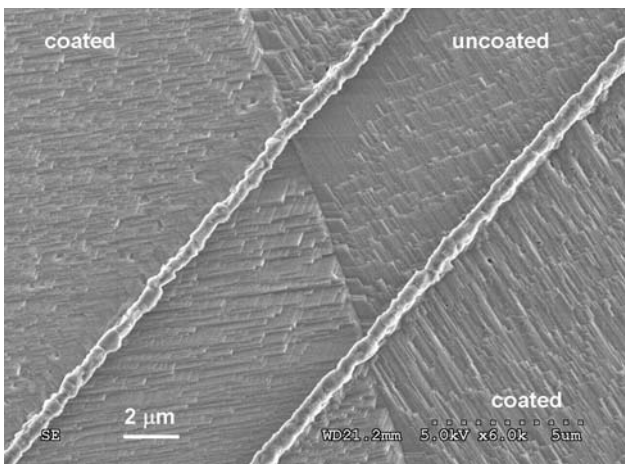

Fig. 4 Appearance of faceting in region where there is a break in the coating (heat-treatment at 1400 °C for 10 h). Note that for a given grain, the morphology of the faceting is similar for the coated and uncoated region (SEM, 5 keV accelerating voltage)

therefore, that the coating has adopted the orientation of the underlying spinel substrate grains.

To provide further confirmation of epitaxial conversion, cross-section thin foils of the coated and heat-treated samples were examined in the TEM. A representative micrograph is shown in Fig. 5. There was no evidence of any delineation between the surface layer and the underlying substrate. Based on the coating observations for different annealing temperatures, the sequence of microstructural changes in the coating is believed to be as follows. The coating is initially converted to a fine-grained polycrystalline spinel. Subsequently, during annealing at the higher heat treatment temperatures (1200 and 1400 °C), these grains are consumed by the growth of the underlying spinel grains, resulting in an epitaxial surface layer. The driving force for the reaction is the reduction in total grain boundary area. Clearly, therefore, successful epitaxial conversion will depend on the rate of grain growth in the spinel coating versus the mobility of the interfacial boundary of the underlying grain. For this reason, full epitaxial conversion is more difficult in thicker films, due to concurrent grain growth in the coating. The templating studies cited earlier [8–14] utilized substrates or seed crystals with low energy surface orientation. It is perhaps noteworthy that in the present study, the epitaxial conversion has been achieved for a polycrystalline substrate with a wide range of spinel grain orientations.

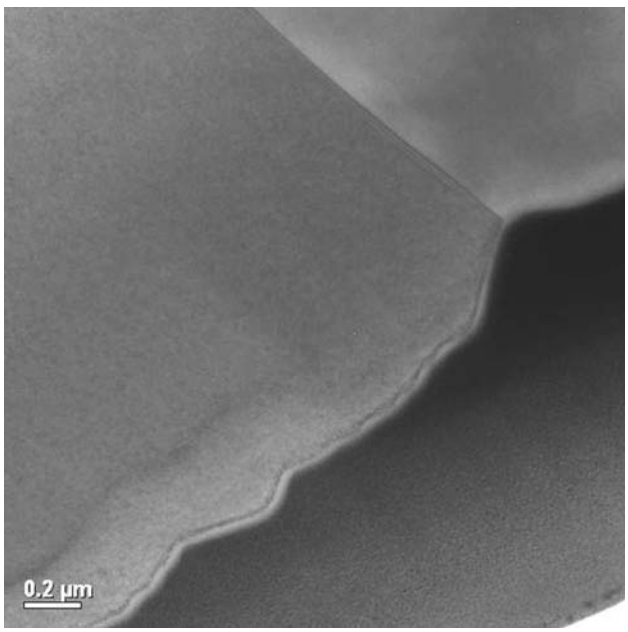

Fig. 5 TEM cross section through spinel sample coated and heat-treated 10 h at 1400 °C. The structure extending from the surface to the underlying substrate is continuous

Surface faceting behavior

As alluded to previously, the surfaces of samples heat treated at 1400 °C exhibited faceting. This process is driven by surface energy considerations, whereby the overall surface energy of a grain can be lowered by the formation of facets parallel to low energy planes. Yanina and Carter [22] have studied terraces and ledges on (001) $MgAl_2O_4$ spinel surfaces using atomic force microscopy. These workers observed that for annealing in the temperature range 1200–1800 °C, the (001) surfaces adopt a terrace and step morphology to accommodate any slight deviation from the exact cube face orientation. The edges of the terraces were found to be aligned along the [110] and [1$\bar{1}$0] directions. Susnitzky and Carter [23] studied the same system using TEM, and reported that for faceting on the (100) plane, the traces of the steps were invariably either {001} or {011}-type.

Somewhat surprisingly, there have been relatively few reported studies on the orientation dependence of surface energy (γ) in spinels [24–28]. Moreover, there is inconsistency not only in the reported values, but (more significantly) in the relative magnitudes for different $\gamma\{hkl\}$. For example, in an early theoretical study Mishra and Thomas [24] reported that comparing the low index planes {100}, {110}, and {111}, the surface energy of the {111} planes was the lowest. In contrast, the atomistic simulation studies of Fang et al. [25, 26] found the {100} planes to have the lowest energy, a result that was consistent with the work of Stewart and Bradt [27], whose values were based on experimental fracture studies. Rice et al. [29] carried out mechanical testing on single crystal specimens of $MgAl_2O_4$, and concluded that both {100} and {110} behaved as cleavage planes, with values of fracture toughness which were within 6%.

Given the relatively small number of direct microstructural observations on this topic, it was decided to survey the morphology of the faceted grain surfaces using SEM, with a view to identifying the lower energy planes. For selected grains, the orientation was determined by EBSD. Magnesium aluminate spinel is cubic, with the space group *Fd3 m* [30]. Because the cubic structure gives rise to unambiguous geometrical relationships between low index planes and directions, in many cases, assignments of the grain facet orientations could be reasonably achieved by visual observation (see for example Fig. 6). A determination of the $\gamma\{hkl\}$ values was beyond the scope of the current study; however, we list some of the pertinent findings in the following. Grains were oftentimes observed where the surface faceting consisted of three perpendicular sets of planes. This would be consistent with either {100} cube face faceting, or a combination of {100}-type planes, with two sets of orthogonal {011}-type planes. Figure 7

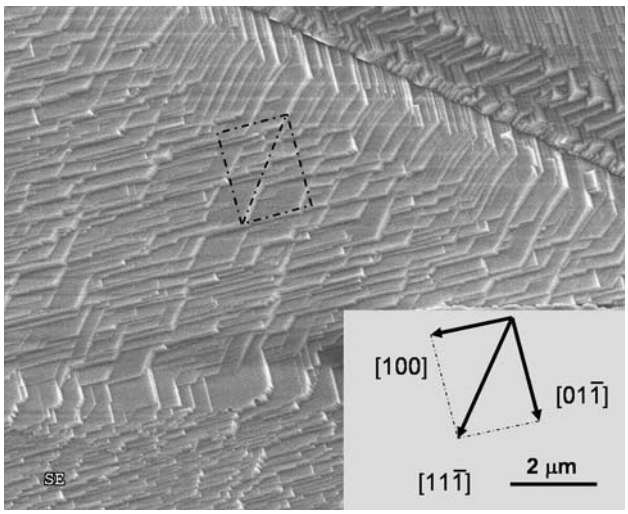

Fig. 6 Appearance of faceting morphology for spinel coated and annealed 10 h at 1400 °C (SEM, 5 keV accelerating voltage)

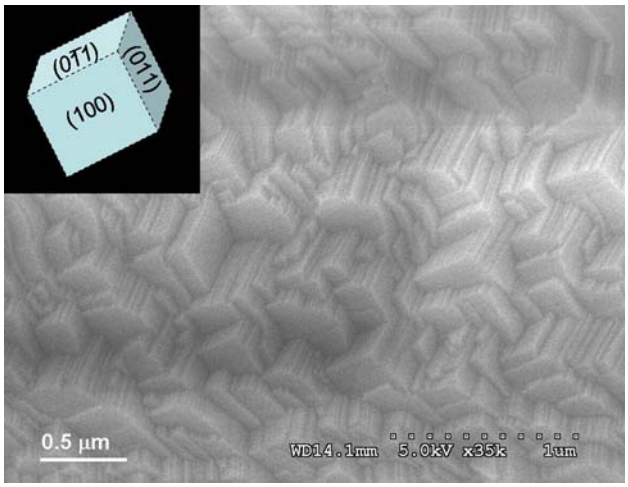

Fig. 7 Appearance of faceting morphology for spinel coated and annealed 10 h at 1400 °C (SEM, 5 keV accelerating voltage)

shows an interesting morphology which was interpreted as an example of the latter case, based on the marked difference in the degree of secondary faceting between one set of planes and the other two. Given that the secondary faceting occurred on the {110}-type planes, it is tentatively suggested that $\gamma\{110\} > \gamma\{100\}$.

Despite the large number of grains studied (>60), in no instance was square base, pyramidal type surface features observed. This type of faceting would be consistent with faceting on {111} planes [31], and has been observed for other spinel systems [32–34]. Overall, the results of the present study suggest that the surface energy of the {111} planes is higher than that of either the {100} or {110}. For example, Fig. 8 shows the faceted surface of a grain with

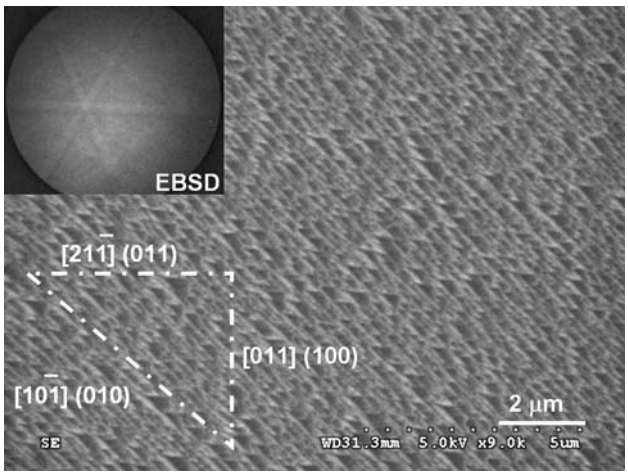

Fig. 8 Appearance of faceting morphology for spinel grain oriented close to {111} orientation. Inset shows EBSD pattern. Line directions are indexed in terms of the surface trace direction [uvw], and the postulated plane of the facet (*hkl*). Sample annealed 10 h at 1400 °C (SEM, 5 keV accelerating voltage)

orientation close to <111>. The surface is not smooth with broad terraces, which would be expected if {111} were the lowest energy plane. Instead small triangular pit-like features have developed. Based on the EBSD pattern, the surface traces of the edges of the triangular features were consistent with faceting on either {100} or {110} planes.

Effect of coating on scratched surfaces

In some cases, the as-received, optically finished samples were lightly abraded with a cloth impregnated with diamond paste (6 μm). The samples were then spin-coated using the methods described earlier in the paper. The number of spin coatings was varied between 1 and 5. The samples were subjected to a drying period of 24 h (under ambient conditions) between successive coatings. The purpose of this part of the study was to determine whether the coating could result in an improvement of the initial surface finish. The results revealed that epitaxial conversion still took place, even for the multiple coatings. However, the faceting of the sol-gel coating tended to exacerbate the appearance of the scratches, although the severity of this effect was influenced by the orientation of the scratch direction. In some cases, there were small pores in the coating along the scratch traces, suggesting that perhaps poor wetting was an issue. The number of coatings did not have a marked effect on these observations. Figure 9 shows a comparison between the morphology of the coated and uncoated spinel, for heat treatment at 1400 °C (10 h). By following the path of the scratches across the coating boundary, it is clear that many are still visible in the coated region, although some of the finer

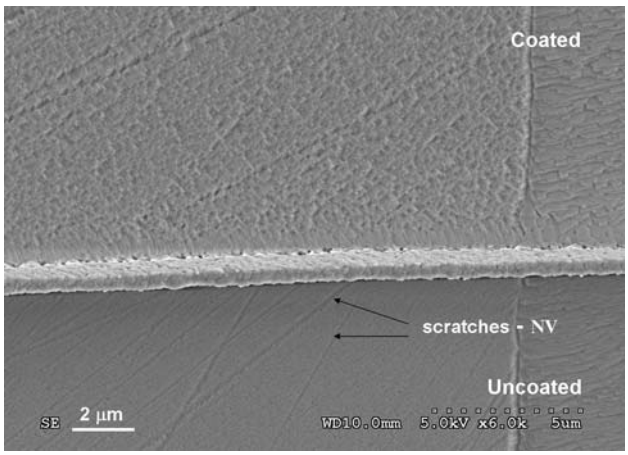

Fig. 9 Boundary between coated and uncoated region for spinel surface abraded (6 μm diamond) prior to coating, heat-treatment 10 h at 1400 °C. Note that some scratches (labelled NV) are no longer visible in the coated portion of the grain (SEM, 5 keV accelerating voltage)

features have disappeared. Work is ongoing to test whether increasing the number of coatings, and/or modifying the heat treatment to reduce the degree of faceting, will yield improved results with respect to the coating of rough spinel surfaces.

Summary

A wet-chemical method was used to produce spin coatings on polished, polycrystalline $MgAl_2O_4$ spinel substrates. For samples that were heat treated at 1100 °C, the surface films developed a porous, fine-grained microstructure. At higher temperatures (1200–1400 °C), growth of the underlying spinel grains occurred, such that the coating became isostructural with the substrate. After heat treatment, coated and uncoated regions of the samples exhibited the same appearance in the SEM. Epitaxial conversion was confirmed by comparing the thermal faceting morphology in coated and uncoated regions of the same grain, and cross-sectional TEM. For a single spin coat, the thickness of the converted films was of the order of 0.6–1 μm. A study on substrates, which prior to coating had been lightly abraded using 6 μm diamond polishing media, was also undertaken. Following heat treatment, some, but not all of the surface features were masked by the epitaxially converted coating. Given the conflicting reports regarding the relative surface energies of low index planes in $MgAl_2O_4$, the morphology of faceting in the polycrystalline spinel was surveyed. The absence of faceting on {111}, suggested that the surface energy values for these planes were higher than that of the {110} and {110} planes.

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