ON THE INFLUENCE OF APPLIED FIELDS ON SPINEL FORMATION

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ABSTRACT

Interfaces play an important role in determining the effect of electric fields on the mechanism of the formation spinel by solid-state reaction. The reaction occurs by the movement of phase boundaries but the rate of this movement can be affected by grain boundaries in the reactants or in the reaction product. Only by understanding these relationships will it be possible to engineer their behavior. As a particular example of such a study, $MgIn_2O_4$ can be formed by the reaction between single-crystal MgO substrate and a thin film of In_2O_3 with or without an applied electric field. High-resolution backscattered electron (BSE) imaging and electron backscattered diffraction (EBSD) in a scanning electron microscope (SEM) has been used to obtain complementary chemical and crystallographic information.

INTRODUCTION

Composite ceramics or coated ceramics are materials of great technological importance. The interfacial reactions that take place at elevated temperatures in these materials may lead to a mechanical and/or electrical failure. In cases where the composite material is used as an insulator, it may also be subjected to high electric fields. The presence of an electric field significantly increases ionic transport, thus leading to higher rate of interfacial reactions. This effect is particularly important along interfaces where the rate of matter transport is much higher than that through the bulk.

The formation of a spinel by the reaction between two oxides is a heterogeneous solid-state reaction [1, 2]. The spinel-forming reaction is important from a technological point of view and also serves as a model reaction system. This reaction can proceed via numerous different mechanisms [1]. If there is no transport of oxygen via the gas phase, the reaction proceeds via the couterdiffusion of cations. The kinetics can be either interface-controlled or diffusion-controlled [1-6]. The formation of $NiAl_2O_4$, $MgFe_2O_4$ and $MgIn_2O_4$ spinels has been previously studied [3, 4, 7-10]. The kinetics of the formation of $NiAl_2O_4$ spinel by the reaction between NiO and different single-crystal substrates of Al_2O_3 has been determined using a thin-film approach [3, 4]. The effect of an applied electric field on the formation of $MgFe_2O_4$ and $MgIn_2O_4$ has been investigated [7-9]. The kinetics of the reaction has been shown to be enhanced for the reactions in the presence of an applied field. The use of Pt markers has been shown to be very effective to mark the position of the interface [8, 9]. This use of markers lends valuable insight into the reactions that take place in the presence of an electric field as opposed to without such a field.

In the present paper, the influence of an electric field on the reaction between MgO and In_2O_3 to form the $MgIn_2O_4$ spinel is investigated. A thin-film approach has been shown to be very useful in the study of the solid-state reactions under an applied field. High-resolution BSE imaging is combined with EBSD to obtain complementary chemical and crystallographic

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information. The use of EBSP has been shown to be very useful in determining the crystallogaphic aspects of thin-film reactions [11].

EXPERIMENTAL PROCEDURE

Indium oxide was deposited by pulsed-laser deposition (PLD) onto a cleaved MgO (001) substrate. The substrate temperature was maintained at 500°C. The thickness of the In_2O_3 layer was about 1-2μm. The MgO substrate contained Pt markers which were produced by solid-state dewetting of a thin (~2 nm) film on the cleaved substrate. The Pt markers serve to mark the initial position of the interface. In the first sample (sample A) the reaction between the layers took place at a temperature of 1350°C under an applied voltage of 200 V for 12 minutes with the MgO substrate in contact with the anode and the In_2O_3 film in contact with the cathode. In the second sample (sample B) the reaction was allowed to continue at 1350°C for 30 minutes under the applied field.

Cross sections of the samples were then polished using the tripod-polishing technique. Microstructural investigation was carried out using a field-emission SEM (Hitachi S900). The cross-section samples were coated with 2 nm of Pt to minimize charging. A large difference in the atomic number between the two cations in the spinel makes it an ideal system for investigation using the BSE imaging in the SEM.

EBSD was performed using a JEOL JSM 6400 XV operating at 20 kV with a LaB filament. The EBSD detector is made up of a 2.5-inch diameter YAG single crystal, 60μm thick, which is epoxied to a fiber optic, 2.5 to 1 inch reducer. The reducer is then coupled to a slow-scan CCD camera, which is cooled to below -10°C. Elemental information was obtained using an energy-dispersive X-ray spectrometry (EDS) system that is also attached to this SEM. The patterns were analyzed by using a Hough transform to locate bands and band edges in the pattern. This crystallographic information, along with the elemental information, is then used to access possible phases through the database of powder diffraction files [12]. The appropriate phase is then selected and an indexed, simulated pattern is created to compare with the original and to give the orientation information.[12].

RESULTS AND DISCUSSION

The deposition of In_2O_3 on MgO substrate at 500°C results in the formation of a polycrystalline film. A plan-view secondary-electron image of the film after annealing is shown in Fig.1. The grain size of the film is comparable to the film thickness leading to the formation of columnar grains of In_2O_3 on the substrate. In such a situation the grain boundaries in the film play an important role in controlling the reaction. A BSE image in cross-section of sample A is shown in Fig.2. The spinel reaction product (with an intermediate BSE contrast) is seen to form at the interface between MgO (dark) and In_2O_3 (bright). A portion of the Pt electrode is seen on the top of the image. At this temperature and time, the reaction has only partially taken place. The Pt markers (bright spots) are seen to remain in the MgO substrate. In the absence of an applied, it has been reported that the Pt markers are located in the spinel layer [8, 9]. However, in the presence of a field, in addition to the counterdiffusion of the cations, there is a superposed flux of cations towards the negative electrode, which leads to a shift of the reaction layer towards the cathode. Thus, the Pt markers are now located in the MgO substrate.

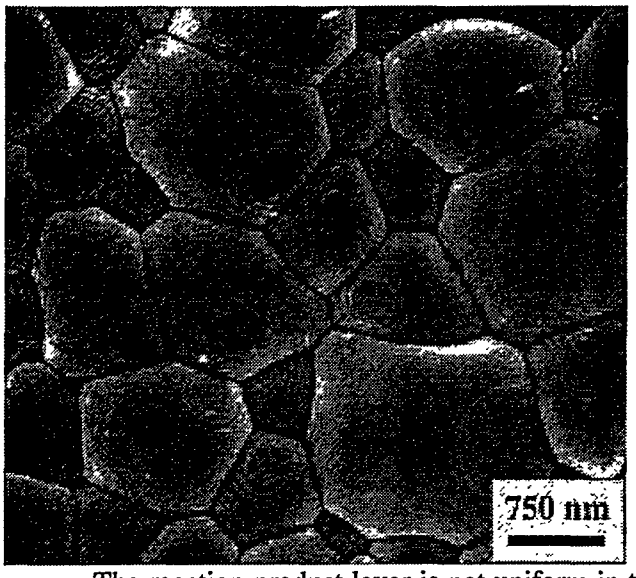

Fig. 1 Plan-view SE image from the In_2O_3 layer after annealing. The grain size (~ 1 μm) is comparable to the thickness of the layer.

The reaction product layer is not uniform in the image shown in Fig.2. Some regions of the spinel phase appear to have grown faster compared to the adjacent regions. Closer examination reveals that the faster growth is associated with the grain boundaries in the In_2O_3 phase.

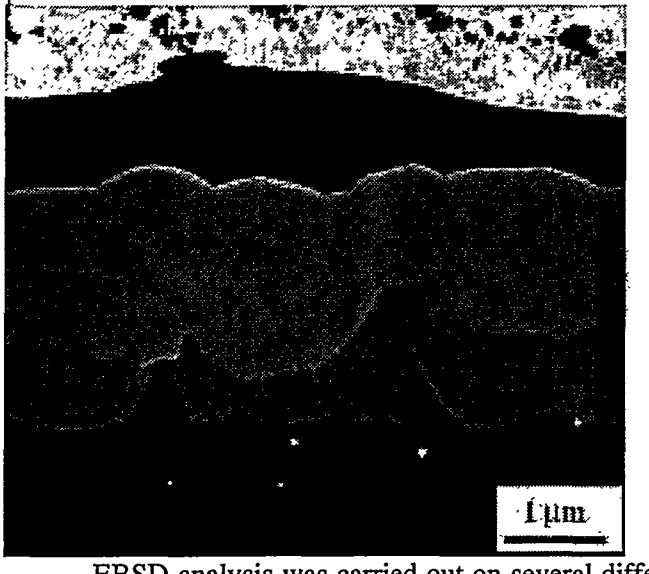

Fig. 2 BSE image from sample A. Only partial reaction to spinel has taken place. The growth of spinel is enhanced along regions where the grain boundaries are present in the In_2O_3 layer.

EBSD analysis was carried out on several different regions of the sample. The objective of the EBSD analysis was to confirm the phase identification and obtain orientations of grains of the reaction layer with respect to the MgO substrate and layer. EBSD patterns were recorded from the MgO substrate and from several grains in the reaction layer and the In_2O_3 layer. The layer was identified as $MgIn_2O_4$ by EDS, and the spinel structure was confirmed by EBSD. EBSD patterns from the MgO substrate and the reaction layer are shown in Fig.3(a-b) with some of the zones indexed. Analysis of these patterns indicates that the [001] direction in the MgO substrate, which is normal to the growth surface, is closely parallel to the [111] direction of the $MgIn_2O_4$ grain within the spinel layer. Additionally, the $[1\,\bar{1}0]$ direction of the MgO substrate is closely parallel to the $[1\,\bar{1}0]$ direction in the spinel grain. Several EBSD patterns were also taken of the In_2O_3 layer, however, there appears to be no simple orientation relationship between the In_2O_3 and the spinel layer.

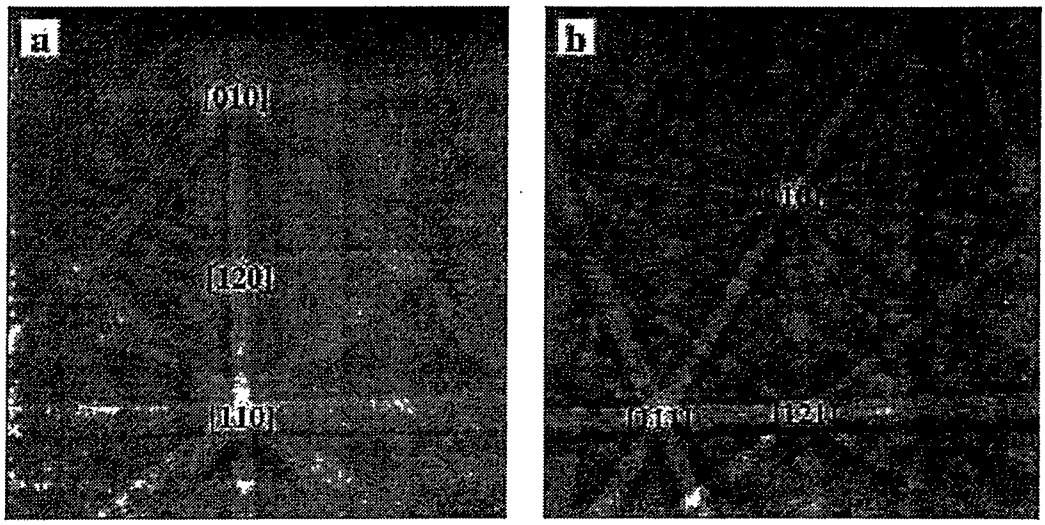

Fig.3 EBSD patterns from the MgO substrate (a) and the spinel layer (b).

Fig.4 shows a BSE image from sample B, which was annealed at 1350°C for 30 mins under an applied field of 200V. Under these conditions, the In_2O_3 film has completely reacted to form the spinel. Further annealing results in the transport of Mg ions across the spinel phase and formation of MgO on the top of the reaction product. The spinel phase is non-uniform and is composed of spikes along regions where the grain boundaries were located in the In_2O_3 layer initially. Again the final products of the reaction were confirmed by EBSD; it was found that the reaction had consumed all of the In_2O_3 and that a layer of MgO was formed on the opposite side of the reaction layer. In order to understand fully the kinetic processes, it is necessary to determine the orientation of the regrown MgO layer with respect to the substrate as well as the spinel layer. Fig.5(a-b) shows EBSD patterns taken from the substrate and from a grain within the MgO layer. It is apparent that the orientations are very close. Fig.6 is a stereographic projection which shows the 001-type directions of the substrate and the various regions within the MgO layer. Most of the regions analyzed were very similar in orientation to the substrate.

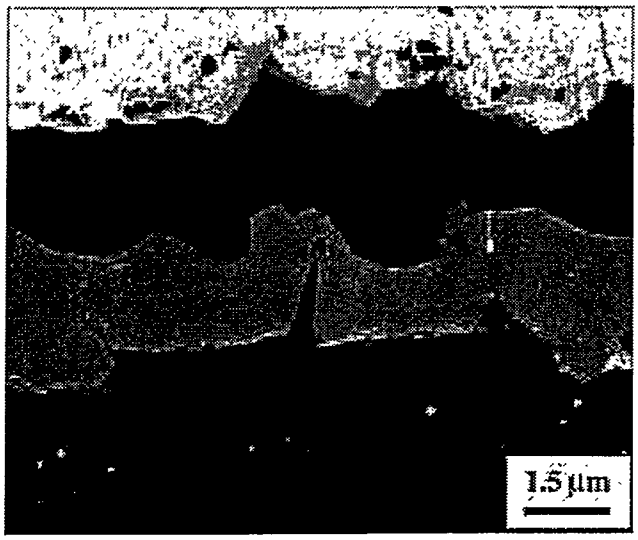

Fig.4 BSE image from sample B indicating that the In_2O_3 layer has fully reacted to form the spinel. The overgrown layer of MgO is seen on top of the spinel layer. The top portion (bright) is from the Pt electrode.

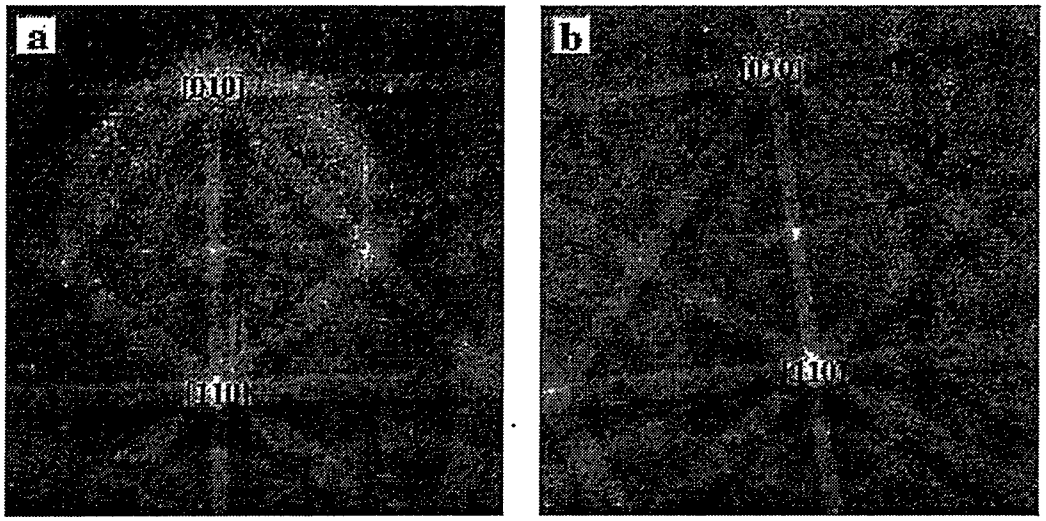

Fig.5 EBSD patterns of the MgO substrate (a) and the overgrown MgO layer (b), indicating that they have approximately the same orientation.

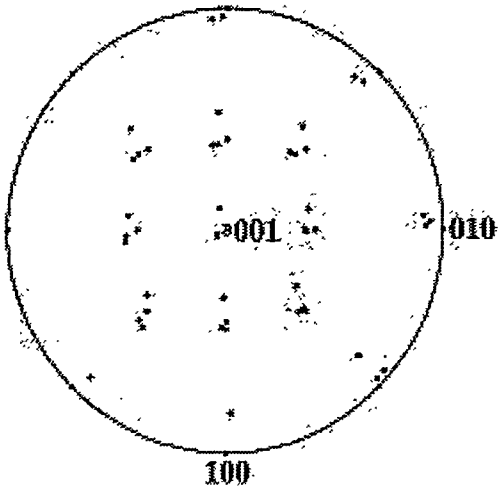

Fig.6 Stereogram showing the 001 projection of the MgO substrate and near 001 projections from several regions of the overgrown MgO layer.

CONCLUSIONS

The results indicate that the morphology during the early stages of growth of the $MgIn_2O_4$ in the electric field is determined by the grain structure of the In_2O_3 layer. The reaction front is seen to progress faster at the places where the grain boundaries are present in the In_2O_3 layer. Annealing for longer times results in the formation of MgO on the top of the spinel layer. EBSP analysis provides essential information regarding the crystallography of the reaction.

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