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The structure of Mg_2SnO_4/MgO topotaxial reaction fronts during gas–solid and solid–solid reactions

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Abstract

Thin spinel films were grown on MgO(001) substrates by a surface reaction between the MgO substrate and (i) a SnO_2 vapour, or (ii) a solid SnO_2 film at temperatures around 1200°C. Regime (i) is called a "gas–solid reaction", regime (ii) a "solid–solid reaction". Investigations by SEM, XRD, TEM/SAED, and HRTEM revealed the films obtained by the gas–solid reaction to grow in almost [001] orientation and to develop a specific morphology. They are composed of domains, the crystal lattices of which are tilted by less than 1° off the overall orientation around two different $\langle 110 \rangle$ axes. A network of interfacial dislocations with Burgers vectors a/2 [011] and a/2 [101] accommodates the Mg_2SnO_4/MgO lattice misfit of +2.5%. The films obtained by the solid–solid reaction grow in the very [001] orientation and do not consist of domains. Here, a network is proven of interfacial dislocations with Burgers vectors a/2 [110] and a/2 $[1\bar{1}0]$, which are parallel to the reaction front. The observations are discussed in terms of the interplay between reaction kinetics, the properties of the misfit-accommodating interfacial dislocations persisting at the moving reaction front, and the differences between gas–solid and solid–solid reactions concerning the starting conditions of the growing spinel phase. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Films; B. Electron microscopy; B. Interfaces; D. MgO; D. Spinels; Solid state reactions

1. Introduction

Solid state reactions between chemically different components frequently occur in heterogeneous thin films or bulk ceramics, if the latter are subject to high temperatures during their production or in use [1]. These reactions usually proceed on the nanometer scale because of the small sizes of the particles constituting the ceramics, or because of the low film thickness. Nanometer scale reactions are distinct in that their kinetics are not diffusion-controlled but interface-controlled [2–4]. Structure and morphology of the interfaces (reaction fronts) therefore decisively determine important characteristics of the reaction as, e.g. product orientation, reaction mechanisms, or reaction kinetics [5,6]. The atomic-scale structure of the reaction front, however, depends on the crystallographic conditions under which the reaction proceeds, particularly on the sign and amount of the lattice misfit at the reaction front [7]. Topotaxial reactions are useful for studying interrelations of the above kind, because they proceed under well-defined crystallographic conditions. Spinel-forming reactions mostly proceed topotaxially, thus representing suitable model systems for investigations of this kind. For five spinel-forming reactions on MgO(001), Sieber et al. studied the influence of sign and amount of the spinel/MgO lattice misfit on the atomic structure of the reaction front, on the mechanism of the interfacial reaction and on the kinetic regime of the solid state reaction [8–9]. The studies reported here were made to extend these experiments with respect to a new system involving a spinel/MgO lattice mismatch of positive sign ($a_S > 2 \cdot a_M$; a_S, lattice parameter of spinel, a_M, lattice parameter of MgO).

2. Experimental

Mg_2SnO_4 films were prepared on epi-polished (001) surfaces of MgO single crystal substrates of $10 \times 10 \times 1$ mm^3 in size, using a reaction with either (i) a SnO_2 vapour or (ii) a solid SnO_2 film. The SnO_2 vapour was obtained either from small polycrystalline pieces of

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SnO_2 (99.9% pure, from CERAC), about 1 mm in size, which were placed on the polished MgO surface heated to 1300°C in air (Fig. 1, left). Alternatively, a SnO_2 vapour incident onto the MgO substrate was produced by heating a solid SnO_2 film located opposite the MgO substrate, but almost contacting it, to temperatures of 1200°C (Fig. 1, right). Here, the SnO_2 film rested on an auxiliary MgO substrate, where it had been deposited beforehand by electron-beam evaporation in high vacuum. Solid–solid reactions were observed at the interface between the SnO_2 film and the auxiliary MgO substrate. Reaction times were typically 1 to a few hours. The samples obtained were first studied by scanning electron microscopy (SEM) in a Jeol 6300 F, and by X-ray diffraction (XRD; $\theta-2\theta$ diffraction, Φ-scans and texture analysis) in a Philips X'Pert MRD system. Plan-view and cross-section samples for transmission electron microscopy (TEM) were thinned by standard methods of mechanical thinning followed by ion etching [10]. TEM investigations were performed in a Philips CM20 T (at 200 keV), a Jeol 4000 EX (at 400 keV) and a Jeol JEM-1000 (at 1 MeV). Experimental details have been reported in a recent paper [11].

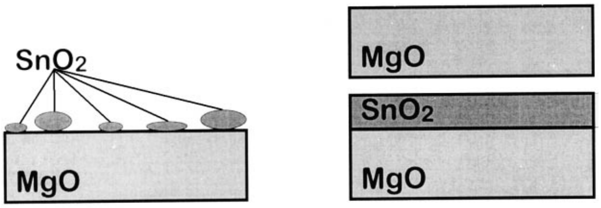

Fig. 1. Schematic of the two reaction geometries used. Left; polycrystalline pieces of SnO_2 are used as the vapour source. Right; a SnO_2 film on an auxiliary MgO substrate serves as the vapour source.

3. Results

3.1. Gas–solid reaction

X-ray diffractometry and texture analysis showed that the Mg_2SnO_4 films grown by a gas–solid reaction are crystallographically almost well-oriented according to the relation

$$MgO(001) \parallel Mg_2SnO_4(001); \quad MgO[100] \parallel Mg_2SnO_4[100], \tag{1}$$

which, however, is not exactly fulfilled, as will be explained below. Films grown from SnO_2 pieces show a dependence of their morphology on the distance from the nearest SnO_2 piece (Fig. 2). The reason is the variation of the incoming vapour flux with this distance, which also means that the different film morphologies of Fig. 2 can be considered as successive stages of film growth. The solid state reaction starts with the formation of isolated islands, which later on coalesce, finally forming a continuous Mg_2SnO_4 film. Remarkably, each of the islands consists of four domains, the boundaries of which form a cross-like pattern (cf. Fig. 2a). The nature of these domains is revealed by X-ray texture analysis (Fig. 3). This pole figure shows a splitting of the spinel (008) reflection into four peaks, which means that the Mg_2SnO_4 film consists of four kinds of tilt domains. The lattice of each domain is tilted off orientation (1) by about ±0.8° around one of two ⟨110⟩ tilt axes, as was revealed by X-ray rocking curves and Φ-scans. The domains shown in Fig. 2a are the tilt domains. TEM plan-view investigations revealed the presence of a network of misfit dislocations running along ⟨100⟩ directions with spacings of about 12 nm (Fig. 4). The dislocations are located at the Mg_2SnO_4/MgO interface

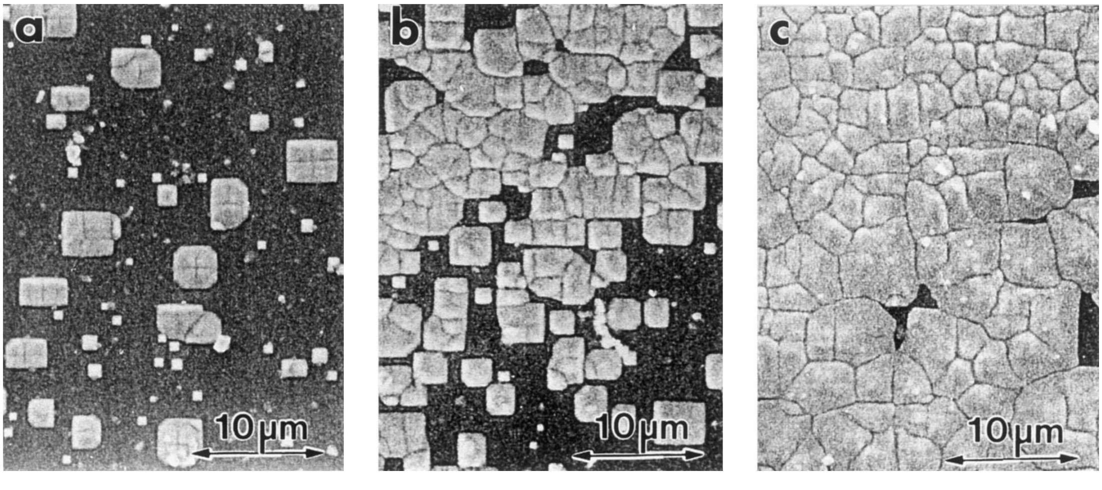

Fig. 2. SEM images of different growth stages of the Mg_2SnO_4 films grown by gas–solid reaction: (a) isolated islands; (b) coalescing islands; (c) continuous film with some residual holes.

as shown by cross-section high-resolution TEM images (Fig. 5). Fourier filtering of the latter revealed the presence of two mutually perpendicular sets of extra planes (Fig. 6), from which the Burgers vectors b = $a/2$ [011] and $a/2$ [101] were deduced. These vectors form angles of about 45° with the interface plane, thus pointing out of the latter. The dislocations are pure edge dislocations. The interface-parallel components $b_{||} = a/2$ [010] and $a/2$ [100] of the Burgers vectors accommodate the Mg_2SnO_4/MgO lattice misfit of +2.5%, while the perpendicular components $b_{\perp} = a/2$ [001] cause the tilt of the spinel lattice by about 0.8° off orientation (1).

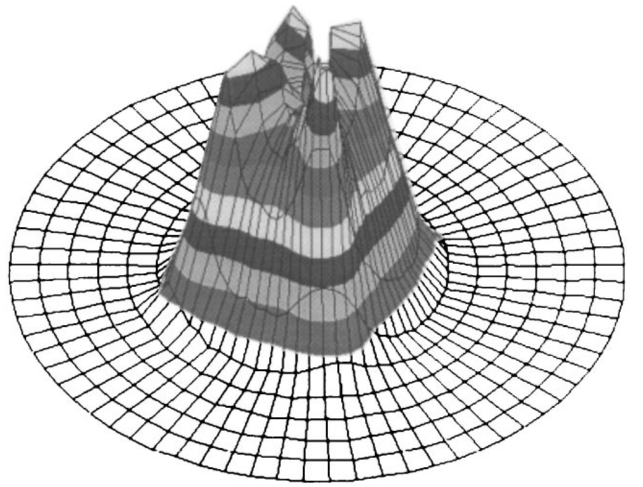

Fig. 3. Part of an X-ray pole figure of a film grown by a gas–solid reaction recorded with the (008) spinel reflection (ψ ranges from 0 to 3°). The (008) peak is almost symmetrically split into four peaks.

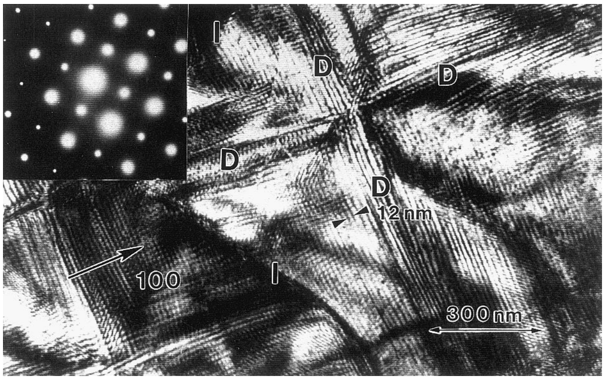

Fig. 4. Plan-view TEM image of a Mg_2SnO_4 film grown by a gas–solid reaction on a MgO substrate. Domain boundaries are marked by 'D', island boundaries by 'I'. The arrow indicates a ⟨100⟩ direction. The inset at the upper left shows a diffraction pattern of the same sample area.

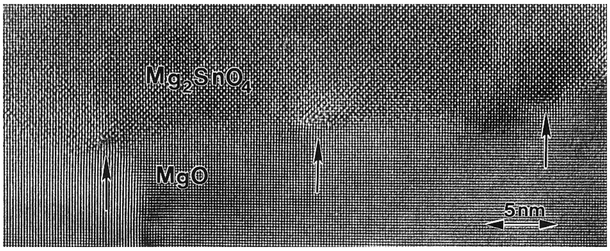

Fig. 5. High-resolution TEM image of the Mg_2SnO_4/MgO reaction front of a film grown by a gas–solid reaction. Extra lattice planes on the MgO side are marked.

3.2. *Solid–solid reaction*

X-ray pole figures (Fig. 7) show that during the solid–solid reaction the spinel films grow exactly in orientation (1). Accordingly, no tilt domains occur. A network of misfit dislocations running along the [110] and [$1\bar{1}0$] directions was identified in plan-view TEM micrographs (Fig. 8). These dislocation lines have spacings of about 17 nm. The analysis shows that their Burgers vectors are of type b = $a/2$ [$1\bar{1}0$] and b = $a/2$ [110], respectively, i.e. perpendicular to the line vectors thus having no component perpendicular to the plane of the reaction front. Again, the dislocations are pure edge dislocations accommodating the Mg_2SnO_4/MgO lattice misfit.

4. Discussion

During both gas–solid and solid–solid regimes of the solid state reaction the Mg_2SnO_4/MgO reaction front

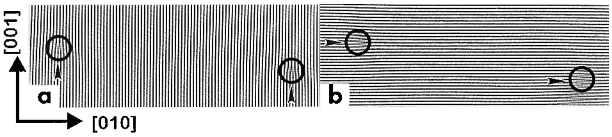

Fig. 6. Fourier-filtered images of a high-resolution TEM image of a Mg_2SnO_4/MgO interface section: (a) MgO (020)-filtered image; and (b) MgO (002)-filtered image. Extra lattice planes are visualized.

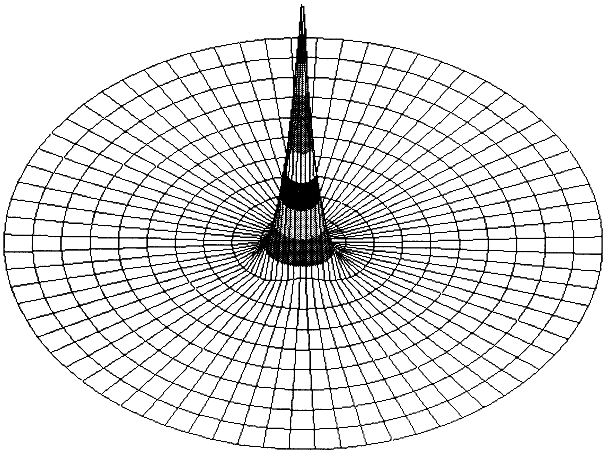

Fig. 7. Part of an X-ray pole figure of a film grown by solid–solid reaction recorded with the (008) spinel reflection (ψ ranges from 0 to 3°). The (008) peak is not split at all.

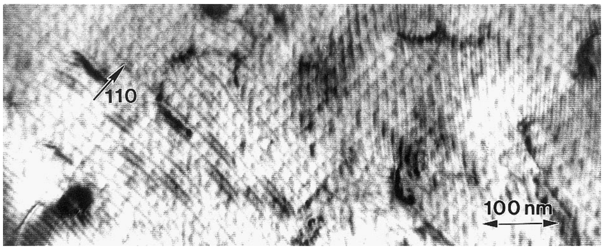

Fig. 8. Plan-view TEM image of a Mg_2SnO_4 film grown by solid–solid reaction on a MgO substrate. The arrow indicates a ⟨110⟩ direction.

moves in [001] direction, and the network of misfit dislocations has to move together with the reaction front. The mode of dislocation movement — glide or climb — determines the overall reaction rate as thin-film solid state reactions are interface-controlled and cation diffusion is sufficiently fast (cf. Refs. [8,9]). The presence of the perpendicular Burgers vector component $b_\perp$ at the reaction front of films grown by the gas–solid reaction allows the misfit dislocations to move by glide on {011} planes thus avoiding climb. Dislocation glide is favourable for rapid reaction kinetics, whereas climb is highly unfavourable kinetically because of the energetically expensive, but unavoidable emission of interstitial oxygen atoms into the dense-packed oxygen sublattices of Mg_2SnO_4 and MgO (cf. Ref. [11]). A fast reaction thus requires glide of the misfit dislocations, i.e. a condition which can only be met by the reacting system using a perpendicular Burgers vector component $b_\perp$. The latter also results in a tilt of the spinel lattice. Most probably, the necessary tilt of the initial spinel islands is facilitated if during gas–solid reactions these islands start to grow on the free surface of the sample.

The situation at the reaction front of the films grown by a solid–solid reaction is entirely different. Here, the network of misfit dislocations has to move by climb, because the interface-parallel Burgers vector does not provide a glide plane, which would allow a dislocation movement into the [001] direction. Obviously, the more rigid conditions at the solid–solid front hinder a tilt of the initial Mg_2SnO_4 islands, thus preventing the formation of a perpendicular Burgers vector component $b_\perp$. It can thus be assumed that the rate of the solid–solid reaction is considerably lower than that of the gas–solid reaction.

5. Conclusions

The rate of topotaxial spinel-forming solid state reactions is controlled by the structure of the reaction front, because the misfit-accommodating lattice defects at the reaction front must be able to move together with the interface into the overall direction of the reaction. Depending on the sign and value of the lattice misfit and also on the initial conditions of the solid state reaction, different structures of the reaction front may occur implying different types of movement of the interfacial dislocation network and accordingly also different reaction kinetics.

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