

## Interfacial Control of Reaction Kinetics in Oxides

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The kinetics of nickel-aluminate spinel formation from the solid-state reaction of thin films of nickel oxide and two different orientations of single-crystal aluminum oxide has been measured. The spinel layer was found to thicken linearly with time, indicative of kinetic control by interfacial reaction. Furthermore, the linear kinetics were found to depend on the orientation of the aluminum oxide substrates, varying by nearly 2 orders of magnitude between the fastest and slowest. The monocrystalline substrate controls the crystallographic orientation of the overlayers (nickel oxide and spinel) and thereby the structure of the interfaces. The interfacial structure controls the kinetics of the interfacial or phase-boundary reactions. [S0031-9007(96)01368-3]

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Thin-film reactions in ceramic systems are of increasing importance as materials such as oxide superconductors and ferroelectrics are applied in thin-film form. Reactions at the epilayer/substrate interface have, for example, been found to occur during the growth of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$  on  $\text{ZrO}_2$  [1]. Additionally, thin-film reactions have also been intentionally initiated for the production of buffer layers for the subsequent growth of high- $T_c$  superconductors [2]. The problem is that the kinetics of ceramic reactions are not well understood when the reaction layer is very thin; that is, when the rate-limiting step is a phase-boundary (or interfacial) reaction as opposed to diffusion of the reactants through the product layer [3,4].

Spinel formation reactions, where a rocksalt-structure oxide, AO, is reacted with a corundum structure oxide,  $B_2O_3$ , to form a spinel  $AB_2O_4$ , are among the most widely studied of solid-state reactions among oxides. The reason for this is that the materials have relatively simple crystal structures, all being essentially close-packed oxides. Additionally, only one product forms as a result of the reaction, namely, the spinel. The majority of studies of reaction kinetics of spinel-forming oxide systems have focused on "bulk" reactions, where polycrystalline compacts were placed in contact and heated to high temperatures for long times [5–7]. Under these reaction conditions, the reaction layer was always found to thicken as the square root of time, the well-known parabolic reaction kinetics characteristic of a diffusion-controlled reaction. Furthermore, marker studies, where the original interface could be followed after reaction, confirmed that the mechanism of the reaction was that first proposed by Wagner [8], counter diffusion of cations with the oxygen anions being essentially fixed. This is the case, for example, when the reactants are in intimate contact, and free oxygen is excluded from the interfaces [4,9]. Implicit in the discussion of diffusion control of reactions is that the interfacial reactions represent a negligible contribution to the overall reaction rate, or in other words that the reaction layer is sufficiently thick that the time it takes the cations to cross the reaction layer is long. In order to study the earliest stages of

spinel formation reactions, Duckwitz and Schmalzried [10] reacted aluminum oxide spheres, attached to a microbalance, with zinc oxide gas. The amount of spinel formed was inferred by the weight increase of the alumina sphere. The result was that, in the earliest stages, the amount of spinel formed increased linearly with time; a characteristic of an interfacial-controlled reaction. More recently, Simpson, Colgan, and Carter [11] demonstrated qualitatively that spinel formed at different rates when nickel oxide was reacted with different orientations of single-crystal aluminum oxide.

Thin-film geometries are particularly well suited to the study of solid-state reactions because the reactants can be brought into intimate contact and the site of the reaction is localized to the immediate region of the thin-film/substrate interface. In what is probably the first demonstration of thin-film reactions in the nickel oxide/aluminum oxide system ( $\text{NiO}/\text{Al}_2\text{O}_3$ ), Thirsk and Whitmore evaporated both Ni metal and NiO (oxidatively evaporated Ni metal) on different orientations of single-crystal  $\text{Al}_2\text{O}_3$  [12]. If Ni metal was deposited onto the  $\text{Al}_2\text{O}_3$  and then oxidized, the NiO was random polycrystalline. If, on the other hand, Ni was oxidatively evaporated, NiO was found to grow epitaxially on  $\text{Al}_2\text{O}_3$ . The orientation relationships they observed with reflection high-energy electron diffraction have been more recently confirmed [13–19]. In more recent studies of thin-film reactions in the  $\text{NiO}/\text{Al}_2\text{O}_3$  system, nickel metal was deposited onto either single-crystalline [11,20,21] or polycrystalline [22–26] aluminum oxide and then heated to oxidize the Ni to NiO. The extent of the thin-film reaction was followed with Rutherford backscattering spectrometry (RBS). Such measurements are indirect, relying on assumptions of the microstructure; a model of the reaction profile, including, for example, enhanced reaction at grain boundaries, is iteratively varied until an acceptable match with the experimental data is reached [27]. In the present study, high-quality, well-characterized, thin-film reaction couples were fabricated for the purpose of directly and quantitatively measuring the kinetics of thin-film reactions.

It has been shown previously, for the case of epitaxial NiO films on single-crystal sapphire, that the reaction (formation of spinel) initiates first along the triple junction where a grain boundary in the film meets the substrate [17]. In this case, the overall rate of reaction is determined by the nucleation rate and by the propagation of interfaces. The problem with this reaction geometry (i.e., NiO on  $\text{Al}_2\text{O}_3$ ) lies in deconvoluting nucleation from growth. It was for this reason that another reaction geometry was developed. In order to avoid nucleation altogether, a 20 nm buffer layer of  $\text{NiAl}_2\text{O}_4$  was first grown on the single-crystal sapphire substrates followed by 400 nm of NiO. Two orientations of sapphire were chosen for this study, (0001), the basal plane, and  $\{1\bar{1}02\}$ , the rhombohedral plane. The thin-film reaction couples were prepared by pulsed-laser deposition [28,29].

In order to determine the reaction kinetics, individual cross-section specimens were imaged in the field-emission gun scanning electron microscope (FESEM) and then taken apart by dissolving the glue. The specimens were subsequently heat treated at 1100 °C and prepared as above for further observation in a FESEM. The thin-film reaction couples were imaged at an accelerating potential of 5 kV in a Hitachi S-900 immersion-objective-lens FESEM equipped with an Aufrata backscattered-electron (BSE) detector [30]. A profile of reaction-layer thickness versus time at reaction temperature is the result of multiple iterations of this procedure. For the purpose of determining the thickness of the spinel layer for a given reaction couple, approximately twenty images were collected over the 3.5 mm length of each cross section at 175  $\mu\text{m}$  intervals. The individual images were acquired digitally at a microscope magnification of 50 000 $\times$  with a Silicon Graphics IRIS (SGI) [31] and then transferred to a Macintosh Quadra 900. NIH Image [32] was then used for measuring the thickness of the reaction layer; the images were calibrated, smoothed to remove noise, and then a density slice (i.e., range of image gray levels) corresponding to the spinel layer was selected and measured giving the area of the spinel layer in  $\text{nm}^2$  in the image. This area was then divided by the measured length of the reaction layer ( $\sim 2.5 \mu\text{m}$ ) to arrive at the spinel layer thickness for the particular image.

Figures 1(a) and 1(b) are FESEM BSE images of the (0001) reaction couple after 32 h and the  $\{1\bar{1}02\}$  reaction couple after 24 min at 1100 °C, respectively. NiO has a backscattered-electron coefficient (i.e., the fraction of the incident electrons backscattered),  $\eta$ , of 0.26 while that of  $\text{NiAl}_2\text{O}_4$  is 0.18 and that of  $\text{Al}_2\text{O}_3$  is 0.12.  $\text{NiAl}_2\text{O}_4$  will therefore appear intermediate in lightness between NiO (lightest) and  $\text{Al}_2\text{O}_3$  (darkest) in a BSE image. This large variation in contrast allowed the measurement of the spinel layer with image processing, as described above, by isolating a distinct range of gray levels in the image corresponding to the spinel. Although both of the reaction couples in Fig. 1 have approximately the same thickness

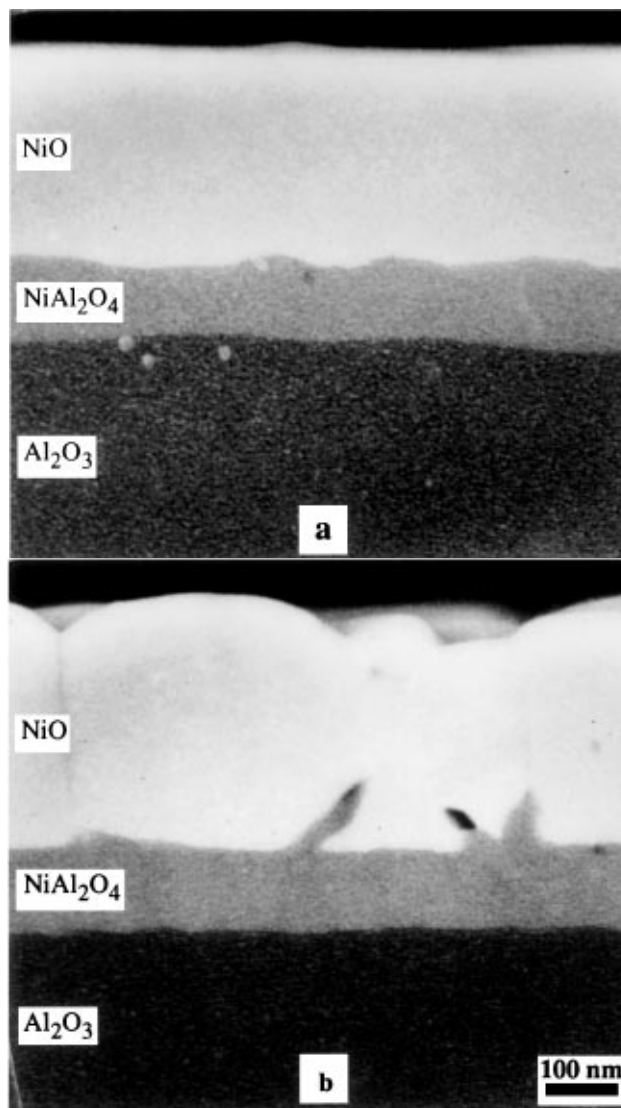


FIG. 1. Backscattered-electron images of thin-film reaction couples heated to 1100 °C. (a) The (0001) reaction couple heated for 32 h. (b) The  $\{1\bar{1}02\}$  reaction couple heated for 24 min. Both reaction couples started with the same thicknesses of spinel buffer layer and NiO.

reaction layer, they were heated for significantly different times to achieve that much reaction. Both of these reaction couples started with a 20 nm buffer layer of spinel and 400 nm of NiO, the only difference being the orientation of the single-crystal  $\text{Al}_2\text{O}_3$  (and therefore the orientation of the overlayers). In both cases, the spinel layer is for the most part uniform: the reaction proceeding by the propagation of nearly planar interfaces. This is in contrast to the irregular reaction profiles observed when no buffer layer was used [17,18]. There are, however, deviations locally from this planarity. This is most clear in the  $\{1\bar{1}02\}$  reaction couple shown in Fig. 1(b). The reaction proceeds more quickly up grain boundaries in the NiO. The extent of this enhanced grain boundary reaction did not change appreciably during the course of the heat

treatments. It is interesting to note, although there was enhancement of reaction at the NiO grain boundaries, the NiAl<sub>2</sub>O<sub>4</sub>/NiO interface elsewhere was still nearly planar. This observation suggests that the NiO grain boundaries are simply local disruptions of the interface allowing the reaction to proceed faster. Such grain-boundary reaction enhancement was not observed in the (0001) reaction couple. This may be because of the structure of the grain boundaries in this case, which are  $\Sigma = 3$  incoherent twin boundaries [13,14,16,17]. These boundaries consist of channel-like defects [33] running parallel to the substrate, thereby not enhancing growth perpendicular to the phase boundaries.

Figure 2 is a plot of the spinel reaction-layer thickness versus time at 1100 °C for a thin-film reaction. The bars on the data points represent 2 standard deviations of the scatter in the measured data. The scale of this scatter is due not to error in measuring, which is typically much smaller (~3 nm, independent of thickness), but rather to an actual variation in the reaction layer thickness along the length of the specimen. The exception is the as-deposited spinel layer where the measurement in the scatter is of the order of the error in measurement. The slopes of the lines represent the linear-reaction-rate constants which vary by a factor of approximately 70. This is clear evidence for interfacial structure controlling the kinetics of interfacial reactions. For the {1 $\bar{1}$ 02} reaction couple, the first data point in Fig. 2 (as-grown thickness of the spinel layer) has not been used to fit the slope of the line because it obviously did not fall on the line with the other data points. Interfacial reactions are time independent only when the interfacial morphology is invariant with time. In this case, the interface propagates at a rate which depends only on the reaction rate as determined by the temperature and activation energy. The reason the first data point does

not lie on the line with the others is that the interfacial morphology or structure has not achieved a steady state. The reaction, in this case, proceeds quickly at first until a steady state is reached. The structure or morphology of the interface includes the physical structure (i.e., where the ions are) as well as electronic structure. Once an interface is propagating, a linear reaction rate will be observed if the interface remains for the most part planar. This does not, however, rule out the possibility of local variations in the amount of reaction as demonstrated by the scatter (the 2 standard deviation bars on each data point) of individual data points in Fig. 2. Each data point is the average of twenty measurements of the reaction-layer thickness from each reaction couple after a given time at 1100 °C. For the (0001) reaction couple, the reaction rate is nearly two orders of magnitude smaller than that of the {1 $\bar{1}$ 02} reaction couple. Since the reaction for the (0001) couple is so much slower, the short-time behavior observed in the {1 $\bar{1}$ 02} couple is not observed.

The fact that the reaction rate varies by nearly 2 orders of magnitude between the (0001) and {1 $\bar{1}$ 02} reaction couples implies that interfacial reactions in oxides are dependent on interfacial structure. It has been suggested that interfacial reactions in spinel-forming systems consist of a number of steps; an ion approaches an interface, crosses it, becomes supersaturated in the reactant, and then “precipitates” to form more reaction product [3]. The rate-controlling step in this process was suggested to be the final stage where ions jump the interface in the “wrong” coordination and subsequently relax to the correct coordination (to form the spinel). Such a process results in a linear reaction which should be independent of crystallography as it is a relaxation process (e.g., similar to a thermal jump in a spinel resulting in a rearrangement of the cations with a characteristic relaxation time) [3]. It is clear that since the interfacial reaction rate depends on interfacial structure, the reaction-limiting step may be an interfacial barrier, hindering movement of the cations or alternatively the rearrangement of the oxygen anions at the sapphire/spinel interface (i.e., from pseudo hexagonal close packed to face-centered cubic, respectively).

The question at this point is then: How are the interfaces different between (0001) and {1 $\bar{1}$ 02} reaction couples? For the (0001) reaction couples, the pseudo close-packed plane of the sapphire, (0001), is parallel to a close-packed plane, (111), of both the NiAl<sub>2</sub>O<sub>4</sub> and NiO with the close-packed directions within those planes being parallel for all three materials [34]. This is true both for the as-grown reaction couples (i.e., with NiAl<sub>2</sub>O<sub>4</sub> buffer layer) and for reacted couples. Thus, this represents a quite coherent set of interfaces. In contrast, for the {1 $\bar{1}$ 02} reaction couples the orientation relationships are more complex with no low-index planes in the NiAl<sub>2</sub>O<sub>4</sub> or NiO being parallel to the rhombohedral (i.e., surface) plane of the sapphire. The NiO and NiAl<sub>2</sub>O<sub>4</sub> do, however, maintain a cube-on-cube orientation relationship with each other, although the

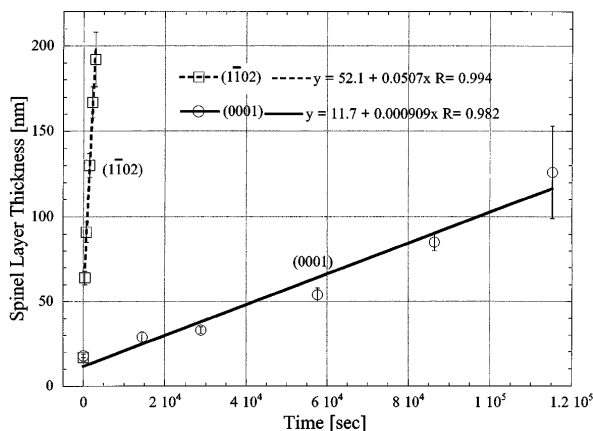


FIG. 2. Plot of spinel layer thickness versus time at 1100 °C for the (0001) and {1 $\bar{1}$ 02} reaction couples. The interfacial reaction rate constants differ by nearly 2 orders of magnitude between the fastest, {1 $\bar{1}$ 02}, and slowest, (0001), reaction couples. The bars on the data points represent 2 standard deviations in the scatter of the data, not the error (see text for details).

