# Chemical kinetics at solid–solid interfaces*

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*Abstract*: The kinetics of solid–solid interfaces controls in part the course of heterogeneous reactions in the solid state, in particular in miniaturized systems. In this paper, the essential situations of interface kinetics in solids are defined, and the basic formal considerations are summarized. In addition to the role interfaces play as resistances for transport across them, they offer high diffusivity paths laterally and thus represent two-dimensional reaction media. Experimental examples will illustrate the kinetic phenomena at static and moving boundaries, including problems such as exchange fluxes, boundary-controlled solid-state reactions, interface morphology, nonlinear phenomena connected with interfaces, and reactions in and at boundaries, among others.

## INTRODUCTION

Solid–solid reactions, in particular those in nonmetallic systems, have been investigated theoretically and experimentally since the early work of Carl Wagner [1], recently with the main emphasis on applications in ceramics. The leading concept was the maintenance of local thermodynamic equilibrium during reaction, which implies that the conditions at the phase boundaries are determined thermodynamically. It also implies that the exchange fluxes across the equilibrium boundaries are large in comparison to the net transport of matter across the boundaries, driven by the Gibbs energy of reaction.

With the advent of micro- and nanotechnology (i.e., with the reduction of the bulk volume in many systems of interest), it is obvious that the role of interfaces and phase boundaries becomes increasingly important, especially in the field of nonequilibrium thermodynamics and solid-state kinetics.

For this reason, this paper is mainly devoted to the basic concepts of interface kinetics in the solid state.

## THE BASIC THERMODYNAMIC CONCEPT: AN EXAMPLE

Let us carefully analyze the situation depicted in Fig. 1. This is a classic solid-state reaction in a binary or a quasibinary system A–B. It is assumed that the boundaries b are not in local thermodynamic equilibrium (i.e., that the boundaries, at least in part, dissipate the free energy of reaction $\Delta G_R$). In other words, the reaction is at least partially controlled by the interface kinetics at boundary AB/B.

In order to have that situation, the series resistance for bulk transport has to be small or vanishingly small relative to the interface resistance, which is always true if the product thickness $\Delta \xi \rightarrow 0$.

Figure 2 illustrates an experimental example of such a situation [2]. We note that A = $Al_2O_3$ is a single crystal, onto which B = NiO is deposited by laser-pulse deposition before the reaction starts. In order to avoid heterogenities from the nucleation process, a nanometer layer of product AB = $NiAl_2O_4$
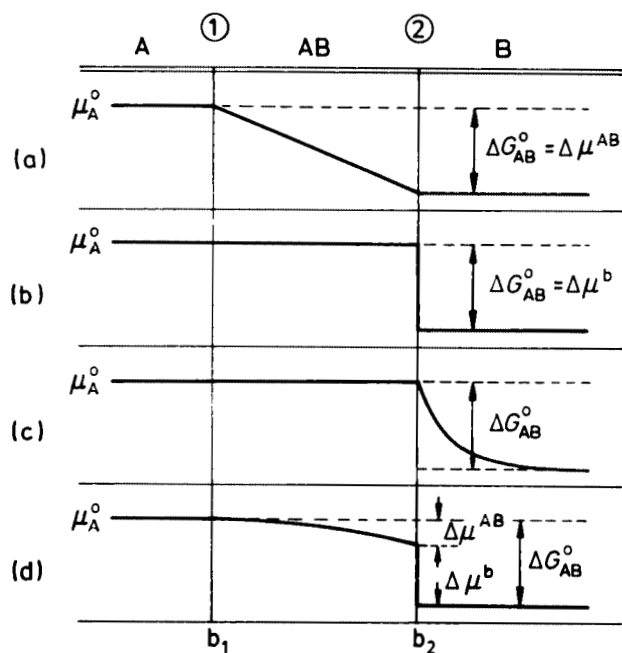
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**Fig. 1** Chemical potential $\mu_A$ during the course of a heterogeneous solid-state reaction A + B = AB. a) diffusion control. b) interface control. c) control by relaxation in B. d) mixed transport-interface control.
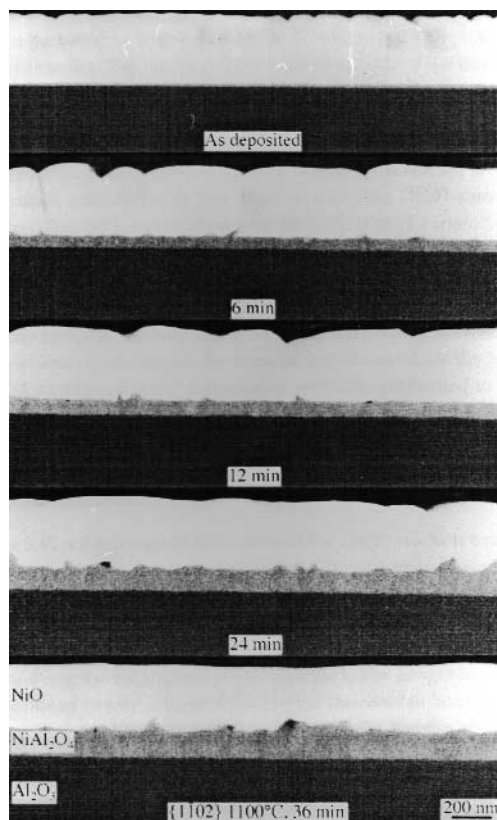


**Fig. 2** Representation of the reaction $NiO + Al_2O_4 = NiAl_2O_4$ in the very early stages according to ref. 2.

was epitaxially deposited onto various *hkl* surfaces of $Al_2O_3$ before the solid-state reaction was started. Figure 3 presents the results. We note the following:

- The solid-state reaction proceeds linearly with time.
- The rate of advancement of the interfaces $v^b$ is a function of the interface crystallography (i.e., $v^b = v^b (hkl)_{Al_2O_3}$. By and large, the rate is the smaller, the higher the density of the oxygen in the *hkl* plane.

There are various ways to state these results. Here is one of them:

Since the "virtual" driving force $\Delta G_R/\Delta V_R = P_R$ is constant, the mobility of the boundary $m^b = v^b /P_R^b$ is a function of the interface crystallography:

$$m^b = f(h,k,l) \tag{1}$$

or, more exactly, $f = f(h_1k_1l_1; (h_2k_2l_2, \varphi, xyz))$. $\varphi$ is the rotation of $hkl_1$ relative to $hkl_2$, $xyz$ are the coordinates of the origin of $hkl_2$ relative to that of $hkl_1$.

The experimental results indicate that $m^b$ is not a function of reaction time t or of the boundary position $\xi^b$ (t). This, in view of the constant driving force $P_R^b$ in the linear regime of the reaction suggests that the structure and the geometry of the phase boundary is stationary, which, in view of the ever-present lattice mismatch, is not at all a trivial result, as will be seen later.

Stationarity does not necessarily mean that the interface geometry is flat and even. Since the interface is normally a source of strain, and the elastic moduli of the adjacent phases are different, the interface may be uneven, even under equilibrium conditions, which has, for example, been shown by Hesse and coworkers [3].

It seems appropriate to make a brief comment on the determination of $P_R^b$. In the present case, $P_R^b$ is known because we know $\Delta G_R$. In general, however, it is necessary to determine the chemical potential drop across the interface by application of reversible potential probes. In view of the physical situation, this is normally almost impossible to achieve without destruction of the solid at the point where it should be measured.

## MOBILITY AND EXCHANGE FLUXES: A KINETIC ANALYSIS

Let us first of all analyze the consequences of the above experimental facts.

a) We know that $m^b$ depends on the *hkl* surface of the anisotropic reactant $Al_2O_3$. Since the other boundary of the spinel, $NiAl_2O_4/NiO$, connects two isotropic phases (epitaxially), it is most unlikely that this interface is rate determining.

b) Both the $Ni^{2+}$ and $Al^{3+}$ ions have to cross the $Al_2O_3/NiAl_2O_4$ boundary for reaction. However, since the $Al^{3+}$ ions are injected into the isotropic spinel, and $Ni^{2+}$ ions into the anisotropic alumina, it is suggested that the crossing of the $Ni^{2+}$ ions over this boundary is the rate-determining step in the linear regime of the solid-state reaction, considering that experimentally we find $m^b = m^b (hkl)_{Al_2O_3}$.

c) The moving boundary here, as any other moving boundary, leaves various defects in its wake: point defects, defect clusters, pores, dislocations. In view of our experimental example, let us look more carefully at the boundary AB/B, where <u>A</u> dissolves in B (as shown in Fig. 1) in the form of point defects. If boundary $b_2$ controls the rate exclusively, the activity of <u>A</u> in B at $b_2$, $a^b(B) = 1$, whereas it is $\exp(\Delta G_R/RT)$ in case of local equilibrium, which follows immediately from the explicit equilibrium condition.

In other words, the supersaturation of <u>A</u> (and the corresponding point defects) in B at $b_2$ is $1/\exp(\Delta G_R/RT) = \exp(-\Delta G_R/RT)$, which may amount to several orders of magnitude, depending on $\Delta G_R$.
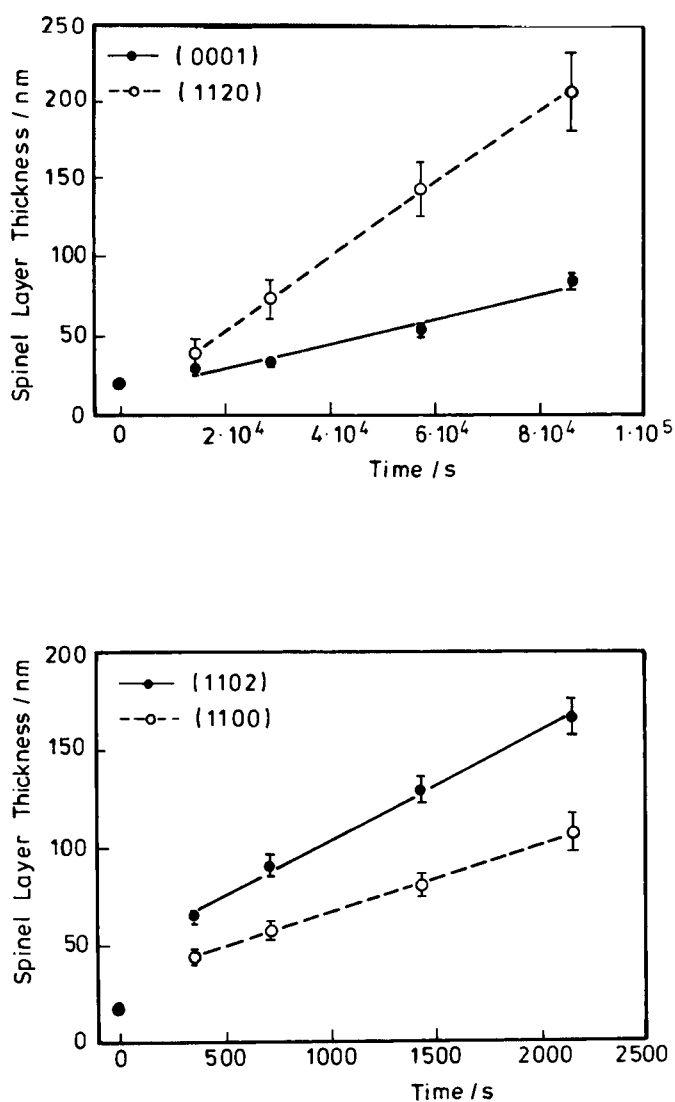
**Fig. 3** The linear rate law of the reaction in Fig. 2. The different $Al_2O_3$ single crystal surfaces are indicated [2].

A will then diffuse off the boundary into the bulk of B. If we neglect the elastic and electric potentials near the interface, a stationary state is attained if $j_A(B)^b/c_A(B)^b = v_A(B)^b = v^b$, which says that the drift velocity of A is equal to the boundary velocity.

We assume that the injected A will rearrange to find its proper sites in the B lattice after a relaxation time $\tau$. If the relaxation process is of first order, $\tau = c_A(eq)/k_R$ with $r = -k_R(c_A - c_A(eq))/c_A$ (eq), the relaxation length is then given as

$$\xi_r = \sqrt{\left(D_A(B) \bullet \tau\right)} \tag{2}$$

With this length, the boundary mobility can be expressed in terms of the drift velocity of A in B as

$$m^b = v^b / P_R^b = \Delta V_R / RT \bullet \sqrt{\left(D_A(B) / \tau\right)} \tag{3}$$

Since $D_A$ (B) in the anisotropic B is anisotropic as well, and since in addition $\tau$ can depend on the directions in which A is injected into B across the boundary b, it is obvious that $m^b$ should be a function of the form $f(hkl)_{Al_2O_3}$.

d) We can generalize the concept of the necessary relaxation processes when phase boundaries move during solid-state reactions as shown in Fig. 4.

The individual rate equations for the relaxation reactions are normally nonlinear. However, the sometimes experimentally observed (quasi-)periodic behavior [4,5] of the boundary advancement (with only an average constant velocity $v^b$) is not necessarily due to point defect relaxations. Structural relaxation at the boundary has to occur as well, as will be discussed later.
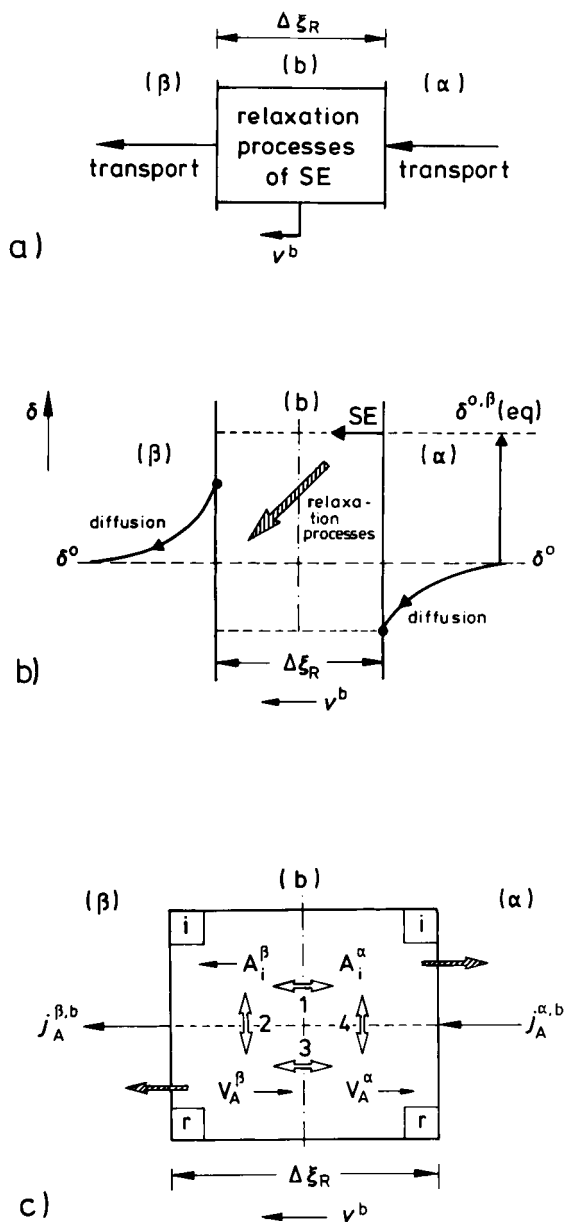


**Fig. 4** Scheme of relaxation processes at a (moving) interface during solid-state reactions.

e)     As always in the linear theory, it is possible to relate reaction rates to kinetic equilibrium parameters. In our case, it is possible to relate $v^b$ to (so-called exchange) fluxes that characterize the boundary b in equilibrium. We then have $\overset{*}{j}{}^b = |\ \overset{\rightarrow}{j}{}^b\ | = |\ \overset{\leftarrow}{j}{}^b\ |$ or, in terms of defect fluxes with $\overset{\rightarrow}{j}{}^b_{A,i}$ and $\overset{\rightarrow}{j}{}^b_{A,v}$ etc. ($i$ denoting interstitial, $v$ vacancy),

$$\overset{*}{j}{}^b_A = |\ \overset{\rightarrow}{j}{}^b_{A,i} - \overset{\rightarrow}{j}{}^b_{A,v}\ | = \overset{\leftarrow}{j}{}^b_{A,i} - |\ \overset{\leftarrow}{j}{}^b_{A,v}\ | \tag{4}$$

$\overset{*}{j}{}^b_A$ is named the exchange flux of A. In the linear regime we then have, with $\eta$ as a general thermodynamic potential:

$$j^b_A = -\ \overset{*}{j}{}^b_A = (\Delta\eta^b\ /\ RT) = (c_A\ (B)^b \cdot D_A\ (B)^b\ /\ RT) \cdot (\Delta G(AB)\ /\ \xi_r) \tag{5}$$

By comparison we find:

$$\overset{*}{j}{}^b_A = c_A\ (B)^b \cdot D_A\ (B)^b\ /\ \xi_r = c_A\ (B)^b \cdot \sqrt{}\ (D_A\ (B)^b\ /\ \tau) = (c_A\ (B)^b \cdot (RT\ /\ \Delta V_R) \cdot m^b \tag{6}$$

Exchange fluxes across solid–solid boundaries have been experimentally determined only in a very few cases. Figure 5 gives an example for the boundary AgS/AgI at T = 260 °C [6]. For

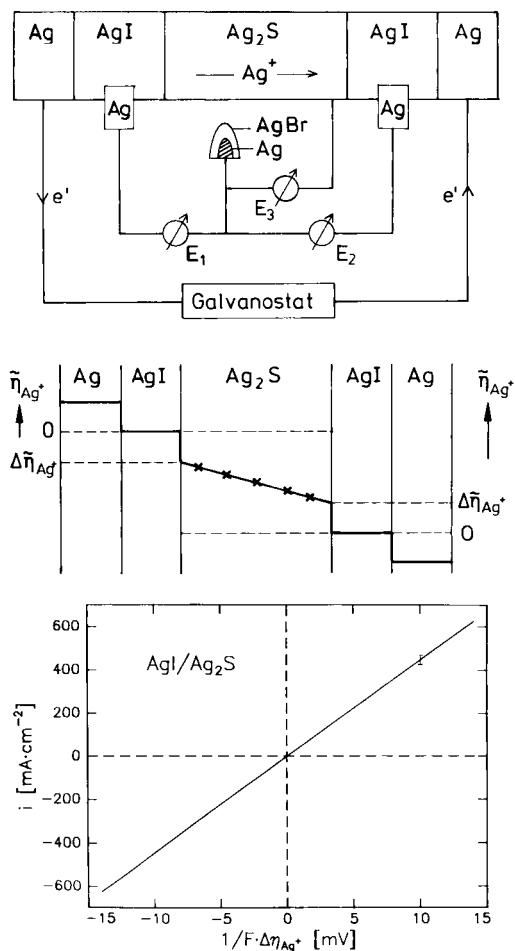**Fig. 5** Determination of chemical potentials across the AgI/Ag$_2$S$^-$ interface and the exchange flux of Ag$^+$ ions derived [6].

$\overset{*b}{j_A}$ one obtains of the order of 1 A/cm$^2$ = 10$^{-5}$ mol/cm$^2$s = 10$^{-10}$ lattice planes per Debye-vibration period, which is quite high. One may compare this number with an exchange flux calculated according to eq. 5 from one of the aforementioned spinel formation reactions [7]. At ca. 1500 K as the reaction temperature, the exchange flux is more than four orders of magnitude less than that of the AgS/AgI boundary, reflecting the high Ag-mobility in structurally disordered silver compounds.

## REDOX PROPERTIES AND DEFECT RELAXATION OF THE BOUNDARIES

In ionic crystals, interface kinetics with resting and sometimes also with moving interfaces are often studied by the application of $\Delta\eta^b = F\cdot\Delta\varphi^b$ as the only thermodynamic driving force and by determining the I/$\Delta\varphi$ (current/voltage) relationship. The situation at a metal electrode is depicted in Fig. 6 and has been studied earlier by Fischbach and others [8,9]. The point is that if the relaxation processes are not sufficiently fast, the interface becomes structurally unstable, for example, by the formation of pores and a subsequent collapse of the crystal lattice. Periodic phenomena have been observed in this context, the periodicities of which were very sensitive to the externally applied pressure.

But with boundaries between nonmetallic compounds one meets a fundamental problem [10]. Let us consider the resting boundary + AX/AY − , where $D_{X(Y)} \to 0$. Even if the transference number $t_A$ in
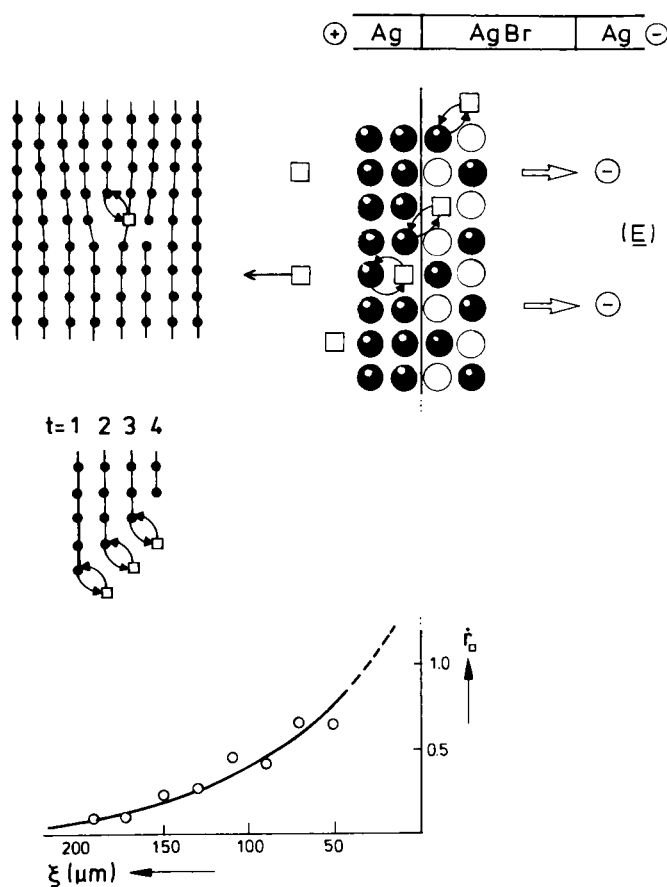


**Fig. 6** Ag/AgBr interface and the electrochemical injection of vacancies into the silver bulk with subsequent defect relaxation.

both AX and AY is almost 1, there is always a nonvanishing electronic transference, which in AX is different from AY. In other words, the interface acts as a partial internal electrode, at which oxidation/reduction processes must take place by necessity. These processes change $a_A^b$ and $a_{X(Y)}^b$ either to a stationary state (if the current density is sufficiently small), or to a value high enough so that eventually precipitation of a new oxidized (reduced) phase takes place at b. This is true even if it is assumed that local equilibrium is still prevailing at interface AX/AY, as can be immediately deduced from the course of $\eta$. In any case, since the AX/AY interface structure depends also on the local component potentials (and not only on interface crystallography), even the resting phase boundary is influenced by the kinetic conditions imposed externally.

## INSTABILITIES OF MOVING BOUNDARIES

Let us treat this topic more generally and turn our attention for this purpose to the study of the interface kinetics at moving boundaries under the action of $\Delta\eta^b = F\cdot\Delta\varphi^b$ only. The following scheme then is appropriate: + AX/BX − . As long as t(cation) is $\cong 1$, the electric current will move the phase boundary in a predictable way, if b is morphologically stable.

   Schimschal in his thesis has shown that if AX = KCl and BX = AgCl, the moving boundary is morphologically unstable, but is stable if the sequence of the phases is reversed [11]. This behavior can be explained theoretically by setting up the kinetic transport equations and performing a stability analysis. It can be shown that not only phase boundaries but even planar diffusion fronts in one-phase systems can become unstable if one superposes a second thermodynamic driving force (e.g., an electric field) to the chemical potential in the solid solution.

   Röttger [12] has investigated the AX/BX boundary for the quasibinary system KBr–AgBr. Small crystals of AgBr were embedded into the larger crystals of polycrystalline KBr. *In-situ* experiments were performed in a high-temperature X-ray camera, and a broadening of the diffraction lines of both AgCl and KCl was occasionally observed under electric load. (It should be mentioned that these experiments are extremely difficult to perform and reproduce.)

   The defects that formed at and by the moving boundary and that led to the diffraction line broadening have not yet been identified. They may stem from the debris of the structural transformation (i.e., essentially dislocations) or from the production of point defects and their clustering. A possible model is shown in Fig. 7.

   We note that the moving interface acts as a source (sink) for lattice molecules while it moves its misfit dislocations along. In ref. 12 the $v^b (\Delta\eta^b)$ − relation has been worked out in terms of the lattice misfit at AX/BX, and the diffusion coefficients of the adjacent phases.

   In general terms we can state again that two processes occur simultaneously at the driven boundary: the structural rearrangement and the matter transport, best to be described by point defect fluxes. In a stationary state, the rate of the two processes must be equal, which determines the fraction of $\Delta G_R$ dissipated by each of the two processes (see Fig. 1d).

   We have seen that the irregular structural elements and the structural debris are formed if the phase boundary moves under the action of an externally applied driving force. Depending on the spatial distribution of the defect sinks and sources, and the relaxation times of the defect annihilation, we expect a disturbed lattice in the wake of the moving boundary. In the extreme, and given a high enough driving force, one may even foresee an amorphous zone behind the moving interface to occur.

## INTERFACE AS A REACTION MEDIUM

This section will be concerned with matter transport during solid-state reactions in a boundary itself and not across the boundary. It is not meant to complement the vast literature on grain boundary diffusion, but to draw the attention on the role of interfaces in the course of solid-state reactions.
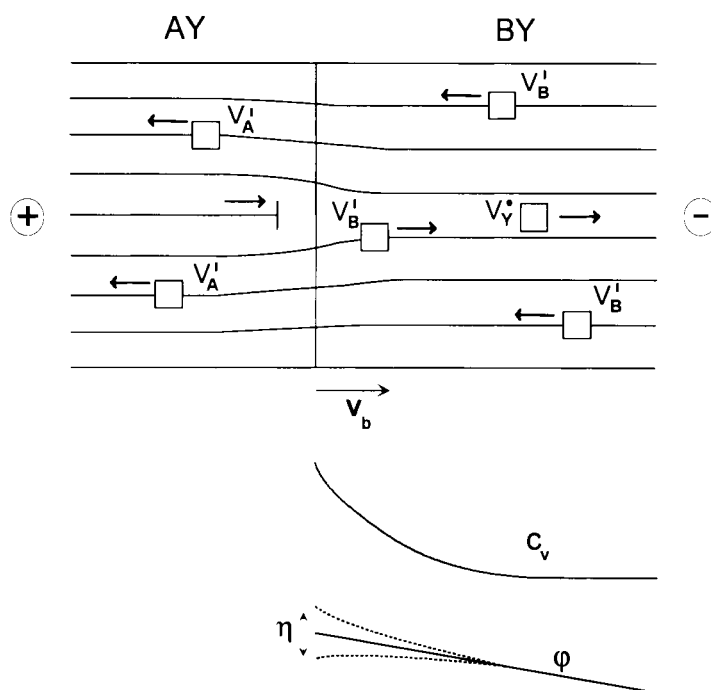
**Fig. 7** Model of the moving AY/BY interface with misfit dislocations which climb by point defect transport under the action of an externally applied electric field [12].

Again, let us first carefully analyze the result of a reaction, namely $MgO + In_2O_3 = MgIn_2O_4$ [13]. This reaction is known to occur by the counterdiffusion of cations Mg and In, as is usually observed in densely packed double oxides.

If the spinel forms between a single crystal of MgO and differently oriented large grains of $In_2O_3$, one observes the following features:

a) The growth rate of the spinel is different at the differently oriented grains of $In_2O_3$, indicating boundary rate control of the reaction at $\Delta\xi < 0.5$ μm. This is in line with other observations [7].

b) Preferred growth of spinel occurs near the grain boundary in the spinel. These boundaries stem from the original $In_2O_3$ grains. This indicates 1) that the grain boundary in the hexagonal $In_2O_3$ is preserved when it reacts to the cubic spinel (i.e., even after the hexagonal to cubic rearrangement of $O^{2-}$ ions) and 2) that the grain boundary has a higher lateral mobility of the components than the bulk lattice has.

c) The fact that the bulging of the spinel takes place essentially at the $MgIn_2O_4/In_2O_3$ interface suggests that $Mg^{2+}$ ions have preferentially been transported laterally in and along the spinel grain boundary. The oxygen necessary to form the additional spinel at the spinel/$In_2O_3$ boundary is driven by the diffusion potential (due to $D^{sp}_{Mg2+} \gg D^{sp}_{In3+}$) which is equivalent to an increase in the oxygen activity at the MgO/spinel interface.

d) It can be seen that the $MgIn_2O_4/In_2O_3$ interface also transports ions faster than the bulk spinel. Therefore, the protrusion at the grain boundary is obviously flattened and spread.

By far, more complex is the effect that the grain boundaries have on the reaction when the above reacting sample is in addition under electric load. This is illustrated in Fig. 8. A mean field of 100 V/cm was applied to the reaction couple under otherwise identical conditions. The cathode was placed in the form of a Pt-foil onto the laser-pulsed $In_2O_3$ deposition layer. The pronounced waviness, in particular that of the $MgO/MgIn_2O_4$ interface, is not the result of the above discussed morphological instability of
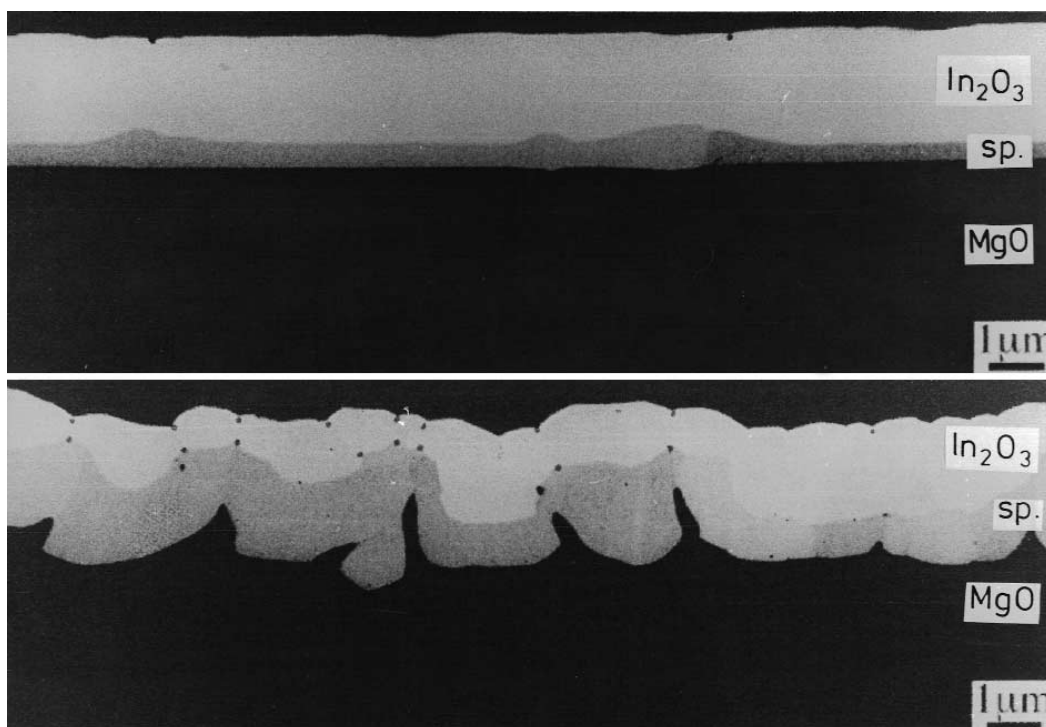
**Fig. 8** Spinel formation between MgO(s.c.) and In$_2$O$_3$ without and with an externally applied electric field [13].
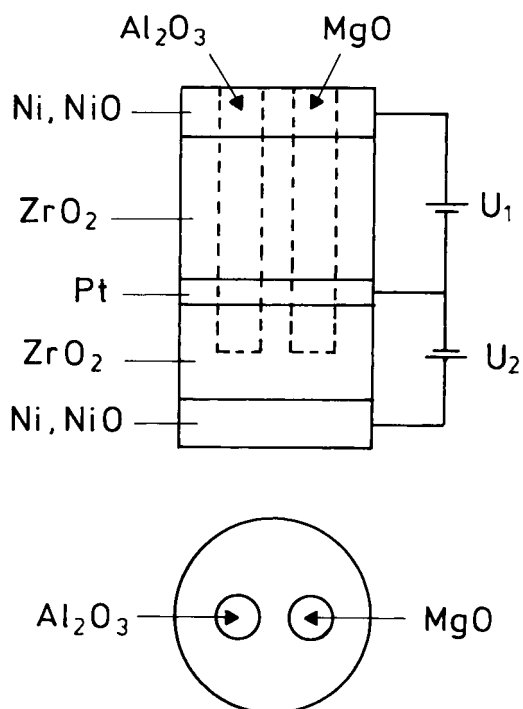


**Fig. 9** Optical micrograph of the Pt/ZrO$_2$ interface (view on the Pt-surface [14b]) and the experimental set-up [14a] for the study of the (lateral) reaction MgO + Al$_2$O$_3$ = MgAl$_2$O$_4$ in the interface (T = 1302 °C, t = 384 h).

moving interfaces which are in local equilibrium, due to the transport properties of the adjacent bulk phases. Rather, it is the action of the grain boundaries that cause the protrusion of MgO along these boundaries towards the cathode.

The MgO/spinel interface motion is due to the displacement reaction $3\ Mg^{2+} + MgIn_2O_4 = 4MgO + 2In^{3+}$. The increased mobility of $In^{3+}$ in the spinel grain boundary causes the MgO − wedge motion towards the cathode.

To conclude, another experiment is presented which illustrates the A/B interface to serve as a reaction medium proper [14]. Fig. 9b shows the scheme of the experiment. The main point is the *in situ* preparation of a zirconia/Pt interface, which is welded together under some pressure at temperature and then contacted *in situ* on one side with $Al_2O_3$, on the other side with MgO.

Although these experiments are difficult to reproduce, one finds occasionally spinel $MgAl_2O_4$ located as lateral bands in the zirconia/Pt interface, indicating that countertransport of Mg and Al took place in the interface. This is also seen in Fig. 9a. The banding could be an indication for a nucleation barrier, in line with other Liesegang phenomena. No influence of the oxygen potential on the interface transport and reaction has been detected, which is somewhat astonishing since the crystallography and the defect structure of the interface depend on the chemical potential of the components.

## ACKNOWLEDGMENTS

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