Intergranular Grooving During Oxidation of Intermetallics

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ABSTRACT

Intergranular grooving in intermetallics during oxidation was treated as a diffusional process facilitated by vacancy generation. Selective internal oxidation alters the concentrations of the alloy's components, leading to interdiffusion and the transformation of structural vacancies into excess vacancies. At low temperatures, when only grain boundary (GB) diffusion takes place, excess vacancies migrate along the GB to the outer surface, where they are annihilated. This may cause propagation of the crack growing as a planar channel along GB. The set of equations, including diffusional equations for vacancies, oxygen, and the alloy's components, and a kinetic equation for the oxide concentration, were solved numerically. The crack propagation velocity was found through the flux of vacancies to the crack tip or through the coalescence of voids beneath the metal/oxide interface. Dependences of this velocity on different parameters, such as diffusion coefficient ratios, vacancy source power, and vacancy sink density, were analyzed. The vacancy source power was recognized as the most important parameter determining whether intergranular crack propagation is fast or not. Results were compared with an analytical solution obtained earlier, and the existence of two different regimes of crack propagation – fast and slow – was confirmed.

1. INTRODUCTION

Internal and intergranular oxidation of some intermetallics is accompanied by grain boundary (GB) voiding and cracking /1-3/. In some cases GB-cracking during oxidation leads to the full disintegration of an intermetallic into a powder – small particles covered with oxides (the "pest" phenomenon) /4-6/. Westbrook and Wood /1/ assumed that the pest phenomenon is connected with GB embrittlement followed by intercrystalline fracture. In recent years, Grabke *et al.* /5,6/ studied in detail the pest-like disintegration of some intermetallics, such as $NbAl_3$ and NiAl. They came to the conclusion that this phenomenon is a complex interplay of the processes ending in strain-cracking along grain boundaries. The stresses may, however, be insufficient for attaining the critical value of the stress intensity factor. In that case, subcritical crack propagation can be due to the crack's diffusional growth /7,8/. A simple diffusional model of the grain boundary disintegration of intermetallics has recently been proposed by the authors /9/. The formation of excess vacancies due to oxidation was taken into account in that model.

In the present work GB grooving during oxidation of intermetallics was treated numerically as the diffusional and stepwise growth of plane channels along grain boundaries. The analysis was made on the basis of a computer simulation of the processes ahead of the GB crack tip during oxidation.

The model

Let us consider the oxidation of an alloy AB. At intermediate temperatures, insufficient for the bulk diffusion of oxygen, oxidation is localized in narrow zones near GBs (Fig. 1).

The oxidation of intermetallics is selective. The oxidized component, A, is consumed at the metal/oxide interface due to reaction with oxygen. Depletion of this component at the grain boundary metal matrix near the interface causes diffusional fluxes of the components, A and B, J_a and J_b, along the grain boundary (GB) and, if diffusivities of the components are different, a vacancy flux, $J_v = -J_a - J_b$, results (Kirkendall effect). The oxide layer formed at the "top" of a grain boundary is assumed to be defective (e.g. due to a low oxygen pressure) which allows oxygen access to the metal/oxide interface. Penetration of oxygen into the GB leads to internal oxide precipitation. Internal stresses caused by these oxides and by a climb of GB dislocations (due to the absorption of the excess vacancies) influence the diffusional fluxes and, at some critical value, may cause a jump forward of the GB crack. The vacancies generated during oxidation diffuse along the GB and accumulate in voids. The formation and coalescence of GB voids may be another reason for GB grooving.

Having regard to the points made, the following processes ahead of the crack tip should be incorporated in the model: i) diffusion of oxygen into the material; ii) external and internal oxide formation; iii) diffusion of the alloy's components; iv) generation, diffusion and annihilation of vacancies; v) voiding; vi) internal stress generation and relaxation by crack jumps.

To develop a quantitative description of these processes, the following equations were used. The concentration of oxygen, C_o, at the GB can be described by the diffusion equation:

$$\frac{\partial C_o}{\partial t} = D_{ox}\frac{\partial^2 C_o}{\partial x^2} - \alpha_1 C_o C_a(1-C_{ox}), \qquad (1)$$

where D_{ox} is the diffusivity of oxygen, α_1 is the kinetic coefficient. The concentration profile of A-atoms, C_a, along the GB beneath the metal/oxide interface follows the diffusion equation:

$$\frac{\partial C_a}{\partial t} = D_a\frac{\partial^2 C_a}{\partial x^2} - \alpha_1 C_o C_a(1 - C_a) \qquad (2)$$

where D_a is the intrinsic GB diffusion coefficient of A-atoms, x is the distance from the external surface, t is the time. The second term in eqns. (1), (2) describes the internal reaction between oxygen and A-atoms to form oxides. Concentration of internal oxides is determined by the kinetic equation:

$$\frac{\partial y}{\partial t} = \alpha_1 C_o C_a(1-y) \; . \qquad (3)$$

The diffusion equation for vacancies, comprising their sources and sinks, can be written as follows:

$$\frac{\partial C_v}{\partial t} = D_v \frac{\partial^2 C_v}{\partial x^2} + (D_b - D_a)\frac{\partial^2 C_a}{\partial x^2} + D_v C_v \frac{\Omega}{kT}\frac{\partial^2 \sigma_{in}}{\partial x^2} + p\alpha_1 C_o C_a - \alpha^2 D_v (C_v - C_{v0}) \; , \qquad (4)$$

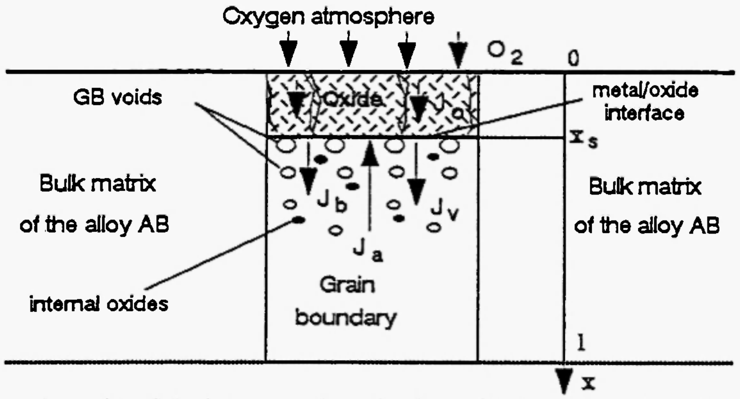

Fig. 1: A model of the intergranular selective oxidation of an alloy AB, schematic.

where D_v and D_b are the GB diffusion coefficients of vacancies and of the nobler component of the alloy, respectively, $\alpha = (1/l_s)$, l_s being the average distance between sinks (i.e. voids), C_{v0} is the equilibrium vacancy concentration, p is a coefficient of proportionality between the rates of oxide formation and vacancy generation. The initial concentration of vacancies was assumed to be at equilibrium at the surface and along the GB:

$$\text{For} \quad t = 0: \qquad C_v = C_{v0}\,, \qquad 0 \le x \le l. \tag{5}$$

The following boundary and initial conditions for concentrations C_a,, C_o and y were used:

$$\text{For } t = 0: \quad x_s = 0; \quad C_a = C_{as}, \text{ and } y = 0 \tag{6}$$

$$\text{for } 0 \le x \le l; \quad C_o(x{=}0) = C_{os}, \quad C_o(x > 0) = 0.$$

$$\text{For } t > 0: \quad C_a(x{=}x_s) = C_{as}\,, \qquad C_o(x{=}x_s) = C_{os}\,,$$

$$\text{and } y(x{=}x_s) = 0;$$

$$\left.\frac{\partial C_a}{\partial x}\right|_{x=l} = \left.\frac{\partial C_o}{\partial x}\right|_{x=l} = 0\,, \tag{7}$$

where x_s is the location of the metal/oxide interface, l is half of the sample thickness.

Growth of the GB plane channels

Consumption of the oxidized component at the metal/oxide interface serves as a surface source of vacancies. The flow of this component to the interface is equivalent to the opposite flow of vacancies:

$$J_v^1 = -\left.J_a\right|_{x=x_s} = D_a \left.\frac{\partial C_a}{\partial x}\right|_{x=x_s}. \tag{8}$$

The vacancies generated during oxidation diffuse along the GB (eqn. (4)) and accumulate in voids. The volume fraction of voids was determined by integration of the last term in eqn. (4), describing sinks of vacancies:

$$\frac{\Delta V_{void}}{V} = k_1 \int_0^t \alpha^2 D_v \left(C_v - C_{vo}\right) dt \tag{9}$$

where the dimensionless parameter k_1 denotes the portion, k_2, of the vacancies annihilated at GB voids (another portion can be annihilated at GB dislocations, or depart from GB to the bulk matrix sinks). The values of parameters k_1 and k_2 depend on the temperature and the initial defect structure. The precipitation of oxides at GB and the climb of GB dislocations lead, as mentioned above, to internal stress formation:

$$\sigma_{in} \quad - \left(\varepsilon_{H1} + \varepsilon_{H2}\right)K\,, \tag{10}$$

where $\varepsilon_{H1} = k_2(\Delta V_{void}/V)$ and $\varepsilon_{H2} = y(\Delta\Omega/\Omega)$ are the hydrostatic strains caused by the dislocation climb and by the volume change during oxide formation, respectively, K is the elastic modulus. In the present work the role of internal stress is not analyzed.

Two different cases of GB channel growth were considered:

i) *Pure diffusional growth.* All vacancies generated due to the consumption of the oxidized component – eqn. (9) – are assumed to be annihilated in the size reduction of the GB metal matrix. The metal/oxide interface serves as an ideal vacancy sink, and equilibrium vacancy concentration is maintained at $x = x_s$:

$$\left.C_v\right|_{x=x_s} = C_{vo}\,. \tag{11}$$

The displacement rate of the metal/oxide interface is determined by the total vacancy flow to the interface:

$$V_{s1} = \left(\frac{dx_s}{dt}\right) = -\Omega \left.J_v\right|_{sur} = \left.\left\{D_v \frac{\partial C_v}{\partial x} + D_b \frac{\partial C_v}{\partial x}\right\}\right|_{sur} \tag{12}$$

ii) *Void-induced propagation.* The displacement rate of the metal/oxide interface was determined as a purely void-induced propagation. The metal/oxide interface was assumed to be impermeable to vacancies. The total vacancy flux to the interface equals zero:

$$\left.J_v\right|_{x=x_s} = -\left[D_v \frac{\partial C_v}{\partial x} + D_b \frac{\partial C_a}{\partial x}\right]_{x=x_s} = 0\,, \tag{13}$$

leading to a zero displacement rate V_{s1}, and then the vacancy concentration is not at equilibrium at the metal/oxide interface, which may lead to the formation of voids immediately beneath the interface. In the computer simulation of this situation we used the following procedure: When the volume fraction of voids reached unity, the metal/oxide interface was displaced to the distance where this condition ($\Delta V/V=1$) was satisfied.

RESULTS AND DISCUSSION

Dimensionless parameters $\xi = x/l$ and $\tau = tD_a/l^2$ were used in the calculations. The set of equations (1)–(4), (11), (12) with initial and boundary conditions (5)–(7), (12) (or (14)), was solved numerically by the explicit finite-difference method /10/. The following cases were considered:

1) The metal/oxide interface is displaced due to an outward vacancy flux to the interface – eqn. (13). Vacancies are generated by a change in the alloy composition, due to the Kirkendall effect and the consumption of A–atoms at the interface ($x = x_s$), where equilibrium vacancy concentration is maintained. The time dependences of the interface displacement were calculated for different parameters (D_b/D_a), (D_{ox}/D_a), (D_v/D_a), and (αl) (Fig. 2). The rate of displacement is substantially higher in the case of slower diffusion of the oxidized component, and it increases with a decrease in the steady-state concentration of the oxidized component at the interface (curves 1, 2, Fig. 2a). Activity of the vacancy source may substantially facilitate the diffusional crack growth (curve 3, Fig. 2a).
2) Growth of the GB crack was calculated as the void-induced propagation of a channel along the GB. Vacancies generated at the GB accumulate under formation of GB voids (k_1 = 1 or 0.5 in eqn. (10)). Formation and coalescence of voids beneath the interface was considered as the only cause of the interface displacement. The interface was advanced for one step $\delta\xi$, when the volume fraction of voids at $x = x_s$ reached unity: $\Delta V/V=1$. The stepwise lines in Fig. 2b describe the stepwise movement of the interface, as calculated. Straight lines average these stepwise dependences. The most important parameters determining the displacement rate are the ratios (D_b/D_a), (D_{ox}/D_a) and the concentration of the oxidized component, C_{as}, at the interface. As can be seen, the rate of the void-induced propagation of the channel is lower than the diffusional rate.

Thus, fast and slow propagation of the GB channels can be realized depending on the system parameters. The fast regime can be related to an intergranular disintegration of the material during oxidation – a process observed for some intermetallics /1,4-6/. The slow regime corresponds to the case when no disintegration occurs. A similar conclusion was reached earlier on the

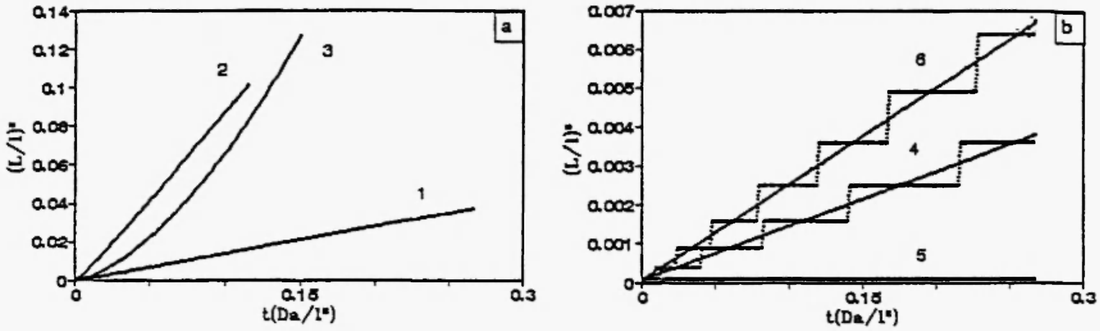

Fig. 2: Calculated GB channel length as a function of oxidation time:
(a) displacement due to the vacancy ffux Eq. (11) only; $C_v(x_s) = C_{vo}$, $D_o/D_a = D_v/D_a = 1$. $C_{a0} = 0.5$, $C_{os} = 0.005$, $(\alpha l) = 100$; diffusion of the oxidized component is slow: $D_b/D_a = 3$; $C_{as} = 0.4$ (1, 3) and $C_{as} = 0.3$ (2); $p = 0$ (1,2) and $p = 10^5.(D_a/\alpha, l^2)$ (3).
(b) displacement due to void formation beneath the interface, $J_v(d_s) = 0$, $D_o = 0$, $(\alpha l) = 100$, $C_{as} = 0.3$ (5) and $C_{as} = 0.1$ (6, 7), $D_b/D_a = 3$ (5), $D_b/D_a = 0.1$ (6) and $D_b/D_a = 1$ (7).

basis of the simplified diffusional model for GB channel growth /9/.

CONCLUSION

A quantitative model of spontaneous GB grooving during oxidation was proposed. The model describes the interplay of different processes in the oxidation zone ahead of the crack tip. Two different mechanisms of the GB channel growth were analyzed: diffusional growth and void-induced growth. Vacancy generation during oxidation was recognized as the most important parameter determining whether intergranular crack propagation is fast or not. Fast GB crack propagation can be responsible for the intergranular disintegration of intermetallics during oxidation.

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