Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 59 (2011) 1389–1399

Acta MATERIALIA

www.elsevier.com/locate/actamat

Theory of the Kirkendall effect during grain boundary interdiffusion

L. Klinger, E. Rabkin *

Department of Materials Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel

Received 30 April 2010; received in revised form 19 July 2010; accepted 31 October 2010
Available online 1 December 2010

Abstract

A grain boundary interdiffusion in a semi-infinite bicrystal under the conditions of negligible bulk diffusion is considered. We show that the inequality of the intrinsic grain boundary diffusion coefficients of the two components leads to plating out of additional material at the grain boundary in the form of a wedge of extra material, which generates an elastic stress field in the vicinity of the grain boundary. We solved a coupled diffusion/elasticity problem and determined the time-dependent stress field and concentration distribution in the vicinity of the grain boundary. We show that diffusion of embrittling impurities along the grain boundary generates tensile stresses at the boundary which are high enough to cause intergranular fracture.

Keywords: Grain boundary diffusion; Grain boundary embrittlement; Elastic behaviour; Theory

1. Introduction

The inequality of intrinsic diffusion coefficients in a binary diffusion couple results in a movement of inert markers, or lattice drift, known as the Kirkendall effect [1]. According to Darken's interpretation of the Kirkendall effect, lattice drift is caused by the divergence of the vacancy flux in the diffusion zone [2]. The excess vacancies are absorbed by edge dislocations climbing normal to the diffusion direction, which results in destruction/creation of atomic planes and concomitant lattice drift. In Darken's original model, only dislocation climb normal to the diffusion direction was allowed; in a diffusion couple with free ends such climb does not result in any incompatibility stresses and the diffusion couple remains stress-free throughout the interdiffusion process. The scarcity of the vacancy sources/sinks, especially during the initial stages of interdiffusion, or the dislocation climb parallel to diffusion direction, result in generation of stresses in the interdiffusion zone. A general treatment of the coupled problem of interdiffusion and stresses was given by Stephenson [3]. To describe the temporal evolution of interdiffusion-generated stresses he introduced a phenomenological viscosity of the solid, η. Small values of η correspond to fast relaxation of stresses, and the Darken result for effective interdiffusion coefficient is reproduced in this case. For large values of η, the differences in atomic fluxes of components is compensated for by the stress gradient developing in interdiffusion zone, rather than by the lattice drift. This results in an expression for interdiffusion coefficient different from that of Darken (Nernst–Planck regime of diffusion in the terminology of Ref. [3]; the same result was obtained earlier by Bokstein and Shvindlerman [4]). Alternatively, dislocation climb parallel to the diffusion direction can result in sample extension/contraction normal to the diffusion direction and give rise to internal stresses; this process was observed during interdiffusion in thin wires [5] and sheets [6].

In contrast with the bulk Kirkendall effect, very little is known about the Kirkendall effect during grain boundary (GB) interdiffusion. Atomistic simulations [7] have demonstrated that diffusion in GBs occurs with the aid of point defects (vacancies and interstitials), which makes the GB Kirkendall effect possible. Experimental evidence of this effect is, however, scarce and mostly indirect. The authors

* Corresponding author. Tel.: +972 4 829 4579; fax: +972 4 829 5677.
E-mail address: erabkin@tx.technion.ac.il (E. Rabkin).

1359-6454/$36.00
doi:10.1016/j.actamat.2010.10.070

of the present work interpreted nucleation and growth of elongated GB pores during diffusion of Cu along the GBs in ordered NiAl intermetallics as a manifestation of the GB Kirkendall effect [8]. The GB pores, formed alongside bulk pores in the Cu–Sn diffusion couple, were interpreted in terms of GBs acting as sinks for vacancy flux caused by the bulk Kirkendall effect [9]. Probably the most convincing evidence for the GB Kirkendall effect associated exclusively with the GB diffusion was provided by Sommer et al. [10]. They observed a diffusion-induced GB migration (DIGM) in thin bicrystalline Au films with a deposited layer of Ag at room temperature, at which any interference of bulk diffusion can be ruled out. It was proposed that the GB Kirkendall effect caused by fast diffusion of Ag along the GBs in Au gives rise to high biaxial stresses in the near-GB region, which in turn can cause GB migration due to anisotropy of elastic moduli in two neighboring grains [10]. However, no estimates of the amplitude of the stresses that may develop due to the GB Kirkedall effect were presented in this work.

To the best of our knowledge, the only attempt to treat the GB Kirkendall effect quantitatively was undertaken by Hwang et al. [11]. In this work, the surface accumulation method for studying the GB diffusion in thin films was developed and applied to measuring the diffusion of Ag along the GBs in polycrystalline Au film. As pointed out by Hwang et al., "The mass gained or lost by the unequal diffusion in the grain boundary is compensated for by a mass flow in a direction perpendicular to the grain-boundary plane" [11]. Hwang et al. have written down the corresponding diffusion equations taking into account mass flow, or lattice drift, normal to the GB plane. It was shown that in the regions gaining mass the effective GB diffusivity is given by Darken's expression, while in the regions losing mass the effective GB diffusivity coincides with the diffusion coefficient of the slow component [11]. It is clear, however, that the variable lattice drift normal to the GB should lead to strain accumulation in the near-GB region. The resulting stresses modify the chemical potentials of atoms diffusing along the GB and, consequently, change the atomic diffusion fluxes. These stresses generated by the GB Kirkendall effect (and mentioned in the later work [10]) were not taken into account in the analysis of Ref. [11]. As demonstrated by a number of stress-related effects during the bulk Kirkendall effect [3–6], such stresses in the near-GB region may be quite significant.

Gao et al. provided a quantitative analysis of stresses and strains caused by divergent GB self-diffusion flux (generating so-called "diffusion wedges") in the initially stressed polycrystalline thin films [12]. A similar analysis was later applied by the present authors for analysis of interdiffusion (with equal intrinsic diffusivities of components) in stressed semi-infinite bicrystal [13]. In the present work we will apply the methodology developed in Refs. [12,13] to analysis of the GB Kirkendall effect in an initially stress-free semi-infinite bicrystal. The aim of our model is to provide quantitative answers to the following questions:

- What is the dependence of "effective" GB diffusivity on intrinsic diffusivities of components? What kind of GB diffusion coefficient is measured in the radiotracer GB diffusion experiments in Harrison's *C*-regime [14], in which the diffusing atoms are confined within the GB core, and the concentration gradients cannot be considered as small, at least at the beginning of diffusion process?
- What are the amplitude and the character of stresses developing in the GB vicinity as a result of GB interdiffusion? Are these stresses high enough to activate GB dislocation sources, or can they lead to GB decohesion in the case of diffusion of embrittling impurity?
- What is the thickness of the wedge of extra material at the GB developing as a result of inequality of GB diffusion fluxes? Can the GB diffusion in Harrison's *C*-regime be confined within the atomically thin GB core?

2. The model

We will consider a semi-infinite bicrystal of solid phase *A* with a GB normal to the external surface (see Fig. 1). The component *B* deposited on the surface of *A* penetrates into the GB. Component *A*, generally, moves in the opposite direction. Furthermore, we neglect the diffusion in the bulk, which approximately corresponds to the temperatures below $0.4T_m$ (where T_m is the melting temperature of *A*).

The concentration gradient itself moves the components *A* and *B* in opposite directions. If the intrinsic diffusivities of the components are different, these fluxes are not balanced. The divergence of the total diffusion flux along the GB causes plating out of an additional material at the GB in the form of a wedge of extra material. The latter causes internal stresses in the bicrystal, which, in turn, affect the GB diffusion.

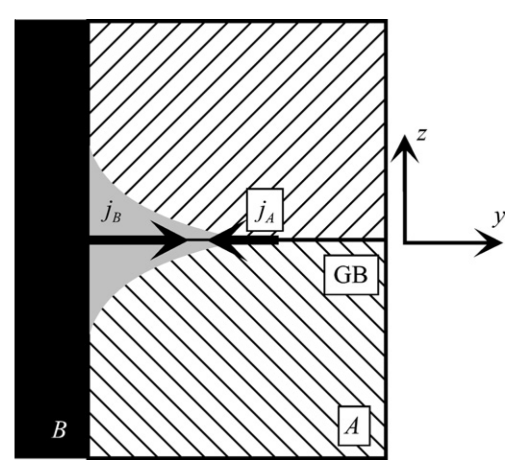

Fig. 1. A bicrystal of *A* with the layer of *B* deposited on the surface. The imbalance of diffusion fluxes of the two components, j_A and j_B, is caused by the difference in intrinsic diffusivities of *A*- and *B*-atoms along the GB. This imbalance leads to the formation of a wedge of extra material at the GB.