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Lateral Diffusion Spreading of Two Competitive Intermetallic Phases along Free Surface (System Cu-Sn)

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1. Introduction

In recent years, formation of sub-micron intermetallic layers has been detected during interdiffusion along a free surface. [1, 2]. Kinetic regularities of spreading and thickening of surface intermetallic phases have been studied for the systems, in which only one compound grew although, according to the phase diagram, several phases could grow [3, 4]. In this paper we study the kinetics of competitive diffusion growth and lateral spreading of two intermetallic layers along a free surface. We apply our analysis to the Cu – Sn system, in which two competitive phases propagate over the surface during surface reactive diffusion. Last years interfacial reactions in Cu-Sn system are under great attention, mainly due to new Pb-free microelectronic technologies, which apply Sn-based solders with preferably Cu under-layers.

2. Experimental

Our samples were composed of contacting Cu and Sn plates of about 2 mm thickness. The cross-section used for studies of surface interdiffusion was polished mechanically and cleaned chemically. The samples were annealed isothermally in a temperature range 160 – 200°C in purified hydrogen atmosphere. After successive stages of isothermal annealing the morphology of intermetallic phases forming along the surface was examined by the methods of optical microscopy, scanning electron microscopy (Field Emission Gun SEM provided with X-ray microanalysis), and by atomic force microscopy (AFM). With these methods the kinetics of lateral phase spreading, concentration distributions in growing compounds and surface profiles of spreading phases were measured.

3. Results and discussion

Two intermetallic compounds, ε – phase Cu_3Sn (i_1) and η – phase Cu_6Sn_5 (i_2), grew and propagated simultaneously both in the bulk and on the surface of the Cu-Sn couple (see scheme in Fig. 1). Bulk phases grew "unipolarly" as a result of Sn diffusion through the growing phase layers [1]. It was caused by inequality $D_{Sn} \gg D_{Cu}$ in both phases (D_{Sn} and D_{Cu} are Sn and Cu bulk diffusion coefficients, respectively). The growth kinetics for both phases in the bulk obeyed parabolic law, indicating diffusion growth regime. On the basis of theoretical analysis made for competitive phase growth in diffusion regime we calculated the Sn diffusion coefficients and diffusion activation energies for both growing phases, Cu_6Sn_5 and Cu_3Sn [5].

Similarly to the bulk phase growth, the kinetics of lateral spreading both Cu_6Sn_5 and Cu_3Sn phases along the Cu surface also occurred in diffusion regime (Fig. 2.) SEM and AFM studies showed that unipolarly spreading phases thicken with time and a depression in the Cu surface appeared near the Cu_3Sn spreading front. The profile peculiarities are caused by two oppositely directed Cu and Sn fluxes over the surfaces of growing phases. Thickening of the phases occurs as a result of two processes: 1) flux of Sn-atom through the spreading phases with successive reaction at the interfaces under spreading layers: 2) surface diffusion of Cu-atoms towards Sn with the reaction between Sn and Cu atoms on the surface of spreading phases.

On the basis of experimental results, a theoretical analysis of competitive surface spreading of intermetallic phases has been done. We supposed that unipolar spreading was accompanied by a leakage of Sn-atoms into the bulk of spreading phases and controlled by reaction at the interfaces. We also estimated a contribution of opposite surface flux of Cu-atom in the thickening of the phase layer. As a result of the analysis, Sn surface diffusion coefficients were calculated and Arrhenius equations were obtained for each of the competitive phases.

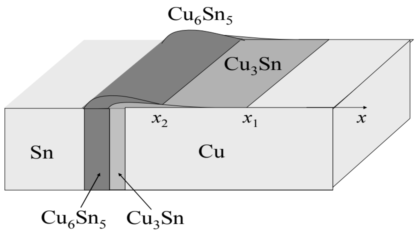

Fig. 1. Scheme of the diffusion experiment. During diffusion of Sn-atoms two phases, Cu_3Sn and Cu_6Sn_5, grow both in the bulk (between Sn and Cu) and on the Cu-surface.

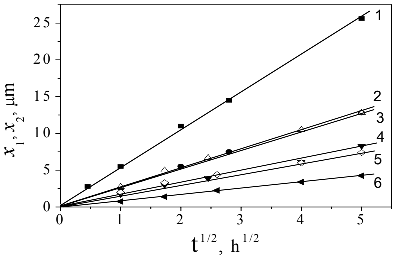

Fig. 2. Kinetics of surface spreading of Cu_3Sn (1, 3, 5) and Cu_6Sn_5 (2, 4, 6) phases; 1, 2 - 200°C; 3, 4 – 180°C; 5, 6 – 160°C.

4. Conclusions

Parabolic kinetic law of lateral spreading of Cu_3Sn and Cu_6Sn_5 sub-micron intermetallic layers during surface interdiffusion in Cu-Sn system has been detected.

Kinetics of competitive propagation has been calculated in assumption that thickening of the layers is controlled by the reaction rate at the interfaces.

A method for the determination of surface diffusion coefficients from the kinetics of competitive phase spreading has been developed and applied to the system under study.

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