Chapter 2

GROWTH KINETICS OF TWO COMPOUND LAYERS
BETWEEN ELEMENTARY SUBSTANCES

Growth kinetics of two chemical compound layers in a binary heterogeneous system have been theoretically treated, from a diffusional viewpoint, by V.I. Arkharov,[1,46] K.P. Gurov *et al.*,[22] B. Schröder and V. Leute,[52] A.T. Fromhold and N. Sato,[53] G.-X. Li and G.W. Powell,[54] and other investigators. Diffusional considerations predict that the thickness of each of two layers as well as their total thickness must parabolically increase with passing time. However, available experimental data provide evidence that this is not always the case. In fact, in many binary systems the layer growth is neither simultaneous, nor parabolic. Instead, a variety of kinetic laws (linear, asymptotic, paralinear, parabolic, *etc.*) are observed. Only a certain portion of the layer thickness-time kinetic dependence in the region of long reaction times and hence large layer thicknesses is close to a parabola. Moreover, one of the layers is often missing from the *A–B* reaction couple over a long period of time, while the other grows from the very beginning of interaction of initial substances. This is the case, for example, with the $NiSi$ and $PdAl_3$ intermetallic compound layers in the Ni–Si and Pd–Al reaction couples, respectively, the first occurred layers being those of Ni_2Si and Pd_2Al_3.[25,100] At 20°C, a single layer of the Cu_6Sn_5 intermetallic compound is known to grow between copper and tin,[64] while above 150°C both Cu_3Sn and Cu_6Sn_5 were observed by M. Oh and M.R. Notis[191] and S. Däbritz *et al.*[192] to occur simultaneously in the same time range, with growth kinetics of the Cu_6Sn_5 layer not always obeying a parabolic law.

There are two compounds of the type *Me*Ag and *Me*$_2$Ag (*Me* = Zr or Hf) on appropriate equilibrium phase diagrams of the Zr–Ag and Hf–Ag binary systems.[193] However, according to O. Taguchi and Y. Iijima, the Zr_2Ag and $ZrAg$ layers grow between zirconium and silver simultaneously,[194] whereas the Hf_2Ag layer occurs in the Hf–Ag couple after an incubation time reaching 432 ks at 900°C.[195] Below about 880°C, it does not form at all. Quite different behaviur of chemical compounds can thus be expected even in very similar binary systems like these.

Y. Fujiwara *et al.*[76] found that the thickness of the $NiSb$ layer in the Ni–Sb reaction couple reaches a maximum value within about 15 minutes and then remains almost unchanged, whereas the Ni_5Sb_2 layer continues to grow (annealing times were

up to 960 min). The maximum thickness of the NiSb layer was 2 μm at 460°C and 6 μm at 600°C. The same applies to intermetallic layers based on the Fe_2Al_5 and $FeAl_3$ compounds, which are formed at the interface between a commercial 18Cr–10Ni stainless steel and aluminium saturated with its components at 700°C.[196,196] When studying the process of simultaneous formation of the Mo_5Si_3 and $MoSi_2$ layers between molybdenum and silicon at 1200-1350°C, V.I. Zmiy and A.S. Seryugina[198] found growth kinetics of the Mo_5Si_3 layer to be linear, whereas the thickness of the $MoSi_2$ layer increased linearly during the first 40 minutes and then parabolically in the 1-20 h time range.

An unambiguous interpretation of these well-known experimental facts in the framework of the diffusional theory is hardly possible. To overcome considerable difficulties arisen, use is usually made of different additional (not very convincing) assumptions and suggestions. In contrast, from a physicochemical viewpoint, the phenomena and dependences observed in practice seem to be quite natural and easily explainable.[134,136,139,141,199] These can therefore readily be expected to hold in binary systems of whatever chemical nature.

It should be noted that a theoretical approach close to, but not identical with, the physicochemical one was proposed by U. Gösele and K.N. Tu[25] (see also Ref.30). It is worth mentioning that both approaches were described in the papers published in the same year 1982 (see Refs 25 and 134). Analysis of various stages of the growth process of two compound layers can be found in works by F.M. d'Heurle and P. Gas,[27] W.S. Johnson and G. Martin,[29] J. Philibert[33,34] and other investigators.

To derive a system of two differential equations describing the rate of formation of two compound layers at the *A–B* interface, it is necessary:

(*i*) to write down equations of partial chemical reactions taking place at layer interfaces. In the case under consideration, there are four such reactions, two for each layer.

(*ii*) to find out relations between the changes in thicknesses of the layers due to those reactions.

(*iii*) to establish mathematical equations relating the differential time, d*t*, to the differential changes, d*x* and d*y*, of the layer thicknesses, using the postulate about the summation of the time of diffusion and the time of chemical transformations.

(*iv*) to write down the required general system of differential equations, taking into account the principle of independency of the elementary acts of chemical reactions.