

## Chapter 3

### OCCURRENCE OF MULTIPLE COMPOUND LAYERS AT THE *A–B* INTERFACE

Many binary systems are multiphase, with the number of chemical compounds on the *A–B* equilibrium phase diagram reaching or even exceeding ten.<sup>120,123,142,145,146,215–225</sup> Therefore, the primary question the experimentalist faced when starting to investigate a particular reaction couple is how many and precisely which compounds, of their variety shown on the phase diagram, can form separate layers at the interface between initial elementary substances under given conditions of temperature and pressure.

In the framework of diffusional considerations all the chemical compounds of a multiphase binary system, whatever their number, are assumed to simultaneously form individual layers which must grow, at a higher or a lower rate, during isothermal annealing of the *A–B* reaction couple according to a parabolic law. Such an assumption can readily be found in numerous papers, monographs and textbooks. Though often stated to follow from the equilibrium phase diagram, it does not seem to have any substantiation. Since now it is practically impossible (and probably not necessary) to find out who was the first to put forward this misleading idea, no citation is made to avoid offending those researchers who have simply mentioned it in their works, following the others, even though their own experimental results provided sufficient evidence for quite opposite conclusions.

In fact, what follows from the equilibrium phase diagram of any binary system is (i) which compounds *may*, not *should*, form individual layers at the interface between substances *A* and *B* and (ii) the final state of the *A–B* reaction couple after prolonged

isothermal annealing, which only depends on the amounts of initial substances taken. The phase diagram by no means dictates that those compound layers must necessarily occur simultaneously. Moreover, from the point of view of phase equilibria, the number of compound layers may rather be expected to decrease, not to increase, with passing time since only two phases must remain in the equilibrium state.

In most reaction couples, part of compound layers are known to be missing, with only one or two layers growing at the  $A$ – $B$  interface, irrespective of the number of chemical compounds on the appropriate phase diagram. The cases where three or more compound layers were present and the more so *grew simultaneously* between elementary substances  $A$  and  $B$  are evidently very rare against the background of the cases where one or two layers were formed. Consider a few characteristic examples.

Of eight intermetallics of the Zr–Al binary system, only the  $ZrAl_3$  layer is known to grow at the Zr–Al interface at temperatures below the melting point of aluminium.<sup>36</sup> This is typical of most transition metal–aluminium binary systems (see a review by E.G. Colgan<sup>36</sup>). A single layer of the  $CuCd_3$  compound was observed by Yu.E. Ugaste and P.A. Kyarsna<sup>115</sup> to occur between Cu and Cd (four intermetallics on the phase diagram). Though there are several oxides in the Ti–O binary system, the  $TiO_2$  layer dominates during oxidation of titanium.<sup>13,120–123</sup>

As already mentioned in Chapter 2, two layers  $Ni_5Sb_2$  and  $NiSb$  are formed at the Ni–Sb interface (five intermetallics on the phase diagram).<sup>43</sup> According to V.I. Zmiy and A.S. Seryugina<sup>198</sup> and P.C. Tortorici and M.A. Dayananda,<sup>226</sup> the  $Mo_5Si_3$  and  $MoSi_2$  layers occur in Mo–Si diffusion couples, while the formation of the  $Mo_3Si$  silicide is not observed. The  $Cu_5Zn_8$  and  $CuZn_5$  layers were found by V.V. Bogdanov *et al.*<sup>227</sup> and M.V. Yarmolenko *et al.*<sup>228</sup> to grow between Cu and Zn, with the third intermetallic compound  $CuZn$  of the Cu–Zn binary system being missing. Simultaneous growth of two intermetallic layers was also observed by T.C. Chou and L. Link<sup>114</sup> in Mo–Ni diffusion couples (three intermetallics on the phase diagram) and by E.K. Ohriner and E.P. George<sup>229</sup> in Mo–Ir diffusion couples (four intermetallics on the phase diagram). Compact layers of one or two compounds are known to form in almost all transition metal–silicon reaction couples.<sup>27,124,125</sup> The same applies to numerous other heterogeneous systems of different chemical nature.<sup>6, 10, 120–123,230, 231</sup>

Note that even in those cases where multiple compound layers were present at the  $A$ – $B$  interface, two layers were dominating. For example, G. Hillmann and W. Hofmann<sup>232</sup> and O. Taguchi *et al.*<sup>233</sup> observed the formation of all six intermetallics

shown on the equilibrium phase diagram in the reaction zone between zirconium and copper, with two Cu-rich compounds occupying more than 90 % of the total layer thickness and layer-growth kinetics deviating from a parabolic law . When investigating this system, K.Bhanumurthy *et al.*<sup>234</sup> have found only two (Cu-rich and Cu-poor) intermetallic layers growing parabolically. As evidenced from micrographs in those works, the specimens of G. Hillmann and W. Hofmann and O.Taguchi *et al.* contained cracks along the layer interfaces, while those of K.Bhanumurthy *et al.* did not. The TiCu and Ti<sub>3</sub>Cu<sub>4</sub> layers are dominant in Ti–Cu diffusion couples, with the thickness of other compound layers being much less and in addition very irregular.<sup>235</sup> Multiple layers were also observed in Hf–Cu diffusion couples in which the intermetallics Hf<sub>2</sub>Cu<sub>7</sub>, Hf<sub>14</sub>Cu<sub>51</sub> and HfCu<sub>5</sub> occupied about 95 % of their total thickness.<sup>236</sup>

It should be emphasised that not always the multilayered structure of the transition zone between elementary substances *A* and *B* is a result of simultaneous isothermal growth of chemical compounds. Certain layers may form during cooling, if slow, because the reaction usually takes place at elevated temperatures, while the layers grown are investigated after cooling down to room temperature. Another main reason for the formation of additional layers may be the disruption of contact between the phases involved in the interaction, due to mechanical stresses associated with thermal expansion and volume effect. As a result, the examined reaction couple is splitted into at least two new independent couples. In those, the other compound layers, lacking in the previous couple, may readily occur. Clearly, in such a case, at least one of the former layers must shrink, up to its full disappearance, as was observed, for example, by S.L. Markovski *et al.*<sup>237</sup> with the PtSb compound layer in Pt–Sb diffusion couples.

However, as evidenced from the available experimental data, not always even these secondary factors do lead to any significant increase in the number of chemical compound layers at the *A–B* interface. Not only the *simultaneous parabolic growth* of eight or ten compound layers, but even their *simultaneous presence* was never observed.

To explain the absence of certain compound layers between initial substances *A* and *B*, two reasons are most frequently put forward (see, for example, Ref.22).

(1) Difficulties with nucleating a new phase. This indeed takes place in particular cases. However, in general, the difficulties with nucleating new phases in a heterogeneous system appear to be too exaggerated. If sufficiently clean surfaces of initial phases capable of forming chemical compounds are brought into intimate contact, the interaction is known to start at relatively low temperatures even in reaction couples

consisting of substances with very high melting points.<sup>124,125,238–245</sup>

(2) The low layer-growth rate due to the small value of the product  $D\Delta c$ , where  $D$  is the diffusion coefficient and  $\Delta c$  is the width of the range of homogeneity of a chemical compound. Firstly, there is no straightforward relation between the width of the homogeneity range and the growth rate of the layer of a chemical compound. Secondly, if the absence of a given compound layer were a consequence of the low growth rate, its appearance in the  $A$ – $B$  reaction couple would only depend on the duration of the interaction between initial substances.

The experiments are known in the literature, providing evidence that these reasons for the absence of some part of the compounds of a multiphase system at the  $A$ – $B$  interface are definitely not decisive.<sup>66,70,89,94,111,124,246</sup> For example, F.J.J. van Loo<sup>66</sup> carried out isothermal annealing of Ti–Ti<sub>3</sub>Al–TiAl–TiAl<sub>2</sub>–TiAl<sub>3</sub>–Al specimens consisting of all the phases of the Ti–Al binary system at 625°C for 15 hours. Instead of the parabolic growth predicted by the diffusional theory, the layers of Ti<sub>3</sub>Al, TiAl and TiAl<sub>2</sub> disappeared and only the TiAl<sub>3</sub> layer remained. Note that all these intermetallic compounds are thermodynamically stable at 625°C. This experiment has convincingly shown that, firstly, all the compound layers of a multiphase system present in the  $A$ – $B$  reaction couple should not necessarily grow during its isothermal annealing and, secondly, the difficulties with nucleating new phases do not play in the solid-state systems that role which is ascribed to them. In the case under consideration, even the layers of the already existing compounds did not grow. Only the layer of the TiAl<sub>3</sub> intermetallic compound, which is known to be the first to occur at the Ti–Al interface,<sup>36,66,247</sup> grew. The layers of the remaining compounds were consumed during its growth and therefore sequentially disappeared with passing time. Working with much thinner artificially prepared Ti–Ti<sub>3</sub>Al–Al and Ti–TiAl–Al specimens, S. Wöhlert and R. Bormann<sup>119</sup> have confirmed the findings of F.J.J. van Loo<sup>66</sup> regarding the complete disappearance of the initially existing Ti<sub>3</sub>Al and TiAl intermetallic layers in the course of formation of the TiAl<sub>3</sub> layer.

It is worth noting that the intermetallic compound TiAl<sub>3</sub> is a stoichiometric phase without any noticeable range of homogeneity, whereas the other intermetallics of the Ti–Al binary system have the homogeneity ranges 1 to 12 at.%.<sup>142,145,193</sup> Nonetheless, the TiAl<sub>3</sub> layer grows much faster than do these. In such a case, in order that the product  $D\Delta c$  be a real reason for its fast growth, the diffusion coefficient  $D$  must clearly have an infinitely high value. Physically, this is scarcely possible.

It should be emphasised that according to the diffusional theory any chemical compound layer once formed cannot then disappear during isothermal annealing of the  $A-B$  reaction couple because its growth rate increases with decreasing thickness:  $dx/dt \sim \partial c/\partial x$ . It is therefore assumed that the layers do not disappear completely, but their thickness decreases to such an extent that they become unobservable experimentally.

Until recently, when it was only possible to examine compound layers with a thickness of the order of 1  $\mu\text{m}$  or greater, experimentalists were forced to accept this explanation. At present, when the phase composition, the structure and the rate of formation of chemical compound layers, a few nanometers thick, can reliably be determined, this explanation is no longer acceptable. At smaller thicknesses of a growing layer the concept *phase* clearly loses its physical meaning since, in order to be identified as such, any phase must contain at least a few crystal-lattice units across the layer thickness.

Therefore, it seems more reasonable to assume that if the layers of certain compounds cannot be revealed in the  $A-B$  reaction couple by means of sufficiently sensitive experimental techniques both in thin films and in massive specimens, then they are simply *missing* from that couple, and to undertake an attempt to find out the reasons for this phenomenon. Such an attempt will be made in this chapter.

### 3.1. Chemical reactions at phase interfaces in a multiphase binary system

To understand the regularities of multiple layer formation, it suffices to consider the  $A-B$  binary system with three chemical compounds  $A_pB_q$ ,  $A_rB_s$  and  $A_lB_n$  on the equilibrium phase diagram (Fig.3.1). The scheme of analysis of the process of their occurrence at the  $A-B$  interface is analogous to that of two compound layers (see Chapter 2). First of all, the equations of partial chemical reactions taking place at phase interfaces must be written. These are as follows.

Layer	Interface	Partial chemical reaction	
$A_pB_q$	1	$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q$ ,	(3.1 <sub>1</sub> )
	2	$(sp - qr)A_{\text{dif}} + qA_rB_s = sA_pB_q$ ,	(3.1 <sub>2</sub> )
$A_rB_s$	2	$(sp - qr)B_{\text{dif}} + rA_pB_q = pA_rB_s$ ,	(3.2 <sub>1</sub> )