3.7. Sequence of compound-layer formation at the A–B interface

From a theoretical viewpoint, predicting the sequence of layer occurrence at the A–B interface would present no difficulties if the values of all the chemical constants entering a system of differential equations like (3.27) were known. For any multiphase binary system A–B, these values are determined by the physical-chemical properties of the elements A and B and their compounds. With their dependence on those properties established, the sequence of formation of compound layers would readily be predicted from the system of equations (3.27) or similar. Unfortunately, the theory of reaction diffusion has not yet reached this stage of its development.

It is obvious that simultaneous occurrence of all compound layers at the A–B interface is highly unlikely since even with three compounds the total probability of the cases where the derivatives dx/dt, dy/dt and dz/dt have different signs (+,–,–; –,+,–; –,–,+; +,+,–; +,–,+; –,+,+) is evidently much greater than the probability of the case in which all three derivatives are positive (+,+,+), with their ratio being 6:1. Therefore, from a physicochemical viewpoint, formation of the A_pB_q, A_rB_s and A_lB_n layers must be sequential, rather than simultaneous, in accordance with experimental observations.

Exact laws governing the sequence of occurrence of compound layers in a particular reaction couple have not so far been established. What is available is a few empirical rules predicting this sequence at a probability level of about 60 to 90 %. These are based either (*i*) on the structure of the equilibrium phase diagram of a binary system or (*ii*) on the thermodynamic properties of its compounds.

3.7.1. Phase-diagram predictions

The equilibrium phase diagram is doubtless the main source from which the researcher obtains the required primary data, when starting to investigate the kinetics of formation of chemical compound layers in a particular binary system. It immeaditely indicates which compounds *may* form separate layers but by no means dictates that those must occur at A–B interface simultaneously.

In the case of binary systems with three or more compounds, generally there is no full correspondence between the microstructure of the A–B transition zone and the appropriate equilibrium phase diagram, whatever the annealing time. Part of compounds

will inevitably be missing, not simply too thin to be observed, for kinetic reasons. Therefore, to confidently judge of the structure of the $A–B$ equilibrium phase diagram from reaction-diffusion experiments, it is necessary to investigate not only the $A–B$ diffusion couple but also a few diffusion couples consisting of initial substances A and B and their compounds.

In binary systems with one chemical compound, there is a full correspondence between what is seen at the $A–B$ interface and the equilibrium phase diagram in the sense that all the reacting phases are available in the microstructure of the transition zone between A and B. During growth of any compound layer under conditions of diffusion control, boundary contents of the components in this layer may reasonably be expected to be equal to the limiting values of the homogeneity range of that compound, if any. Note that even in this simplest case, there can be no equilibrium between all three reacting phases. One of them is 'superfluous' since, according to the Gibbs phase rule, in any binary system only two phases can coexist under equilibrium at constant temperature and pressure.

In binary systems with two compounds, a full correspondence between the microstructure of the $A–B$ transition zone and the appropriate equilibrium phase diagram can in principle be achieved at prolonged annealing. The only obstacle for this may be a very great difference in growth rates of compound layers. In such a case, one of them occurs after a considerable time delay and then over a long period of time is much thinner than the other. As soon as both compound layers grow under conditions of diffusion control, boundary contents of the components in these layers are again equal to the limiting values of the homogeneity ranges of those compounds, if any. The concentration distribution within layer bulks must be close to linear.

It should be noted that both stable and metastable compounds may occur in reaction couples. Analysis of the available experimental data shows that the growth of metastable compound layers is observed relatively rarely. The possibility of formation of metastable compounds is usually mentioned in the explanatory text accompanying the equilibrium phase diagram of any binary system. For certain systems, diagrams of both stable and metastable equilibria have been proposed.[142,145,193,215-225]

At a large difference in melting points of components A and B, the compound enriched in a low-melting component can evidently be expected to occur and grow first. According to an empirical correlation formulated by F.M. d'Heurle[32] as the ordered Cu_3Au phase rule, the first compound to occur should have the highest content of a

component with a lower melting point and diffusion of atoms of that component prevails during formation of this compound. R.W. Walser and R.W. Bene[249] suggests that the first compound formed in a planar reaction couple must be the most stable, congruently melting compound bordering with the lowest-melting eutectic on the equilibrium phase diagram of a binary system. If congruently melting compounds are present at both sides of this eutectic, the layer of the compound with a higher melting point will be the first to grow.

According to a correlation established by B.Y. Tsaur *et al.*[54] when analysing the sequence of formation of transition metal silicides, the second compound to form is the nearest congruently melting compound enriched in the unreacted element. If all the compounds are non-congruently melting phases, then B.Y. Tsaur *et al.* proposes that a criterion for the sequence of their further formation should be the difference, ΔT, in temperatures between the liquidus curve and the peritectic horizontal, with the second phase to form being the compound having the lowest value of ΔT existing on the equilibrium phase diagram between the composition of the first phase and the unreacted element.

Clearly, if diffusion of one of the components (either *A* or *B*) prevails in all the compounds of a multiphase binary system, then only the layer of one of those compounds will grow. Probably, the previously mentioned Ti–Al system just belongs to such systems. Therefore, the results obtained by F.J.J. van Loo[66] with artificially prepared Ti–Ti_3Al–TiAl–$TiAl_2$–$TiAl_3$–Al specimens at 625°C becomes easily explainable.

The melting point of titanium is 1670°C, while that of aluminium is 660°C.[142] In kelvins, these are 1943 K and 933 K, respectively. Thus, the temperature 625°C (898 K) amounts to 0.46 T_{melting} of titanium and 0.96 T_{melting} of aluminium. Hence, at this temperature the aluminium atoms may be expected to be much more mobile in the crystal lattices of the titanium aluminides than the titanium atoms. This appears to be the case even with the Ti_3Al intermetallic compound. The duplex structure of the Ti_3Al layer in the Ti–TiAl diffusion couple (see Fig.5.13 in Ref.66) provides evidence that aluminium is the main diffusant. Otherwise, its microstructure would be homogeneous. This point will be explained in more detail in the next chapter devoted to the consideration of growth kinetics of the same compound layer in various reaction couples of a multiphase binary system.

Under conditions of diffusion control, the $TiAl_3$ layer known to be the first to

occur between titanium and aluminium consumes all the aluminium atoms diffusing across its bulk exclusively for its own growth, not sharing them with the other intermetallic compound layers. Therefore, those or at least one of them can grow only at the expense of diffusion of the titanium atoms.

It seems likely that the self-diffusion coefficient of aluminium in the $TiAl_3$ lattice does not exceed its self-diffusion coefficient in pure solid aluminium. According to the data by L.N. Larikov *et al.*[119] (see also Ref.250), at 625°C the value of this coefficient is of the order of 10^{-12} m^2 s^1.

On the other hand, by extrapolating the data of H. Nakajima and M. Koiwa,[251] the self-diffusion coefficient of titanium in α-titanium at 625°C is found to be of the order of 10^{-18} m^2 s^1. It is reasonable to assume that the the self-diffusion coefficient of titanium in Ti_3Al and other titanium-enriched aluminides does not differ from this figure by more than one or two orders of magnitude. As for any compound, the ratio of the reaction-diffusion coefficients may be expected to be close, if not equal, to the ratio of the appropriate self-diffusion coefficients, it becomes obvious that the reaction-diffusion coefficient of aluminium in $TiAl_3$ is at least four orders of magnitude greater than the reaction-diffusion coefficient of titanium in titanium-enriched aluminides. Since (*i*) diffusional (physical) constants are identified with corresponding reaction-diffusion coefficients (see Section 1.9) and (*ii*) the ratio of layer thicknesses in the course of simultaneous growth of two compound layers is proportional to those constants (see equation (2.48)), at 625°C the thickness of the $TiAl_3$ layer must be about four orders of magnitude greater than that of any other aluminide layer. Thus, if the former is 100 μm, then the latter may be (very roughly) estimated as 10 nm. Such layers are difficult to identify with the help of most frequently employed experimental techniques. Until recently, this fact was used to justify the belief in invisible, but really existing layers.

Experiments like those of S. Wöhlert and R. Bormann[119] clearly indicate, however, that there are no grounds for such a belief. When investigating the Ti–Ti_3Al–Al and Ti–TiAl–Al reaction couples with initial thicknesses of the deposited Ti_3Al and TiAl layers of around 200 nm, they found those layers to fully dissappear during growth of the $TiAl_3$ layer, with no indication of the formation of the $TiAl_2$ layer. Note that the beam spot had a diameter of about 2 nm. For comparison, lattice spacings of the titanium aluminides lie in the range of approximately 0.4-2.5 nm.[142,214] Evidently, any really present intermetallic layer could hardly be overlooked by S. Wöhlert and

R. Bormann.

From a physicochemical viewpoint, those are indeed missing from the Ti–Al reaction couple. This is due mainly to large rates of their consumption in the formation of the TiAl$_3$ layer, not simply to small rates of diffusion in their bulks.

Note that in the framework of purely diffusional considerations any diffusing atoms are assumed to be available for any growing compound layer. In other words, the existence of any interface barriers to prevent diffusion of appropriate atoms is not recognised. From this viewpoint, it would be more logical to compare the diffusion coefficients of aluminium, as the more mobile component, in all the titanium aluminides. In such a case, the absence of most aluminide layers becomes quite unexplainable. It is highly unlikely that the diffusion coefficients of aluminium in different titanium aluminides are so different as to exclude the formation, say, of the TiAl$_2$ layer.

Definitely, more experimental work is desirable with thin films, but even already existing data provide sufficient evidence for rejecting the erroneous idea about the simultaneous formation of compound layers, with some being invisible due to their small thickness.

The second apparent factor influencing the mobility of the atoms and hence the sequence of compound-layer formation is atomic radii of reacting elements. Clearly, the direct juxtaposition of the melting points to decide which compound has a greater chance to occur first is only justified if the atomic radii are identical or close for both elements, as is the case with titanium and aluminium, the atomic radius being 0.146 nm and 0.143 nm, respectively.[152,153] Similarly, the juxtaposition, with the same purpose, of the atomic radii is valid only if the melting points of both elements are close. An example of this kind is the Al–Mg binary system already considered in Section 2.8.3 of Chapter 2.

If both the melting points and the atomic radii of the elements are close, two compound layers may well be expected to grow at comparable rates. The melting point of molybdenum is 2620°C, while that of iridium is 2447°C.[152,153] Appropriate atomic radii are 0.139 nm and 0.135 nm. Therefore, as established by E.K. Ohriner and E.P. George,[229] two intermetallic layers MoIr and MoIr$_3$ grow between iridium and molybdenum simultaneously at close rates in the temperature range 1200-1475°C.

Generally, these factors can act either in the same direction, strengthening the effect of each other, or in the opposite direction, thereby weakening this effect. In the

former case, the final result is quite obvious, whereas in the latter it is hardly predictable *a priori*. For example, in the Ni–Bi binary system the melting point of nickel is 1455°C, while that of bismuth is 271°C. Atomic radii are 0.124 nm and 0.182 nm, respectively. From the point of view of melting temperatures, bismuth may be expected to be more mobile in the nickel bismuthides in the solid state, whereas from the point of view of atomic radii smaller nickel atoms must diffuse much faster. In this particular case, the effect of the difference in the melting points is known to prevail over effect of the difference in the atomic radii.[149,150]

As the atomic radius of nickel is much less than that of titanium, not only $NiAl_3$ but also Ni_2Al_3 can occur at the Ni–Al interface, especially at elevated temperatures. According to the data of E.G. Colgan *et al.*,[89] X.-A. Zhao *et al.*[95,96] and E. Ma *et al.*,[252,253] only one layer of the nickel aluminide $NiAl_3$ is formed between nickel and aluminium at temperatures 300-425°C. The layer of this compound is known to grow in the artificially prepared Ni–NiAl–Al specimens, whereas the existing NiAl layer disappears.[89] S.B. Jung *et al.*[110] observed the simultaneous growth of the Ni_2Al_3 and $NiAl_3$ layers between pure aluminium and the NiAl phase (49.5 at.% Ni) at temperatures of 550-635°C, with the Ni_2Al_3 layer being much thicker than the $NiAl_3$ layer. According to M. Lieblich *et al.*,[254] the $NiAl_3$ layer is formed first in the Ni_3Al–Al specimens at 350-500°C, while then (at longer times or a higher temperature in that range) the Ni_2Al_3 layer starts to grow between the initial Ni_3Al phase and the growing $NiAl_3$ layer. A. Thevand *et al.*[75] found the Ni_2Al_3 layer to occur and grow in the NiAl–Al specimens at temperatures of 760-1100°C.

With purely ionic compounds, appropriate ionic radii must evidently be compared. Complications arise, however, with compounds formed by a metal with a non-metallic element, having partly covalent bonds. Though the values of covalent radii are available as well,[152,153] the precise nature of the chemical bond in any particular chemical compound is usually not known. It is yet unclear whether the tabular values can be used to predict the mobility of the components, for example, in the crystal lattices of transition metal carbides, borides or silicides.

Therefore, even under close temperature and pressure conditions, the sequence of occurrence of silicide layers in metal-silicon reaction couples may be different. Indeed, A. Noya *et al.*[255] found that Ta_5Si_3 is the first compound to form in the Ta–Si thin-film couple at 650°C. At 700°C, in addition to Ta_5Si_3 the $TaSi_2$ layer also occurs, whereas at higher temperatures only the latter grows. According to the data by

T. Nakanishi *et al.*,[256] the Nb$_3$Si compound is formed in the Nb-Si thin-film couple at 550°C, while Nb$_5$Si$_3$ grows at 600°C. At 650°C three phases Nb$_3$Si, Nb$_5$Si$_3$ and NbSi$_2$ were revealed, whereas only the NbSi$_2$ layer grew at 700°C. The reason for the disappearance of the tantalum- or niobium-enriched layers is again kinetic. The TaSi$_2$ or NbSi$_2$ layer rapidly growing at the expense of diffusion of silicon fully consumes the layers of other silicides having insufficient growth rates.

At least with intermetallics, the effect of melting points and atomic radii on the sequence of occurrence of compound layers at the *A–B* interface seems to be more or less straightforward. On the contrary, the influence of the crystal structure of the compounds is rather obscure. Probably, those with less symmetrical and loosely packed structures may be expected to form first under highly non-equilibrium and stressed conditions usually encountered in reaction-diffusion experiments.

Thus, looking at the equilibrium phase diagram and knowing the physical-chemical properties of the elemets *A* and *B* and their compounds, it is possible to draw certain conclusions concerning the sequence of compound-layer formation in a multiphase binary system. It must be remembered, however, that any predictions based on the above-mentioned or other criteria hitherto proposed are only weak correlations, rather than the precise rules. As both the researcher and technologist are always interested in knowing the sequence of occurrence of chemical compounds in a *particular* reaction couple, they can hardly be satisfied even with a correlation valid in 99 out of 100 cases, because it remains unknown whether this couple falls in the range of those 99 or is the only exception. Further theoretical work in this direction is badly needed.

3.7.2. Thermodynamical predictions

The most stable compound of a multiphase binary system is often assumed to be the first to occur and grow at the *A–B* interface. The change, $\Delta_f G_T^0$, of the isobaric-isothermal potential (Gibbs free energy) in the reaction of formation of any compound from the elements under given conditions is usually considered to be a measure of its thermodynamic stability. The more negative the value of $\Delta_f G_T^0$, the more stable the compound is.