

Chapter 1

FORMATION OF A CHEMICAL COMPOUND LAYER AT THE INTERFACE OF TWO ELEMENTARY SUBSTANCES

1.1. Description of the kinetics of solid-state heterogeneous reactions

Consider first the main characteristic features of formation of the layers of chemical compounds common to solid-solid, solid-liquid and solid-gas systems (Chapters 1 to 4). Then, the effect of dissolution of a solid in the liquid phase of a solid-liquid system or of its evaporation into the gaseous phase of a solid-gas system on the growth kinetics of a chemical compound layer will be analysed in Chapter 5. Thus, under the conditions of occurrence of a chemical reaction its product will be assumed to be solid and to form a continuous compact layer adherent to at least one of the initial phases.

Let us begin an analysis of the process of formation of chemical compounds in heterogeneous systems with the simplest case of growth of a solid layer between elementary substances A and B which form, according to the equilibrium phase diagram of the A - B binary system, only one chemical compound A_pB_q , p and q being positive numbers (Fig.1.1). The substances A and B are considered to be solid at reaction temperature T_1 and mutually insoluble.

It is easy to notice that the usual concepts and laws of the kinetics of homogeneous chemical reactions can hardly be used in analysing the examined heterogeneous process. Indeed, difficulties already arise when employing the main concepts of chemical kinetics, namely, the *concentration* of a reactant or a product in the system and the *rate* of a chemical reaction.

In the case of any homogeneous system in which all reacting substances are mixed at the atomic or molecular level, the definition of the concentration as the amount of a substance per unit volume is applicable to the entire system consisting of initial substances and reaction products as a whole. By contrast, in the case of any heterogeneous system, it is only rational for components A and B within each of its homogeneous parts (phases).

In the examined case of the A - A_pB_q - B system, it is clearly possible to define the concentration (content) of component, for example A , in initial phases A and B or in a

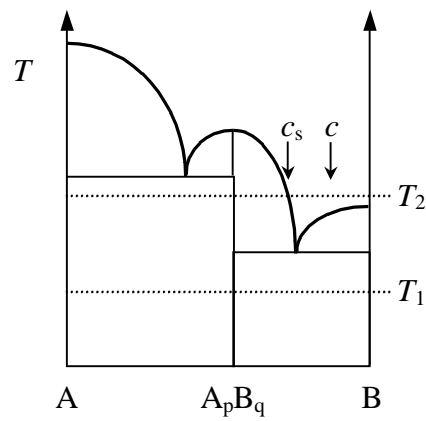
growing layer of the compound A_pB_q . However, it is quite irrational to consider the concentration of substance A , A_pB_q or B in the entire heterogeneous system consisting of non-mixing phases A , A_pB_q and B . In contrast to a homogeneous system in which the concentration of a given substance at any moment of time is the same at all points or at least changes continuously from point to point, in a heterogeneous system the concentration of components is in general different at different points, and at the phase interfaces its value changes abruptly (see Fig.1.1). Therefore, the distribution of the concentration of components A and B with distance becomes important in heterogeneous systems.

By definition, the chemical compound is an ordered phase of constant composition. Ordering means that in the crystal lattice of any compound each component forms its own sublattice in which all the sites are occupied by atoms or ions of only this component. The constancy of composition is a consequence of the valency rule as, for example, in the case of oxides (Al_2O_3), or of more complicated (and still poorly understood) laws as in the case of intermetallics where compounds of a somewhat strange composition ($NiBi_3$) are formed. Though the solids contain no molecules of Al_2O_3 or $NiBi_3$ as such, the composition of the Al_2O_3 and $NiBi_3$ phases is on the average described by these chemical formulae.

Obviously, such a measure of the rate of a chemical reaction taking place in any homogeneous system as the change in *concentration* of reacting substances or its products per unit time at constant reaction volume¹²⁶⁻¹²⁸ cannot be applied to the examined heterogeneous systems. In any heterogeneous system, the concentration (content) of components A and B in initial phases and in a growing layer of the A_pB_q compound having no homogeneity range remains constant, in spite of the occurrence of any chemical reaction. Therefore, a quantitative characteristic of the rate of a chemical reaction in any heterogeneous system is the change per unit time of the *thickness* or *mass* of a solid layer formed. Choice of the method of following the growth process of any compound layer (either by its thickness or by mass) depends entirely upon the efficiency of experimental techniques available for the investigation of interaction of initial substances in a particular heterogeneous system.

In this book, attention will only be paid to the parallel-plane layers whose thickness is the same over the entire surface of contact of the reactants. In addition, the length of the layer in the direction normal to the direction of diffusion of components A and B (see Fig. 1.1) is assumed to be considerably greater than its thickness. In this

**Equilibrium
binary phase
diagram A–B**



**Reaction
couple
A–B**

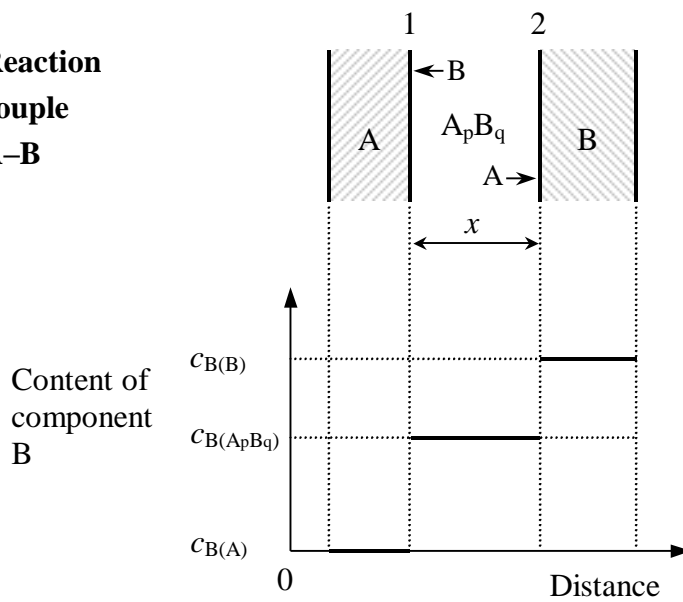


Fig.1.1. Schematic diagram to illustrate the growth process of the $A_p B_q$ chemical compound layer at the interface between mutually insoluble elementary substances A and B .

case, the edge effects on the process of layer growth can be neglected.

It should be noted that the compound layers observed in practice seldom have an ideal appearance. Firstly, one or both boundaries of a layer with initial phases may be uneven. As an example, Fig. 1.2 shows optical micrographs of the Fe_2Al_5 intermetallic compound layer formed at the interface between aluminium and commercial iron or steels of differing carbon content.¹²⁹ Bimetallic specimens were prepared by interaction of solid iron or steel with molten aluminium at 700°C followed by their subsequent joint cooling in water until the solidification of the melt. As seen in Fig. 1.2, the interface of the Fe_2Al_5 layer with aluminium is relatively flat, while that with iron or steel is irregular, with the irregularity becoming progressively less, the higher the carbon content of steel. Secondly, the compound layers formed often contain cracks, pores and other macrodefects. Undoubtedly, this has a considerable (sometimes, even controlling) effect on the kinetics of their growth.

Hereafter, attention will only be paid to the growth of a compound layer which is ideal both in the chemical (constant composition) and the physical (ordered structure, no macrodefects) sense. Influence of secondary factors such as stresses, strains, specimen geometry, *etc.*, will be neglected.

1.2. Reaction diffusion

Reaction diffusion is a physical-chemical process resulting in the occurrence of a continuous solid compound layer at the interface between initial substances.¹³⁰ The term *reaction diffusion* reflects the most important feature of the layer-formation mechanism, namely, that the layer growth is due to a continuous alternation of the two consecutive steps:

- (1) diffusion of atoms (ions) of the reactants across its bulk in the opposite direction;
- (2) subsequent chemical transformations taking place at the layer interfaces with the participation of diffusing atoms of one of the components and the surface atoms of another component.

It should be emphasised that the term *diffusional growth* only reflects one aspect of the layer-growth mechanism, namely, atomic diffusion. The differences in terminology are not so unimportant as it may seem at first sight.