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.
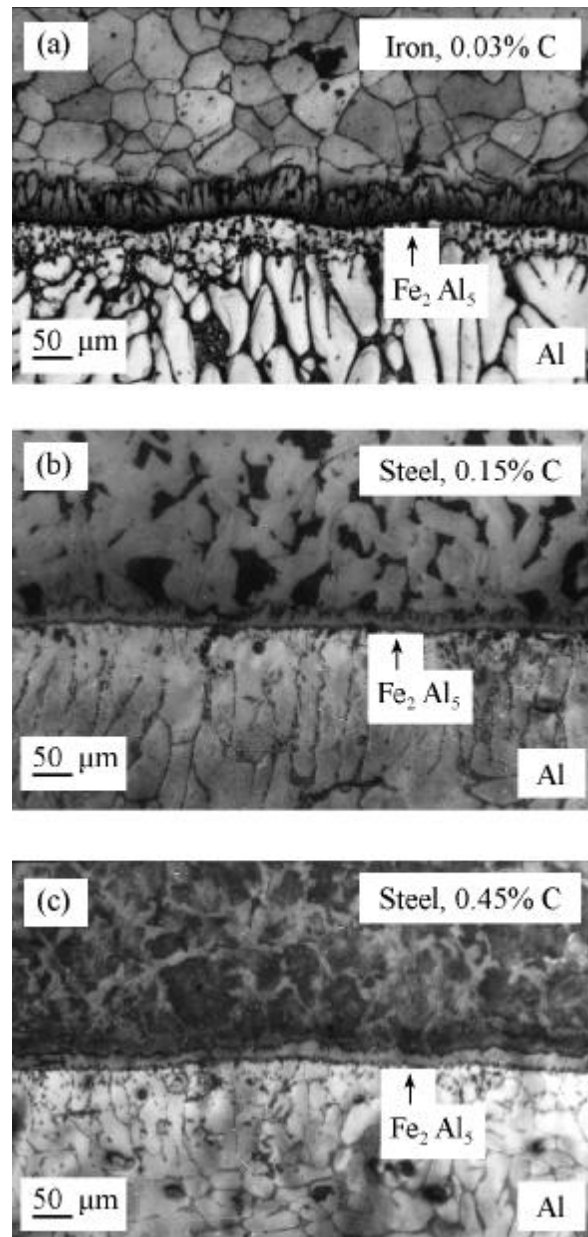
Fig.1.2. Optical micrographs of the transition zone between commercial purity iron or steel and aluminium. The Fe_2Al_5 intermetallic compound layer becomes progressively flatter and thinner with increasing carbon content of steel. The 'Al+an intermetallic compound' eutectic is distributed at grain boundaries of aluminium solid solutions.

In the case under consideration, the concept *chemical transformations* (synonyms: *chemical reaction*, *chemical interaction*) unites the following processes.

(1) Transition of the atoms (ions) of a given kind through the interface from one phase into the other. This is *external* diffusion, according to the terminology proposed by B.Ya. Pines.[9,131]

(2) Redistribution of the electronic density of atomic orbitals resulting in the formation of molecules, ions, radicals or other stable groupings of atoms included in a growing compound layer.

(3) Rearrangement of the crystal lattice of an initial phase into the crystal lattice of a chemical compound formed.

It should be noted that something like to the elementary act of external diffusion also occurs in homogeneous reactions taking place in solutions or gases. Indeed, in order to be combined into a molecule, the reacting particles must move (diffuse) towards each other. The second of these processes in a liquid-phase or a gas homogeneous system results in the formation of an individual molecule which is able to travel relatively freely within the reaction bulk. In the examined solid-state heterogeneous system, however, the 'molecule' formed is rigidly fixed in the crystal lattice of a chemical compound together with a number of other similar 'molecules', thus lost their individuality. What is only possible in this case is the substitution of atoms of any of the 'molecules' comprising the layer for equivalent atoms, not disturbing the stoichiometry of a compound and the total balance of atoms in the entire system.

In the general case of comparable mobilities of components A and B within the A_pB_q crystal lattice, the A_pB_q compound layer grows at the expense of diffusion of the B atoms to interface 1 (see Fig.1.1) where a *partial* chemical reaction then takes place in accordance with the equation

$$qB_{\text{dif}} + pA_{\text{surf}} = A_pB_q \tag{1.1}$$

and also at the expense of diffusion of the A atoms to interface 2 followed by the *partial* chemical reaction

$$pA_{\text{dif}} + qB_{\text{surf}} = A_pB_q . \tag{1.2}$$

In general, the rates of these reactions are different. Indeed, before entering reaction (1.1), the B atoms must lose any contact with the main mass of substance B and be transferred across the A_pB_q layer from interface 2 to interface 1. On the contrary, component A enters reaction (1.1) in the form of particles (atoms or ions) located onto the surface of phase A and therefore bonded with the bulk of substance A. The A atoms diffusing across the A_pB_q layer from interface 1 to interface 2 and the surface B atoms enter reaction (1.2). In addition, reactions (1.1) and (1.2) take place at different interfaces of the A_pB_q layer and are therefore separated in space. Hence, the equality of their rates is a rare exception rather than the rule. In fact, these are two different chemical reactions.

Note that in any heterogeneous system which attained constant temperature-pressure conditions from below (from smaller to higher values), no reaction proceeds within the bulk of the A_pB_q layer. Inside the A_pB_q layer, the A and B atoms (or ions) can and do exchange of their positions but this act by no means represent any chemical reaction.

It should also be emphasised that an initial period of interaction of elementary substances when there is still no compound layer and consequently there is only one common interface at which substances A and B react directly, is outside the scope of the proposed macroscopic consideration. The stage of nucleation of a chemical compound between initial phases is to be the subject of examination within the framework of a microscopic theory which would have to provide, amongst other parameters of the process, a minimal thickness sufficient to specify the interaction product formed at the $A-B$ interface as a layer of the chemical compound A_pB_q possessing its typical physical and chemical properties. However, it can already now be said with confidence that this value is small in comparison with really measured thicknesses of compound layers and therefore can hardly have any noticeable effect on the shape of the layer thickness-time kinetic dependences observed in practice.

Indeed, refined experiments carried out using modern methods of investigation including various kinds of electron microscopy, X-ray diffraction, Rutherford backscattering of light ions, electron probe microanalysis, ion mass spectrometry, *etc.*, showed the layers of chemical compounds, a few nanometers thick, to possess all the properties of bulk phases. For example, in the nickel-aluminium reaction couple R.J. Tarento and G. Blaise[99] were able not only to identify the nickel aluminides $NiAl_3$, Ni_2Al_3, $NiAl$ and Ni_3Al in the layers, 5 nm thick, but also to determine the ranges of

homogeneity of the aluminides having such ranges (Ni_2Al_3 and NiAl). It should be noted that the homogeneity ranges determined by them were in good agreement with the values indicated on the equilibrium phase diagram of the Ni–Al binary system. The same applies to the transition metal-silicon systems which have been studied sufficiently well as the objects of primary importance for microelectronics.[124,125]

As the lattice spacings of chemical compounds are usually of the order of 0.5 nm or greater, it follows that any compound layer, 5 nm thick, can contain at most 10 crystal- lattice units. Therefore, the results of an analysis of the nucleation process obtained by F.M. d'Heurle[31] for transition-metal silicides appear to be quite realistic.

F.M. d'Heurle evaluated the specific thickness (an analogue of the critical radius of nuclei in a homogeneous system, for more detail, see Ref.31) for compounds of the Ni–Si binary system. For Ni_2Si, its value was found to be 0.15 nm, *i.e.* the 'nucleus' does not contain even one lattice unit. Although higher values were obtained for other nickel silicides, they never exceeded 1 nm. Therefore, the nucleation process can hardly play any significant role in the formation of most transition-metal silicides, except in some special cases.[27,31] This conclusion is likely to be valid for any other chemical compound layer. It should be noted, however, that there is also a different viewpoint.[38,132]

1.3. Growth of the A_pB_q layer at the expense of diffusion of component B

Let us assume that reaction (1.1) is the only one in the A–A_pB_q–B system, *i.e.* the diffusivity of component A in the crystal lattice of the A_pB_q compound is negligible in comparison with that of component B. The kinetic equation expressing the growth rate of the A_pB_q layer as a result of diffusion of the B atoms and subsequent reaction (1.1) can readily be found using the following assumptions (postulates):[133-141]

(1) The time, dt, required for increasing the thickness of the A_pB_q layer by dx_{B1} (from x to $x + $ dx_{B1}, Fig.1.3) is the sum of the time, d$t_{dif}^{(B)}$, of diffusion of the B atoms across its bulk to the reaction site (interface 1) and the time, d$t_{chem}^{(B)}$, of their subsequent chemical interaction with the surface A atoms at interface 1:

$$dt = dt_{dif}^{(B)} + dt_{chem}^{(B)}. \tag{1.3}$$