$$k_1^{(Al_3Mg_2)} = 3.5 \times 10^{-8} \exp\left(-69\, kJ\, mol^{-1} / RT\right) m^2\, s^{-1},$$ (2.55$_1$)

$$k_1^{(Al_{12}Mg_{17})} = 0.1 \exp\left(-165\, kJ\, mol^{-1} / RT\right) m^2\, s^{-1}.$$ (2.55$_2$)

As the melting points of aluminium (660°C) and magnesium (651°C) are very close, the large difference in growth rates of the Al_3Mg_2 and $Al_{12}Mg_{17}$ intermetallic compound layers, revealed by E.M. Tanguep Njiokep et al.,[208] appears to be due to the difference in atomic radii of those elements. The atomic radius of aluminium (0.143 nm) is less than that of magnesium (0.160 nm).[152,153] Therefore, the Al_3Mg_2 layer growing at the expense of diffusion of smaller aluminium atoms can reasonably be expected to grow faster compared to the $Al_{12}Mg_{17}$ layer growing at the expense of diffusion of greater magnesium atoms, the more so that both intermetallic compounds have similar (cubic) structures.

This binary system is worth further investigation, especially in the region of non-parabolic layer-growth kinetics. Marker experiments are also desirable, with inert markers embedded in both intermetallic layers.

2.9. NiBi: missing or too thin?

As pointed out in Section 1.8.2 of Chapter 1, the NiBi intermetallic layer is not observed in the Ni–Bi reaction couple for a very long period of time. At least, after a 70 h anneal at 250°C no indication of its presence was found, though the $NiBi_3$ intermetallic layer reached a thickness of almost 230 μm.[149,150] This may seem somewhat surprising, especially in comparison with the just considered Al–Mg couple.

The question whether the NiBi layer is indeed missing or only too thin to be observed could be answered by carrying out experiments with the artificially prepared Ni–NiBi–NiBi$_3$–Bi specimens. The disappearance of the already existing NiBi intermetallic layer would provide direct evidence for its kinetic instability. Such an attempt was made by M.S. Lee et al.[209] Unfortunately, the specimens they prepared proved to be not so easy to handle, and the final goal was not achieved. This example shows how difficult the reaction-diffusion experiments are, even with *best* binary systems. *Best* means the minimal influence of (*i*) thermal expansion and (*ii*) volume effect associated with compound formation. In the Ni–Bi couple the coefficients of

thermal expansion of the components are identical,[210-213] while the volume effect[209] is within a range typical of intermetallic compounds.[214] With respect to the influence of thermal expansion, the Ni–Bi system is even better than the Al–Mg one in which the coefficients of thermal expansion of the components are slightly different.
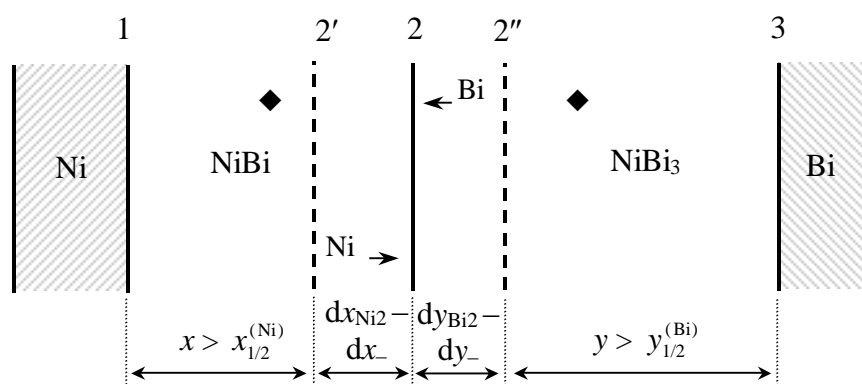
Consider the growth process of the NiBi and $NiBi_3$ intermetallic layers between nickel and bismuth in more detail to explain the difference in diffusional and physicochemical approaches to the same problem of the apparent absence of a chemical compound layer. From a physicochemical viewpoint, in the reaction controlled regime ($x < x_{1/2}^{(Ni)}$, $y < y_{1/2}^{(Bi)}$) both layers grow at the expense of diffusion of both components, as shown in Fig.2.19a. In the diffusion controlled regime ($x > x_{1/2}^{(Ni)}$, $y > y_{1/2}^{(Bi)}$) the NiBi layer grows at the expense of diffusion of the nickel atoms and their subsequent chemical reaction with the $NiBi_3$ compound at interface 2, whereas the $NiBi_3$ layer grows at the expense of diffusion of the bismuth atoms and their subsequent chemical reaction with the NiBi compound at the same interface 2, as illustrated in Fig.2.19b. From a diffusional viewpoint, *both* layers grow at the expense of diffusion of *both* components, *whatever* their thicknesses.

Another principal distinction relates to the time of the occurrence of the NiBi and $NiBi_3$ intermetallic layers. In view of the very large difference in melting points of nickel (1451°C) and bismuth (271°C), at temperatures below 271°C the mobility of the bismuth atoms in the $NiBi_3$ crystal lattice may reasonably be expected to be much greater than that of the nickel atoms in the NiBi crystal lattice. From a physicochemical viewpoint, the NiBi layer can hardly survive under such conditions, and therefore there must be a long delay with its occurrence between Ni and $NiBi_3$. According to diffusional considerations, however, it should occur from the very beginning of the interaction of nickel and bismuth but is too thin to be observed experimentally. To unambiguously judge of which of the two approaches is more correct in this particular case, long-term experiments with Ni–Bi couples are badly needed.

From layer thickness-time plots presented by M.S. Lee *et al.*,[209] the NiBi layer thickness in Ni–$NiBi_3$ couples after their annealing during 100 h can be estimated as about 10 μm at 330°C, 25 μm at 370°C, 40 μm at 410°C and 50 μm at 450°C. This provides evidence that the growth rate of the NiBi layer is indeed very low, though in
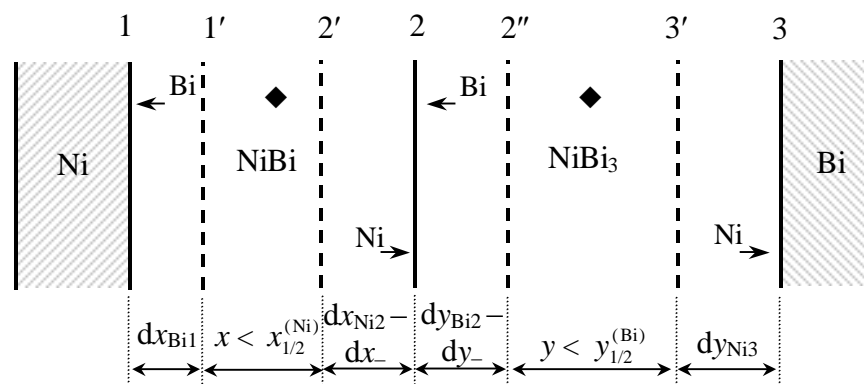
(a)

(b)

Fig.2.19. Schematic diagram to illustrate the growth process of the NiBi and NiBi$_3$ intermetallic compound layers between nickel and bismuth.

(a) reaction controlled regime of layer formation ($x < x_{1/2}^{(Ni)}$, $y < y_{1/2}^{(Bi)}$);

(b) diffusion controlled regime of layer formation ($x > x_{1/2}^{(Ni)}$, $y > y_{1/2}^{(Bi)}$).

 The symbol ⊔ designates an inert marker.

those couples it can readily grow at the expense of diffusion of *both* components (Ni and Bi) and *additionally* at the expense of decomposition of the $NiBi_3$ compound (see Chapter 4).

In order to visualise the NiBi layer at temperatures below the melting point of bismuth, experiments with Ni–Bi couples must evidently be carried out in the 100-1000 h time range. At such annealing times, its thickness will probably exceed a few micrometres. The NiBi layer formed should therefore be seen even under optical microscope at moderate magnifications. A serious obstacle to performing such experiments may be the rupture of Ni–Bi specimens with thick $NiBi_3$ intermetallic layers.