Dividing all the terms of equation (1.53) by $(x - x_0)$ gives

$$x + x_0 = 2k_1\left(\frac{t}{x - x_0} - \frac{1}{k_0}\right). \qquad (1.55)$$

As x_0 can be taken with the plus or minus sign, the experimental data should produce a straight line in the coordinates either $(x + x_0) - t/(x - x_0)$ or $(x - x_0) - t/(x + x_0)$. This form of presenting the experimental results was used by N.A. Kolobov and M.M.Samokhvalov,[17] who found the values of the reaction-diffusion constants for the SiO_2 layer in the oxidation of silicon by oxygen listed in Table 1.2. The temperature dependence of both the chemical constant k_0 and the physical (diffusional) constant k_1 is well described by the Arrhenius relation (see equation (1.34)) with the activation energy 155 and 120 kJ mol^{-1}, respectively.

It should be noted that the chemical constant depends on the surface density of the atoms of a reacting substance. Therefore, the values of the chemical constant are different for various crystallographic faces of a single crystal. In the case of silicon, the packing density of the atoms decreases in the series (110)>(111)>(100), with the ratio of the densities being 1:0.82:0.71. According to J.R. Ligenza,[57,58] E.A. Irene,[60] Y. Kamigaki and Y. Itoh[61] and N.A. Kolobov and M.M. Samokhvalov,[17] the values of the chemical constant in the oxidation of different faces of a silicon single crystal change in about the same proportion but in general this dependence appears to be a weak correlation rather than the exact relation. Clearly, in addition to the packing density of the single-crystal faces, the rate of chemical transformations also depends on (*i*) the interplanar distances in single crystals of different crystallographic orientations and (*ii*) the nature of the chemical bond between the atoms onto a given crystallographic face.

1.8. Growth kinetics of the $NiBi_3$ layer at the nickel-bismuth interface

G. Voss[147] found two intermetallic compounds, NiBi (50 at.% or 78.08 mass % Bi) and $NiBi_3$ (75 at.% or 91.45 mass % Bi), to exist in the nickel-bismuth binary system (see also Ref. [113]). P. Feschotte and J.-M. Rosset[148] thoroughly reinvestigated the phase diagram of this system and confirmed the existence of those two intermetallics (Fig.1.15). However,

Table 1.2. Reaction-diffusion constants for the SiO_2 layer in the oxidation of silicon by oxygen[17]

Temperature (°C)	900	1000	1100	1200
k_1 ($m^2\ s^{-1}$)	5.2×10^{-17}	1.3×10^{-16}	3.1×10^{-16}	6.0×10^{-16}
k_0 ($m\ s^{-1}$)	1.4×10^{-11}	4.8×10^{-11}	1.3×10^{-10}	3.3×10^{-10}

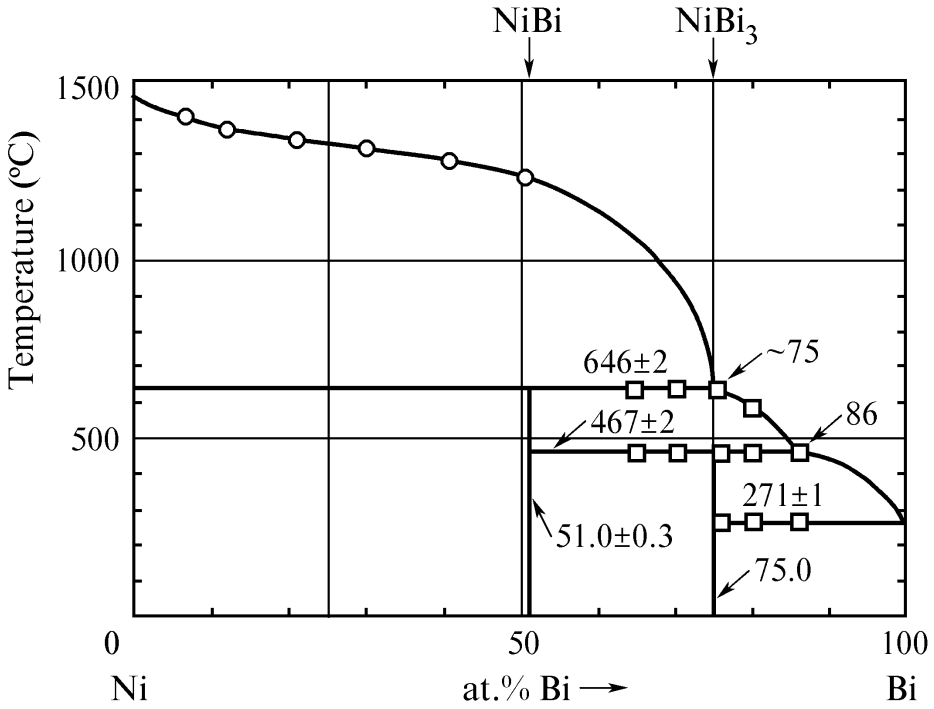

Fig.1.15. Equilibrium phase diagram of the Ni–Bi binary system according to the work of P. Feschotte and J.-M. Rosset.[148]

contrary to the expectations of G. Voss[147] and M. Hansen and K. Anderko[113], they have not revealed a wide range of homogeneity of the NiBi compound. The composition of this compound was found to be 51.0±0.3 at.% Bi. Thus, its range of homogeneity is very narrow, if any. The $NiBi_3$ intermetallic compound is stoichiometric. Both compounds melt incongruently: NiBi at 646°C and $NiBi_3$ at 467°C .

Consider characteristic features of layered compound formation at the Ni–Bi interface, with particular emphasis on the determination of (*i*) the main diffusing species in the growth process and (*ii*) the values of the reaction-diffusion constants.[149,150]

1.8.1. Experimental details

Electrolytic-grade nickel (99.98 mass % Ni) was used in the form of polished plates $3\times9\times14$ mm^3. Their final treatment involved electrolytic polishing, both to remove the surface contaminations and to reduce mechanical stresses.

The plates were mounted into graphite crucibles, 11 mm inner diameter, and heated to about 350°C under a previously dried low-melting flux consisting of the eutectic mixture 82 mass % $ZnCl_2$ – 18 mass % NaCl (melting temperature 280°C). The crucibles were then filled with molten bismuth (> 99.999 mass % Bi) at 350°C and allowed to cool until its crystallization. The time of contact of a Ni plate with liquid bismuth was 60 s, while that of cooling from 350°C down to room temperature was around 180 s.

A continuous, coherent intermetallic layer, 1.5±0.5 μm thick, was found to form during the specimen preparation. Hence, this technique ensured an intimate contact between the nickel and bismuth phases, so that the reaction started simultaneously anywhere along the entire Ni–Bi interface. Therefore, both intermetallics, NiBi and $NiBi_3$, had favourable nucleation conditions.

Each bimetallic specimen thus obtained was cut into two pieces using an electric-spark machine. The surface of the Ni–Bi couples was first ground mechanically and then polished electrolytically using an ‘Elypovist’ apparatus and a special electrolyte.[129]

The Ni–Bi couples were annealed in sealed glass ampoules, filled with high-purity helium (0.25 atm), at 150, 200 and 250°C for 1 to 300 h. Each couple was annealed successively a few times. After each anneal, the specimen surface was examined in the as-